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Development of methods for the treatment of water containing potentially toxic elements using low-cost adsorbents

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LIST OF ABBREVIATIONS AND ACRONYMS

BDDT – Brunauer, Deming, Deming, and Teller

BD – Bulk Density

BET – Brunauer-Emmett-Teller

BMW – Biodegradable Municipal Waste

CBT – Conical Bottom Tube

CCD – Charged Coupled Device (Type of a detector)

EU – European Union

FF – Filtered Fraction

FPS – Fraction Particle Size

FTIR – Fourier Transform Infrared Spectroscopy

HD – Hypotheses of Dimension for qualitative factors

HPLC – High-Performance Liquid Chromatography formerly High-Pressure Liquid Chromatography

HR – Hypotheses of Relationship

HS – Supplementary Hypotheses

IAST – Ideal Adsorbed Solution Theory

ICP-OES – Inductively Coupled Plasma Optical Emission Spectrometer

IUPAC – International Union for Pure and Applied Chemistry

LCA – Low-cost adsorbent

MARS – Microwave Accelerated Reaction System

MSW – Municipal Solid Waste

NATO – North Atlantic Treaty Organization

NIST – National Institute of Standard Technology

OECD – Organization for Economic Co-operation and Development

PTE – Potentially Toxic Element

PVDF – Polyvinylidene Fluoride

REE – Rare Earth Element

SWOT – Strength, Weakness, Opportunities, Threat

UNESCO – United Nations Educational, Scientific and Cultural Organization

W/V – Weight to Volume Ratio of LCAs to aqueous solution

Chapter 1

INTRODUCTION

1.1 BACKGROUND

Water is the most precious thing for human beings which is known to sustain all class of existence on our planet. Availability of pure and clean water is of extreme value to the whole world. With the increase in world's population, demand of pure and clean water will also be increasing (Ruut, 2009). Several surveys on access of clean water to the growing world population shows that by the year 2025, half the world's population will be going to be facing the problem of water scarcity or a water crisis (European Union, 2012; Landner and Reuther, 2005). Increasing unavailability of water in required quantity will also have a great impact on the biodiversity comprising life of flora and fauna.

Growing contamination of water is the main problem (Burakov et al., 2018) all over the world because it is the major cause of water borne diseases resulting illness and mortality worldwide. So, to create awareness for the discharge of industrial as well as heavily polluted domestic wastewater, pretreatment and appropriate decontamination of water is the primary responsibility of the civic bodies. Numerous acts, laws, policies and a number of technological advancement have been (Wamba et al., 2018; Wegener and Malone, 1983) made for treatment and recycling of industrial and domestic wastewater before it is discharged into the surface water bodies.

There are so many causes of water pollution on our planet (Simate et al., 2016; Thines et al., 2017). The causes of water pollution are categorized into two namely natural causes and anthropogenic causes. Natural causes include disasters like floods, calamities and volcanic eruptions. Volcanic eruptions releases huge amount of oxides of sulphur (SO_x) in the environment which causes acid rain. Most of the water pollution on this Earth happens due to anthropogenic activities. Anthropogenic activities include use of pesticides, and fertilizers in agricultural sector, use of detergents and soaps in daily life (Cegłowski et al., 2018), and major pollution is cause by industrial sectors (such as textiles, electroplating, mining and other chemical industries) which release highly toxic chemicals. Fig. 1.1 shows a schematic diagram of water pollution due to anthropogenic activities.

PTEs such as Cd, Cr, Cu, Pb, and Zn (Chu et al., 2015; Gupta et al., 2018) are very harmful and are generally found in almost all kind (sewage, industrial etc.) of wastewater (Simate et al., 2016). Out of the above mentioned PTEs lead (Pb) and zinc (Zn) are very common one. These PTEs enter water through various industries such as metal plating, smelting, mining, phosphate fertilizers, cadmiumnickel and lead batteries, textiles and alloy industries, paint industries, leather tanning, pigments, as well as from sewage. These contaminants are very precarious for humans and other living organism, aquatic environments, and the existing ecosystems.

Besides these some other pollutants which poses serious risk for human health (Chu et al., 2015; Gwenzi et al., 2017; Hui et al., 2018) are chloride (Cl^-), fluoride (F^-), nitrate (NO_3^-), oxalate ($C_2O_4^{2-}$), phosphate (PO_4^{3-}), and sulfate (SO_4^{2-}). Presence of nitrate in high concentration in water causes blue babies disease (methaemoglobinemia) in children. Consumption of water with high concentration of fluoride cause fluorosis. World's population by the year 2050 is expected to reach about 10 billion which means world will be in need of huge quantity of fresh water (European Comission, 2014; European Union, 2012). So, treatment of wastewater, it's recycling and reuse (European Comission, 2012; UNESCO, 2003) is an urgent need to avoid the problem of huge water scarcity (Goh and Ismail, 2018; Gupta et al., 2018) for our future generations.

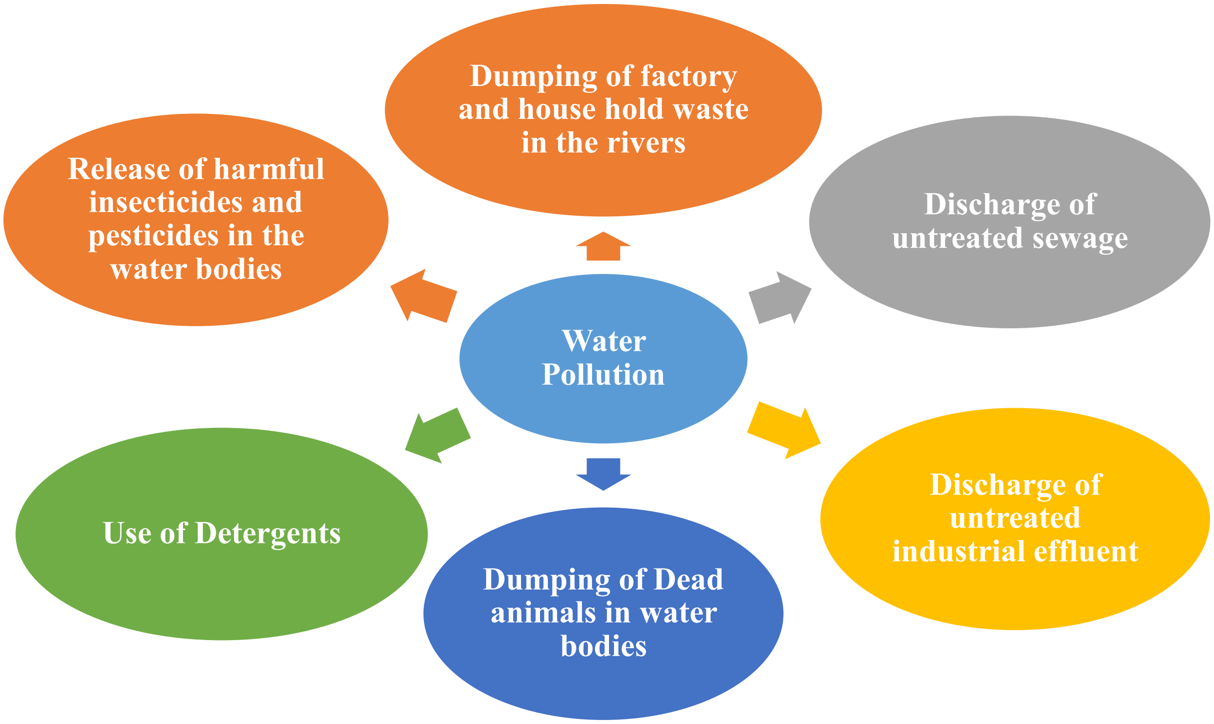


Fig. 1.1 Anthropogenic sources of water pollution

1.2 ADSORPTION TECHNOLOGY

Increasing demand of water quality management have risen the use adsorption technology (Gwenzi et al., 2017; Mo et al., 2018) because of its easy installation and operation (Shakoor and Nasar, 2017). Emphasis have given to research different types of water treatment (Khan et al., 2018; Panahi et al.,

2018) by adsorption using cheaply and easily available adsorbents. Adsorption is a phenomena which can remove several adsorbate (pollutant) at a time. In the process of adsorption, adsorbates (molecule, ion etc.) are adsorbed on a solid surface that is why it is also known as surface phenomena.

Since, adsorption is a surface phenomenon, adsorption of an adsorbate happens by physical strengths. In some cases weak chemical bonds also take place in the process of adsorption. The strong surface which fasten the pollutant or contaminant (atom, ion or molecule) is known as adsorbent and the contaminant held fast to the strong surface is known as adsorbate. The process of adsorption is controlled by the parameters like temperature, nature of the adsorbate and adsorbent, and the presence of other pollutants (Iakovleva et al., 2017; Siswoyo et al., 2014). It can also be controlled by varying the reaction conditions such as pH, concentration of pollutants, contact time, and particle size (Gupta et al., 2018; Vukelic et al., 2018).

Process of adsorption ends once it reaches equilibrium. Equilibrium will be established between the amount of adsorbate adsorbed and the amount of adsorbate in solution if the adsorbent and adsorbate are in contact long enough (Hamed et al., 2018). The plot between the amount adsorbed and the initial amount of adsorbate is known as adsorption isotherm. Column studies are done following batch process to develop a sound adsorption technology. Pilot studies are conducted with small columns to validate the developed adsorption technology. Following the pilot scale studies, the developed adsorption technology is applied at industrial scales using larger columns.

1.3 DEVELOPMENT OF LCAs

Development of low-cost adsorbents (LCAs) becomes an important aspect of study while developing a method for the treatment of water containing PTEs using LCAs. Since, in this study LCA is used for the development of the method for the treatment of contaminated water so, in this section method of development of LCAs is discussed.

1.3.1 Selection of the Precursors

Selection of the precursor for the development of LCAs depends upon many factors. The precursor should be freely available, inexpensive and non-hazardous in nature (Hamid et al., 2017; Vukelic et al., 2018). Moreover, for good adsorption results, high contents of carbon or oxygen in the adsorbent moiety are very necessary (Abo-El-Enein et al., 2017; Cusack et al., 2018). Other characteristics include high abrasion resistance, high thermal stability and small pore diameters, which results in higher exposed surface area and, hence, high surface capacity for adsorption.

1.3.2 Types of Precursors

The choice of the precursor depends upon the nature of origin, i.e. inorganic or organic. Organic precursors include plant, animal and other materials having high carbon content, like fruit waste, rice husks, bark, seaweed, algae, peat moss, hair and keratin etc. (Abdel Salam et al., 2011). Industrial organic products include petroleum and fertilizer products (Ahmaruzzaman, 2011). The inorganic precursors include soil, clay, mud, zeolites, ore materials, metal oxides and hydroxides. The precursors chosen for this study were organic in nature and were mostly plants and other high carbon content materials that is why the compost samples used as adsorbent in this study were categorize as green compost adsorbent (plant as precursor), mushroom compost adsorbent (plant as precursor), and sewage sludge compost adsorbent (high carbon content material as precursor).

1.3.3 Processing Method

Use of activated carbon as an adsorbent for wastewater treatment is found since 1940s. But activated carbon is costly and cannot be used at large scale (Demirbas, 2008). This situation compelled scientists toward the development of LCAs i.e. alternatives of activated carbon and other high cost adsorbents. The use of waste products for developing LCAs contributes to the waste minimization, recovery and reuse (Leal et al., 2018). Continuous search for the inexpensive alternatives, resulted into development of LCAs from industrial waste products, agricultural waste products and house hold wastes etc. The LCAs used in this study were processed from agricultural wastes. The waste was decomposed in waste management plants and compost was prepared. The prepared compost was then processed into granular form and the fine grains were used as adsorbents in this study.

1.4 AIM AND OBJECTIVES OF THE STUDY

Aim of this study was to treat the water contaminated with PTEs using LCAs so that the cost of treatment could be reduced drastically. LCAs used in this study were the compost samples obtained from different materials. To achieve the aim, following objectives were setup.

1. Construction of a test system for study of the cleaning process of contaminated water samples using LCAs.
2. Analysis of compost and polluted water by ICP-OES for PTEs content before and after treatment.
3. Study of the adsorption behaviour of several PTEs on various composts e.g. their fractions of different particle size.
4. Optimization of the parameters in the cleaning process in order to elaborate a functional system.

1.4.1 Specific Goals of the Study

In this study empirical analysis of adsorption behaviour of potentially toxic elements (PTEs) on LCAs was undertaken. Specifically the main focus of this study was to consider the utility of identifying the comparative strengths and weaknesses of compost samples obtained from different waste management plants in Hungary, as LCAs which in turn would reduce the costs of removal of PTEs from polluted water. Thus, aim and objectives of the study were attained by setting the following related specific goals.

1.4.1.1 Development of an optimal method for removal of PTEs

Aim and objectives of the study suggested that a test system needs to be developed and a preliminary study was conducted to have the knowledge of the parameters which were needed to carry out the study on a larger scale. So to extend the study on larger scale –

a) Adsorption columns of larger size were constructed based on the results of preliminary studies.
b) Optimal ratio of adsorbent weight and volume of contaminated water was estimated, and a set of experiment with larger adsorbent columns were performed using selected composts and PTE concentrations respectively.
c) Adsorption isotherms were recorded for certain types of adsorbents with different metallic species and modelling of the adsorption process was carried out in order to support the planning of the optimal procedure.
d) Interaction of the original metal content of the adsorbent and PTEs in the contaminated water was also studied.

1.4.1.2 Evaluation of environmental risk of the adsorbents

Simple biotests with higher plants can be performed to study the potential toxic effects of the composts after being used as adsorbents in the adsorption experiments. Germination and growth tests (e.g. using *Sinapis alba, Lepidium sativum, Lolium perenne* as test organisms) could be suitable and relevant in terms of possible reuse of these composts. In this study concentration of PTEs in the contaminated water used was not so high so, only one plant bioassay test was performed to see the effect of adsorbed PTEs on plants. Mustard plant was used in the experiment.

1.4.1.3 Mitigation of environmental risk

As the adsorbents after use can contain significant amount of PTEs, the treatment of the same as hazardous waste may be necessary that can be achieved by high temperature burning or by incineration, therefore study of the used composts at high temperature can be performed followed by the analysis of the remaining ash. In this study mitigation was not needed because the compost samples used as adsorbents did not pose any significant environmental risk.

1.5 RESEARCH VARIABLES

Factors affecting the use of LCAs for removal of PTEs are the study variables that were studied during the course of this study. A wide range of materials including naturally occurring, synthetic and hybrid adsorbents has been investigated for adsorption of PTEs under different operating conditions such as pH, adsorbent dose and contact time (Ahmaruzzaman, 2011; Bailey et al., 1999; Sajid et al., 2018). However, efforts are required to systematically analyze the wealth of studies to estimate operating conditions (Abdel Salam et al., 2011; Abo-El-Enein et al., 2017; Briso et al., 2018; Oliveira et al., 2018) to achieve efficient PTEs adsorption. In this section, the influence of operating conditions on PTE adsorption process by LCAs is elucidated based on the review of literatures presented in this study. The factors affecting the adsorption of PTEs using LCAs were divided into two (physical factors and chemical factors).

1.5.1 Physical Factors

The factors that affect the process of adsorption externally are categorized as physical factors. The physical factors that were studied in this study are explained below.

1.5.1.1 Effect of contact time

The contact time significantly affects the adsorption process. Also, contact time can influence the economic efficiency of the process (Briso et al., 2018). Therefore, contact time is another performance governing factor in adsorption process. Review of literature indicates that optimum contact time for PTE removal by different LCAs is highly variable. In this study the mean contact time for removal of Cu^{2+} and Zn^{2+} was found to be 6 hours.

1.5.1.2 Effect of temperature

The temperature of the solution mainly affects the enlargement nature of adsorbents, mobility of PTE ions and solid-liquid interface. A number of literature have reported that 298 K has the highest frequency of occurrence (Romero-Flores et al., 2018; Schreiber et al., 2018), indicating that majority of studies were conducted at room temperature. Along with temperature, thermodynamic parameters may also be used to determine the nature of adsorption process viz. exothermic or endothermic, spontaneity and randomness and also to determine whether the temperature is favorable for the process or not (Ahmaruzzaman, 2011). The important thermodynamic parameters are ΔG^0, ΔH^0 and ΔS^0 representing the change in Gibbs free energy, enthalpy and entropy. The negative values of ΔG^0 are associated with the adsorption process being spontaneous. Similarly, the positive values of ΔH^0 indicate that the process is endothermic. Also, the magnitude of ΔH^0 seems to be related with the type of sorption viz. physisorption (ΔH^0 < 50 kJ/mol) and chemisorption (ΔH^0 > 50 kJ/mol). Moreover, the positive values of ΔS^0 could be explained as the increase in entropy occurred due to the exchange of metal ions by more mobile ions during adsorption process.

1.5.1.3 Effect of surface area

Adsorption is a surface phenomenon and as such the extent of adsorption is proportional to specific surface area. Specific surface area can be defined as that portion of the total surface area that is available for adsorption (Briso et al., 2018). Thus the amount of adsorption accomplished per unit weight of solid adsorbent is greater, if the solid is more finely divided and more porous. To increase the effective surface area granular adsorbents of varying particle size were used in this study.

1.5.1.4 Effect of agitation speed

In the process of adsorption, adsorbate molecule has to first encounter the boundary layer effect and then it has to diffuse from the boundary layer film onto adsorbent surface and then finally it has to diffuse into the porous structure of the adsorbents. This phenomenon will take relatively long contact time. Therefore, a higher agitation speed will be required to improve the diffusion of the adsorbate toward the surface of the adsorbent (Abo-El-Enein et al., 2017; Cusack et al., 2018). Equilibrium time is a very important factor to study when considering an economical wastewater treatment to reduce the contact time to reach the equilibrium a proper agitation speed needs to be selected for faster diffusion of the adsorbate to reach the adsorbent surface.

1.5.1.5 Effect of Flow Rate

While dealing with optimizing the operating conditions of the continuous treatment of wastewater, the flow rate of such influent wastewater is a very essential parameter to evaluate for development of a sound method for removal of PTEs which could later be converted into an effective technique. It has been proven that rapid uptake is noticed in the initial stages of flow rate and the rate of uptake starts to decrease thereafter and finally reaches saturation. As the flow rate becomes higher, the contact time between the adsorbate and the adsorbent decreases, and hence the adsorbate molecules do not have enough time to get into the binding sites in the adsorbent surface or diffuse into the pores of the adsorbents, causing the adsorbate solutes to leave the column before equilibrium to occur and breakpoint time to be reached earlier. So, an optimal flow rate should be determined to obtain the maximum adsorption (Hamid et al., 2017) and to provide the enough time of contact for adsorption.

1.5.1.6 Effect of column height

In the continuous flow adsorption experiment, column height is used to provide the larger surface and greater exhaustive time for diffusion of adsorbate molecules. As the bed height increased, the adsorbate molecules would have more time to be in contact with the adsorbents (Mashile et al., 2018; Mehta et al., 2015), which in turn would result in a higher adsorbate molecule removal efficiency in the column. Greater the column height, greater will be exhaustive time and adsorption efficiency. Column height cannot be increased beyond a certain range so it should be calculated according to the contact time and exhaustive time needed for the process of adsorption.

1.5.1.7 Effect of particle size

The particle sizes of adsorbent materials is an important parameter in the adsorption process. It helps in increasing the specific surface area (effective surface area available for the adsorption of adsorbate). Greater the specific surface area, higher will be adsorption efficiency. So, finer particles should be used instead of larger particles. In this study particles in three range (FPS ≤ 0.32 mm, 0.32 mm < FPS ≤ 1.00 mm, 1.00 mm < FPS ≤ 1.40 mm) of particle size were used for adsorption test.

1.5.2 Chemical Factors

The factors which are known to affect the mechanism of adsorption internally are categorize as chemical factors. The chemical factors which affected the removal of PTEs under this study are described as follows.

1.5.2.1 Effect of pH

Potential of hydrogen ions (pH) is one of the most important process variables that can directly affect the uptake of PTEs by adsorbents because it can affect the extent of PTEs ionization as well as the surface characteristics of an adsorbent. Based on the literature reviewed (Ahmaruzzaman, 2011; Garmia et al., 2018) it was found that adsorption of PTEs depends on the solution pH. So, it is important to determine the solution pH because it can influence the mechanism of PTEs adsorption. Normally PTEs are adsorbed below pH 6, over this pH (particularly beyond pH 7) precipitation of PTEs dominates over adsorption due to formation of hydroxides via hydrolysis.

1.5.2.2 Effect of adsorbent dose

In general, the extent of adsorption of a solute increases with the increase in the concentration of an adsorbent because the increase in adsorbent concentration translates into increased active exchangeable adsorption sites. However, the overall solute adsorption per unit weight of an adsorbent can decrease following the increase in adsorbent concentration due to interference (Gupta et al., 2018) caused by the interaction of active sites of an adsorbent. That is why investigating the influence of dose along with its optimization is the mandatory component of PTE adsorption.

1.5.2.3 Effect of competing ions

In the process of adsorption removal efficiency of adsorbate is greatly influenced by the presence of co-existing ions in solution leading to competitive adsorption on the adsorbent surface. Review of literature also reported that the hindrance of competing ions with regards to adsorbate adsorption could be largely influenced by the process pH. For instance, recovery of adsorbates like rare earth elements (REEs) from the acidic solutions pose challenges from the competing ions such as Fe^{3+}, quite common in industrial waste waters or mine waters. At lower pH, besides Fe^{3+}, interference from noble elements and palladium group elements such as Au^{3+}, Pd^{3+} and Pt^{3+}, could be fairly excessive. On the other hand, at higher pH, ions such as Mn^{2+}, Al^{3+}, Cd^{2+}, and Co^{2+} could deter the adsorption process of REEs. It should also be mentioned that poor REEs adsorption was commonly recorded in multicomponent (Ahmaruzzaman, 2011) systems which is quite common in any multicomponent adsorption systems including a multicomponent system for PTEs like Cu^{2+} and Zn^{2+} also.

1.5.2.4 Nature of adsorbate

The solubility of the solute is to a large extent, a controlling factor for adsorption equilibrium (Siswoyo et al., 2014). The Landelius rule states that an inverse relationship can be anticipated between the extent of adsorption of a solute and its solubility in the solvent from which adsorption occurs. Adsorption increases with decrease in the solubility of the solvent (Vukelic et al., 2018). Greater the solubility, stronger the solute-solvent bond and the smaller the extent of adsorption.

1.5.2.5 Effect of mixed solutes

In the application of adsorption for purification of water and wastewater, the material to be adsorbed commonly will be mixture of many compounds rather than a single one. The compounds may mutually enhance adsorption, may act relatively independently or may interfere with one another (Burakov et al., 2018). In mixed solutes, each solute competes in some way with the adsorption of the other. The degree of mutual inhibition of competing should be related to the relative size of the molecules being adsorbed (Gupta et al., 2018), to the relative adsorptive affinities and the relative concentrations of the solutes. In most cases, presence of the other solutes in the mixture adversely affects adsorptions of the first, leading to much more rapid breakthrough of this material.

1.5.2.6 Nature of adsorbent

The physicochemical nature of the adsorbent can have profound effects on both rate and capacity of adsorption (Vukelic et al., 2018). Since, adsorption is a surface phenomenon, it is affected by the parameters like surface functional groups and structural details. The behavior of adsorbents have to be related to the surface of the material (Mo et al., 2018) and the evidence for chemical interaction at the surface. The adsorption capacity may well be accomplished by increasing the concentration of the appropriate functional groups (Panahi et al., 2018) on the surface of an adsorbent.

1.5.2.7 Effect of initial adsorbate concentrations

It has been shown by many researchers (Gupta et al., 2018; Gwenzi et al., 2017; Mo et al., 2018) that increasing the concentration of adsorbates increase the amount of adsorption but at the same time it decreases the percentage adsorption. In a continuous adsorption process, a higher initial concentration of adsorbate will definitely encourage the sorption process. But, once the decrease in percentage adsorption become significant (unavoidable), concentration should not be increased any further. So, the experiment should start with an optimal initial concentration (Ahmaruzzaman, 2011) which maintains the balance between percentage adsorption and the amount of adsorption.

1.6 SELECTION OF STUDY VARIABLES

Development of method for the treatment of water containing PTEs using LCAs require deep understanding and careful selection of study variables because this will pave the way to convert the method into a working technology. In this study both physical as well as chemical variable (as mentioned in section 1.5) were studied. Although, the development of model required for this study needed only two variable viz. quantity of adsorption at equilibrium (q_{eq}) and equilibrium concentration (C_{eq}) of the adsorbate, other variables like weight to volume ratio (W/V), fraction particle size (FPS) and the variables mentioned in section 1.5 were also taken into consideration for the development of whole method which was the ultimate aim of this study. The variable studied other than q_{eq} and C_{eq} for the development of method also helped in getting as correct values of q_{eq} and C_{eq} as possible because these were the primary variable which were used to set up the experimental method for removal of PTEs from aqueous solution using LCAs.

The choice of variable was governed by the fact that together these variable constitute a substantial part of the total operating costs which the removal of PTEs using LCAs incur in the effort to produce effluent content that meets the quality criteria required by legislation at the lowest possible cost. In this study, the method developed was considered as multicomponent adsorption system which was used to remove two PTEs (Cu^{2+} and Zn^{2+}) from aqueous solution. So, equilibrium concentrations of Cu^{2+} and Zn^{2+} were considered as the primary variables for the study and these variables were applied directly in the model to obtain the model parameters. The other variables were considered as secondary variable which did not had the direct influence on the model but had influenced significantly the developed method and methodology of the study.

1.6.1 Justification of the Chosen Research Variables

Many other variables, apart from the identified variables, indirectly affect the adsorption of PTEs from aqueous solution. However, the mindset in choosing the study variables for this study was to consider the variables that directly affect the adsorption of PTEs using LCAs, as otherwise the study would have been unmanageable. Since, in this study development of method for the removal of PTEs from aqueous solution was completed in two stages (Preliminary treatments and Model development), variables were also selected for both the stages.

In the preliminary treatments mostly physical variables were taken into consideration. In this stage the variables studied were, variation in particle size, weight to volume ratio, and amount of adsorbent used to determine the height of the columns. The rationale behind selecting these variables is substantiated by the fact that together these variables provided the structure to the developed method. In the model development stage the variables chosen for the study were equilibrium concentration (C_{eq}) and the amount of adsorption at equilibrium (q_{eq}). These variables justify their selection by the fact that the model developed for this study needed only these two variables for the determination of parameters. Other variables were supposed to affect the process of adsorption but they were not used in the model as such.

1.7 HYPOTHESES FORMULATION

Literature survey and deep understanding of removal of PTEs from water using LCAs has resulted in the formulation of the following Research Hypotheses. Three sets of hypotheses have been formulated. The first set is ‘Hypotheses determining dimensions of qualitative factors’ (HDs) i.e. factors that are to be assessed qualitatively. The second set is ‘Hypotheses of Causal relationships’ (HRs) which tests the effect of identified quantitative factors affecting the adsorption of PTEs using LCAs. The third set covers ‘Supplementary Hypotheses’ (HSs).

1.7.1 Hypotheses Determining Dimensions of Qualitative Factors

HD1: Scientific world is looking at LCAs as sustainable alternatives for wastewater treatment.

HD2: There are no studies which aimed to highlight the affinity of LCAs with respect to more pollutant classes.

1.7.2 Hypotheses of Causal Relationships

HR1: LCAs with higher affinity have larger adsorption capacity.

HR2: High cost of removal of multiple pollutants simultaneously encourage the use of LCAs in water and wastewater industry.

1.7.3 Supplementary Hypotheses

HS1: It is perceived that removal of PTEs from contaminated water using LCAs leads to significant benefits with respect to wastewater treatment techniques.

1.8 DELIMITATIONS OF SCOPE

This section helps to identify a planned, justified scope of the study beyond which generalization of the results was not intended. The identified delimitations are additional to the limitations and key assumptions. ‘Delimitations’ are within the control of the researcher and ‘limitations’ are not. Limitations caused by the methods used are identified and explained in Chapter 5 as summary of all the limitations that became evident throughout the course of the study. Key assumptions are described in relevant sections. The identified delimitations of the scope are listed as follows.

a) The study was conducted for development of LCA from agricultural waste and primary data were used for carrying out the study. Although, type of compost, its elemental content and the particle size used in the adsorption test is mentioned, results could be generalized for larger particle size only after carrying out some pilot scale studies.
b) The adsorption behaviour was studied for small amount of adsorbents while it may be different for larger amounts.
c) Though this study was carried out for a small amount of adsorbents, physical properties like particle size and bulk density can be generalized for larger scale study also.
d) Reusability and the methods used for environmental risk evaluation and mitigation can also be generalized for larger scale studies.
e) Present study is arrived at after studying technical and economic feasibilities of the LCAs. But, the technical issues are studied in terms of the applicability, usage and standardization of features and not with respect to development of technical features.

Chapter 2

REVIEW OF THE LITERATURE

2.1 AVAILABILITY OF WATER RESOURCES

Today’s world cannot be imagined without the technological advances that have occurred over the past 10 decades. Technology continues to develop and cannot exist without the use of natural resources such as water and metals (European Union, 2012). Water is one of the most important resources for sustainable life on the planet. Water covers more than 70% of the Earth, but less than 3% is fresh water, and less than 1% of fresh water is easily available for human consumption (European Union, 2012), Fig. 2.1. More than a third of the world’s population live in conditions of water stress. Industry consumes a fifth of the total water in use, which is about 750 km^3 a^{-1} (European Comission, 2014).

In the past few years adsorptions has been used as one of the most effective (Anastopoulos et al., 2018) pollutant removal technology (Ayawei et al., 2017) because of its easy installation and low operational cost. Cost of treatment could even further be reduced by using LCAs in the process of adsorption. So, in this chapter a strong theoretical background about adsorption phenomena, characterization of adsorbents and mathematical aspects of adsorption equilibrium is also given.

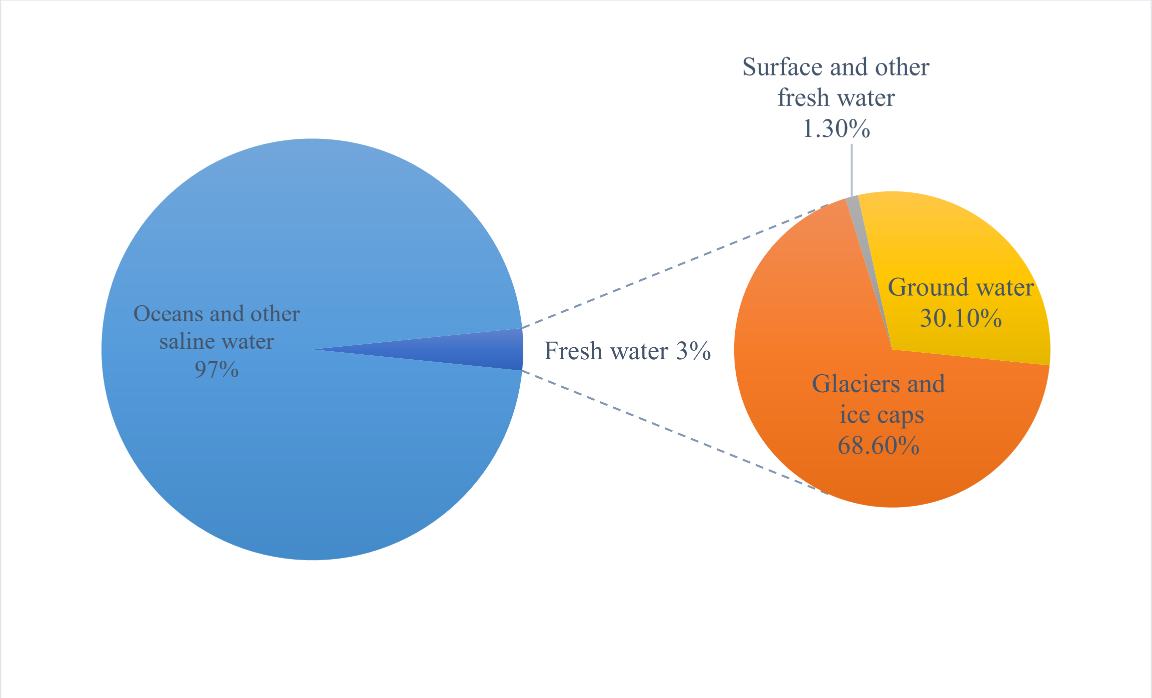


Fig. 2.1 Globally available water resources

(Source: Created & modified from data using ygrapth.com)

2.2 ADSORPTION AS A SURFACE PROCESS

Adsorption is also the study of surface chemistry at the liquid/solid interface (Zaera, 2011). The whole process is described in the Fig. 2.2 with the basic terms used in it. The material which surface is used for adsorption is called adsorbent and the substances that are adsorbed on the adsorbent surface are called adsorbate. Being a physical phenomenon, adsorption can be reversed which is known as desorption and it ensures reuse of LCAs. Lower cost of LCAs allows them to be investigated as a replacement for current costly methods of removing heavy metals from solution (Bailey et al., 1999).

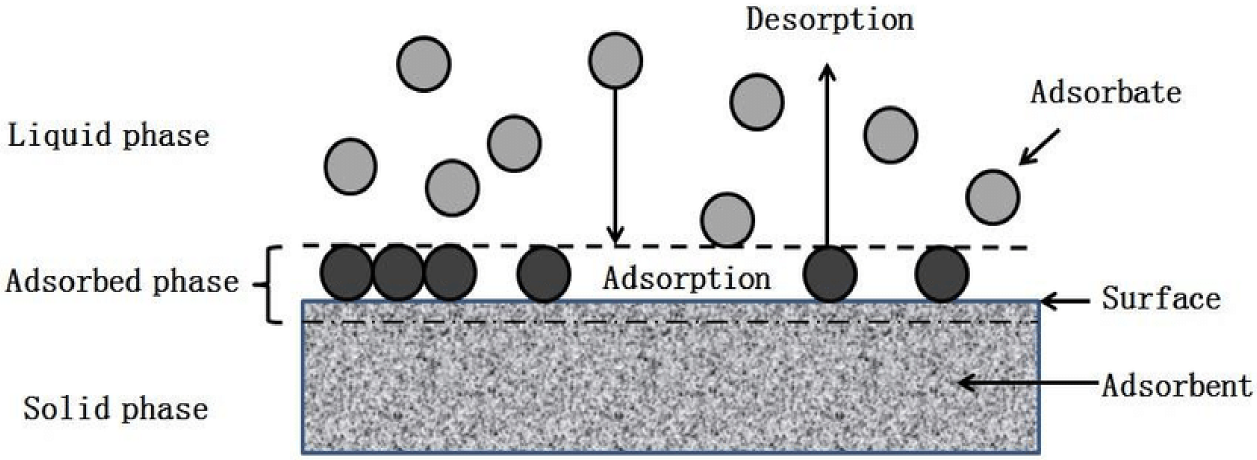


Fig. 2.2 Adsorption from a liquid phase on a solid surface
(Source: www.researchgate.net)

The effectivity and selection of adsorbents depends upon their surface area because adsorption is a surface process so surface area and surface forces (Wang et al., 2012) play a key role in deciding the quality of adsorbent. Engineered adsorbents are preferred over natural adsorbents (De Gisi et al., 2016) because they are the one which are prepared using highly porous materials. The surface area of engineered adsorbents are typically found in the range between 10^2 to 10^3 m^2/g.

2.2.1 Thermodynamic Considerations to Explain Adsorption

The Gibbs free energy, G, is a thermodynamic potential which is used to describe surface processes (Kazeem et al., 2018). For surface processes G depends on temperature (*T*) of the surface, pressure (*P*) applied on the surface, composition of the surface material (number of moles, n_i used for the surface process) and the surface, A_s itself. Change of Gibbs free energy for a surface process can be represented by the following fundamental equation –

$$dG = -SdT + VdP + \sum_i \mu_i \, dn_i + f dA_s \qquad (2.1)$$

Where S is the entropy, V is the volume, μ is the chemical potential, and f is the surface free energy, also referred to as surface tension which can further be elaborated as follows.

$$f = \left(\frac{\partial G}{\partial A_s}\right)_{T,P,\,n_i} \tag{2.2}$$

With the progress in adsorption, the value of surface free energy starts reducing from its initial value $f_{w\text{-}s}$ (surface tension at the water-solid interface) to the value $f_{a\text{-}s}$ (surface tension at the interface between adsorbate solution and solid). The difference of the two values $f_{w\text{-}s}$ and $f_{a\text{-}s}$ is the function of amount adsorbed. This difference is known as spreading pressure, π.

$$f_{w-s} - f_{a-s} = \pi > 0 \tag{2.3}$$

The basis of the ideal adsorbed solution theory (one of the most frequently applied competitive adsorption model) is the relationship between spreading pressure and adsorbent loading, and change in Gibbs free energy (Eq. 2.1). Heat of adsorption can be estimated by estimating the change in Gibbs free energy of adsorption which indicates the degree of spontaneity of the adsorption process (Bhattacharya et al., 2006) and its dependence on the changes of enthalpy and entropy of adsorption. For a spontaneously proceeding reaction the change in free energy of reaction must be negative (De Gisi et al., 2016). Based on the relationship among free energy, enthalpy, and entropy of a spontaneously proceeding reaction, adsorption will be spontaneous if and only if –

$$\Delta G_{ads} = \Delta H_{ads} - T\Delta S_{ads} < 0 \tag{2.4}$$

The change in entropy of a system is the measure of degree of disorder in the system. For adsorption, degree of disorder decreases with time because as the adsorption of chemical species (Particles, molecules or ions) starts, number of species gets reduced in the system and degree of immobilization also reduces thereby reducing the surface interactions (Wang et al., 2012). This indicates that change of the entropy of adsorption is negative ($\Delta S_{ads} < 0$). Dissociation and/or displacement during the process of adsorption may be an exception (if the number of species produced by dissociation or replacement are more than the number of species adsorbed) to the above mentioned situation because with the increase in number species degree of disorder increases. Now, with $\Delta S_{ads} < 0$ enthalpy has to be negative ($\Delta H_{ads} < 0$) for the adsorption to be spontaneous. That is adsorption must be an exothermic process. Adsorption is categorized as physical adsorption (physisorption) or chemical adsorption (chemisorption) a mechanisms involved in the biosorption process (Demirbas, 2008). If mean ΔG_{ads} < 8 kJ/mole then adsorption is known as physisorption and adsorption will be chemisorption if the mean ΔG_{ads} is in the range of 8–16 kJ/mol (Hamed et al., 2018).

2.2.2 Description of Adsorption Theory

Since adsorbates get adsorbed on surface of the adsorbent, adsorbate uptake (adsorption loading) is expressed as surface concentration, ω (in mol/m^2), which is defined as the ratio of adsorbed amount, n_a, and adsorbent surface area, A_s –

$$\omega = \frac{n_a}{A_s} \tag{2.5}$$

In practice, it is not possible to estimate the surface area of adsorbate as accurate as measuring its mass so mass concentration, q is used instead of surface concentration, ω –

$$q = \frac{n_a}{m_A} \tag{2.6}$$

Where m_A is the adsorbent mass. Since, adsorbate gets loaded on the adsorbent surface, q is also known as adsorption loading.

To develop an adsorption model it is pertinent to study the dependence of q, on characteristic process parameters and to derive a relationship among them. Development of a theoretical adsorption model requires study of three main elements (adsorption equilibrium, adsorption kinetics, and adsorption dynamics) of adsorption theory.

The adsorption equilibrium describes adsorption loading as a function of adsorbate concentration (C) and the temperature (T). It can be written mathematically as –

$$q = f(C,T) \tag{2.7}$$

At constant temperature adsorption loading, (q) will be a function of C only and it can be represented mathematically by Eq. (2.8). Curves drawn from Eq. (2.8) are known adsorption isotherm.

$$q = f(C) \quad T = constant \tag{2.8}$$

Adsorption capacity is a vital factor (Shahat et al., 2018), determination of which requires deep understanding of adsorption kinetics. Progress of adsorption with time is described by the adsorption kinetics, that is amount of adsorption and value of concentration at a time can be determined by adsorption kinetics. That is for adsorption kinetics –

$$q = f(t) \quad and \quad C = f(t) \tag{2.9}$$

Based on Eq. (2.9), rate of adsorption can be determined either by rate of change of concentration or by mass transfer rate. For convenience, rate of adsorption is determined most often by slow mass transfer rate from the liquid to the solid phase. Adsorption dynamics is used to describe the time as well as the space dependence of the adsorption process for example thermodynamic investigations reveal the spontaneity (Mohebali et al., 2018) of the process of adsorption. The time (t) and space (z) dependence of q and C can be represented mathematically as –

$$q = f(t, z) \quad and \quad C = f(t, z) \tag{2.10}$$

The elements of practice oriented adsorption theory and their interdependence are shown in Fig. 2.3. Three major concepts of adsorption theory shown in Fig. 2.3 are valid for both single solute adsorption and multisolute adsorption as was successfully done for single solute adsorption of Methylene blue by (Mohebali et al., 2018). Multisolute adsorption is characterized by the presence of multiple chemical species in a single solution which fight for the available adsorption sites. Based on the data obtained for single-solute adsorption model, a model for multisolute adsorption could be developed by considering each solute a separate entity.

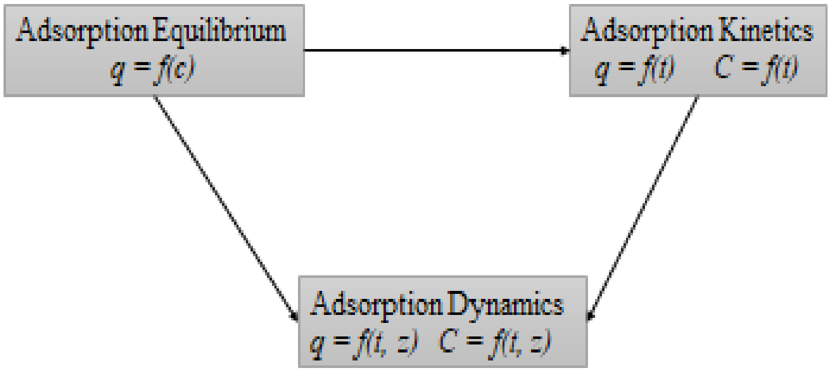


Fig. 2.3 Interdependence of constituent of adsorption theory

2.3 WATER PURIFICATION AND ENGINEERED ADSORPTION PROCESSES

Adsorption is the most widely applied technique in water and wastewater treatment because polluted water normally contains multiple pollutants. Polluted water contains both dangerous organic contaminants like synthetic dyes such as Methylene Blue (Kazeem et al., 2018; Shakoor and Nasar, 2017) as well as harmful inorganic elements such as Fe, Si, S and Cu (Isique et al., 2017). Some selected engineered adsorbents and their application for removal of a specific kind of adsorbents from different type of polluted water is given in Table 2.1. It is clear from Table 2.1 that activated carbon can be used for removal of pollutants (Kyzas et al., 2015) form more type of contaminated water (including drinking water, wastewater, groundwater, landfill leachate, and aquarium water) so activated carbon is considered as one of the most important synthesized adsorbents.

Table 2.1 Type of water treatment and recommended adsorbents

Type of Water Treatment	Removal of Impurities	Recommended Adsorbent
Drinking water treatment	Dissolved organic matter, Organic micropollutants	Activated carbon
	As	Aluminium oxide, iron hydroxide
Urban wastewater treatment	Phosphate	Aluminum oxide, iron hydroxide
	Micropollutants	Activated carbon
Industrial wastewater treatment	Removal or recycling of specific chemicals	Activated carbon, polymeric adsorbents
Swimming-pool water treatment	Organic substances	Activated carbon
Groundwater remediation	Organic substances	Activated carbon
Treatment of landfill leachate	Organic substances	Activated carbon
Aquarium water treatment	Organic substances	Activated carbon

(Source: Shirtcliffe, 2008)

The adsorbents mentioned above are the engineered one which requires preparation to maintain the same energy level. But we have some naturally occurring adsorbents which does not require specific preparations. So, in the next sections classification of adsorbents, characteristic of adsorbents and use of adsorption technique for water treatment, are given.

2.4 CLASSIFICATION OF ADSORBENTS

Adsorbents used for water treatment are classified as natural adsorbents and engineered adsorbents. Natural adsorbents are found in the environment naturally. Natural adsorbents used for water treatment include clay minerals, natural zeolites (Shirtcliffe, 2008), oxides, and biopolymers etc. Engineered adsorbents are produced in the industries by mechanical means. Engineered adsorbents used for water treatment include carbonaceous adsorbents (for example activated carbon), polymeric adsorbents, oxidic adsorbents, and zeolite molecular sieves etc. In recent decades, an increasing interest in using wastes and by-products as alternative LCAs can be observed. So, in the following sections properties of LCAs and their classification are discussed.

2.4.1 Natural LCAs

High cost of engineered adsorbents has shifted the interest of researchers towards development of efficient LCAs using naturally occurring materials in recent times. The main aim of studies dealing with this field has been to develop LCAs which can easily replace high cost engineered adsorbents. Speedy industrialization of the world has led to the generation of wastewater in huge quantities resulting in large scale environmental pollution. Thus, a treatment technology providing effective removal of contaminants (Zhou et al., 2018) at a low cost is needed to reduce the cost of treatment and environmental pollution. To overcome this problem, search of novel LCAs has gained pace and a number of articles dealing with LCAs have emerged recently. Review of literature allowed a broad classification of LCAs as shown in Fig. 2.4. It is evident from Fig. 2.4 that agricultural and industrial by products can be used as LCA (Ahmaruzzaman, 2011; Demirbas, 2008). Agricultural and industrial by products can truly come under the category of LCAs because fast industrialization and mechanization of agriculture have resulted in generation of these byproducts in large amount. So these byproducts are available cheaply and can be used as adsorbents untreated or with a minor physical and chemical pretreatment processes, such as heating or treatment with hydrolyzing chemicals. Since industries generate the wastewater on large scale so the study of adsorption properties of LCAs were mainly directed towards removal industrial pollutants.

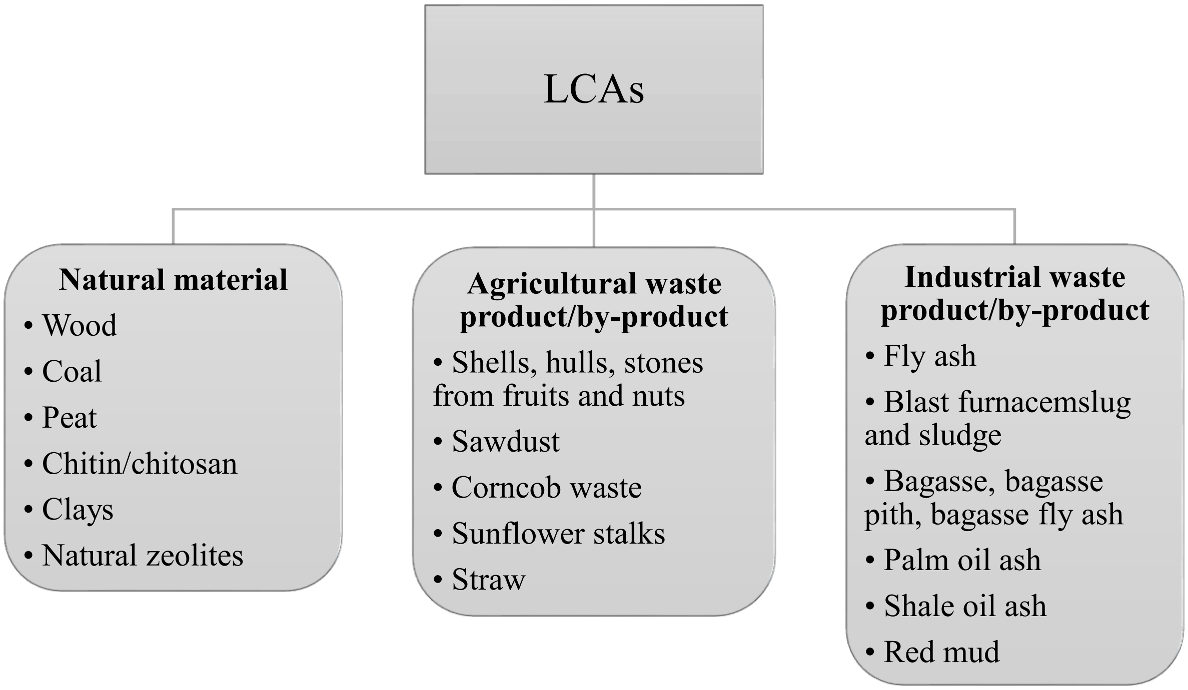


Fig. 2.4 LCAs obtained from different sources

(Source: Shirtcliffe, 2008)

Although a number of studies have evolved on the application of LCAs, it is still a new field of research. So, the prospect of application of LCAs is still in developmental phase because comprehensive adsorption mechanism with defined theoretical base and comparative studies under defined boundary conditions are yet to be developed. Hence, evaluation of practical importance of LCAs is still challenging. So, in this study well prepared compost sample having the property of clay as well as natural materials were used for the removal of PTEs from aqueous solution.

2.4.2 Properties of LCAs

In recent time use of LCAs have been increasing due to increasing cost of treatment of water and wastewater. In particular, there is considerable interest in LCAs, which may be suitable for use in the treatment of water contaminated by pollutants such as heavy metals (Callery et al., 2016). So, it becomes pertinent to understand the properties and characteristics of LCAs. This section provides some properties of LCAs with the next discussing the characterization of LCAs.

- Occur naturally so no extra preparation effort is needed.
- Due to occurrence in nature availability is not an issue.
- As the name suggests, LCAs are cheaply available in large quantities.
- Due to low cost, LCAs decreases the cost of treatment significantly.
- Environment friendly and can be regenerated and reused.
- Provide sustainable solution to the technologies employed in water and wastewater treatment.

2.5 ADSORBENT CHARACTERIZATION

Adsorbents characterization are done by the properties of adsorbent material so in this section properties of materials used as adsorbents are discussed in detail.

2.5.1 Densities

Porous material have different kind of volumes so they have different kind of densities too. Adsorbents are porous materials so material density, particle density (apparent density), and bulk (bed) density for it are defined in the following sections.

2.5.1.1 Material density

The material density, ρ_{mat}, is defined as the ratio of adsorbent mass, m_{ads}, and volume of the solid material, $V_{mat,}$ without pores. It is also known as true density or skeletal density.

$$\rho_{mat} = \frac{m_{ads}}{V_{mat}} \tag{2.11}$$

The instrument used for measuring the material volume is called pycnometer. Pycnometer does not measure the volume of material directly, it measures the volume of a gas or liquid that is displaced after introducing the adsorbent. So, material volume can be evaluated by using a suitable compound (gas or liquid) with small atom or molecule sizes which can fill the pores completely. For example, helium can be used to determine the material volume because it has an effective diameter of 0.2 nm which is small enough to fill the adsorbent pores (Shirtcliffe, 2008).

2.5.1.2 Particle density

The ratio of adsorbent mass, m_{ads}, and total adsorbent volume is known particle density, ρ_p. Sum of material volume and the volume of pores is defined as the total adsorbent volume.

$$\rho_p = \frac{m_{ads}}{V_t} = \frac{m_{ads}}{V_{mat}+V_{pore}} \tag{2.12}$$

Where V_t is the total adsorbent volume and V_{pore} is the volume of pores. The particle density is also referred to as apparent or superficial density (Shirtcliffe, 2008).

2.5.1.3 Bulk density (bed density)

An important parameter used in the design of adsorber is the bulk density, ρ_b, it is also known as bed density. It is the ratio of mass of adsorbent in the reactor and the total reactor volume V_R. Total reactor volume V_R is the sum of adsorbent volume, V_t, and the volume of liquid, V_l present in the reactor during the process of adsorption.

$$\rho_b = \frac{m_{ads}}{V_R} = \frac{m_{ads}}{V_l+V_t} = \frac{m_{ads}}{V_l+V_{mat}+V_{pore}} \tag{2.13}$$

Like the steady state adsorption tests of this study, batch reactors contain low amounts of adsorbent in a large volumes of wastewater so the bulk density of a reactor is more like concentration rather than that of a conventional density. There are two types of adsorbers used in the treatment of wastewater, fixed-bed adsorbers and batch reactors. Bulk density for fixed-bed adsorbers is known as bed density because a bed of adsorbent particles is used for adsorption of pollutants. Granules of material should be used to produce a uniform adsorbent (Iakovleva et al., 2016) in the bed. A bed of two solid adsorbents with magnetic properties for treatment of industrial wastewater polluted with heavy metals (Briso et al., 2018; Vukelic et al., 2018) could be used. To improve the adsorption effectivity composite material like PA-NCu or polyurethane foam coated with chitosan film could be used in fixed bed columns (Contreras et al., 2017; Machado Centenaro et al., 2017). This should be done because the void volume varies with filter backwashing and adsorbent resettling.

2.5.2 Porosity

Porosity is defined as the fraction of void space on the total volume. Like particle density and bulk density, particle porosity (ψ_P) and bulk porosity (ψ_B) are defined for adsorbent materials. Both the porosities depend on the volume considered and therefore can be derived from the densities (material density, particle density and bulk density). Bulk porosity is also called bed porosity (Shirtcliffe, 2008).

2.5.2.1 Particle porosity

Particle porosity is also known as internal porosity because it used to estimate the fraction of void volume available for adsorption. It can be obtained by dividing pore volume (V_{pore}) by the volume of the adsorbent particle, V_t.

$$\psi_P = \frac{V_{pore}}{V_t} = \frac{V_{pore}}{V_{mat}+V_{pore}} \tag{2.14}$$

Since, the porosities are generally calculated using densities, particle porosity is discussed in the form of densities (Shirtcliffe, 2008) as follows –

$$\psi_P = \frac{V_{pore}}{V_t} = \frac{V_t - V_{mat}}{V_t} = 1 - \frac{V_{mat}}{V_t} = 1 - \frac{\rho_p}{\rho_{mat}} \tag{2.15}$$

2.5.2.2 Bulk porosity

Bulk porosity, ψ_B, is also known external porosity. It is used to estimate the fraction of external void volume available for adsorption. Mathematically it is the ratio of V_l and V_R.

$$\psi_B = \frac{V_l}{V_R} = \frac{V_l}{V_t+V_l} \tag{2.16}$$

Bulk porosity can be written in the form of densities as follows –

$$\psi_B = \frac{V_l}{V_R} = \frac{V_R - V_t}{V_R} = 1 - \frac{V_t}{V_R} = 1 - \frac{\rho_b}{\rho_p} \tag{2.17}$$

As mentioned earlier, the term bulk porosity and bed porosity can be used interchangeably for fixed-bed adsorption. It is used to define characteristic conditions occurring in adsorber design equations in terms of different volume/volume or solid/volume ratios. Bulk porosity can be reduced by doing the Nanomaterials-enabled water and wastewater treatment as reviewed by (Zhang et al., 2016).

2.5.3 Surface Area

Rate of mass transfer in the process of adsorption is given by the following equation –

Mass transfer rate = mass transfer coefficient × area available for mass transfer × driving force

$$i.e. \qquad \frac{dm}{dt} = \tau AF \tag{2.18}$$

Where τ is the mass transfer coefficient, A is the available surface area and F is the driving force. The rate of mass transfer is affected both by external and internal surface areas. So, external and internal surface areas play an important role in characterization of adsorbents (Shirtcliffe, 2008).

2.5.3.1 External surface area

As explained above characterization of adsorbents depends on both internal and external surfaces. But external adsorption sites are available for adsorption of adsorbates first so external surface area affects the rate of mass transfer more than internal surface area does. So, for porous adsorbents external and internal mass transfers should be quantified separately. The mass transfer that occur through hydrodynamic boundary layer around the adsorbent particle is known as external mass transfer. The available surface area for adsorption can be approximated by external surface area as solute transport in porous media is also related to solute adsorption on a solid surface (Romero-Flores et al., 2018) in the mass transfer equation (Eq. 2.18) because the boundary layers around the particles are very thin (IUPAC, 1985).

Counting-weighing method is used for the determination of external surface area. By this method, If N_{ads} is the number of the adsorbent particles in a representative sample and $A_{S,P}$ is the average surface area of the particles. Then the external surface area, $E_{A,S}$ available for mass transfer is given by –

$$E_{A,S} = N_{ads} A_{S,P} \tag{2.19}$$

2.5.3.2 Internal surface area

Since, almost all adsorbents used are porous, they possess large internal surface area which is many times larger than the external surface area. So, internal surface area plays a huge role in determination of the whole adsorption capacity. Internal surface area is used in the selection of adsorbents because greater the adsorption capacity, better will be the adsorbent. Although, internal surface area is a quality parameter, it is alone cannot be used for characterization of adsorbent or prediction of the adsorption capacity of the adsorbent, because adsorption is also affected by many other properties of adsorbent and adsorbates including their interaction (IUPAC, 1994). Brunauer-Emmett-Teller (BET) isotherm and low-temperature gas adsorption are used in the determination of internal surface area using standard method. Since BET isotherms are used in this method, it is also known as BET method and the internal surface area determined is known as the BET surface area.

If, $Q_{F,L}$ is quantity of adsorbate adsorbed in the first layer and A_M is the area occupied by adsorbate particle (molecule, atom or ion) then the BET surface (A_{BET}) is given by –

$$A_{BET} = Q_{F,L} A_M N_A \tag{2.20}$$

Where N_A is Avogadro number (6.022×10^{23} mol^{-1}). For adsorption of nitrogen at 77 K, the value of A_M is $16.2 \cdot 10^{-20}$ m^2.

2.5.4 Pore Size Distribution

Shapes and sizes of the pores of adsorbents are not evenly distributed. Pore size varies significantly so the International Union for Pure and Applied Chemistry (IUPAC) have classified the pores into micropores, mesopores and macropores as shown in Table 2.2 (IUPAC, 1985). The interior mass transfer happens through the macropores and the mesopores because sizes of these pores are large enough for the mass transfer within the adsorbent particles. Micropores are too small for the interior mass transfer so these pore are used in the determination of the internal surface area and adsorption capacity. So, more the number of micropores available, greater will be adsorption capacity of the adsorbent. But larger adsorbate specicies can limit the extent of adsorption by size exclusion there by reducing the adsorption capacity of the adsorbents. Size exclusion can be seen in the adsorption (on microporous adsorbents) of organic matters which generally have larger molecular weight. Size exclusion may reduce the adsorption capacity significantly. In practice to avoid the size exclusion it becomes pertinent to develop mesoporous material like KIT-6 (Fernandes et al., 2018).

Table 2.2 IUPAC, 1985: Classification of pore size of adsorbents

Class of Pore	Range of Size
Micropores	< 1 nm
Mesopores	1 nm to 25 nm
Macropores	> 25 nm

2.5.5 Surface Chemistry

Surface chemistry has a major influence on the adsorbate-adsorbent interaction but it depends on the type of adsorbent used. This influence is more for the adsorption of ionic species onto oxidic adsorbents, but it can be relevant for adsorption onto engineered adsorbents and natural adsorbents.

2.5.6 Desorption Regeneration and Reactivation

Some of the important parameters which are used in characterization of adsorbents are its ease of desorption, regeneration, and reactivation. Easier the desorption, regeneration and reactivation better will be the adsorbent. Desorption is the reverse of adsorption which is essential for regeneration. In desorption adsorbates are removed from adsorbent surface so all the conditions that hinder the process of adsorption are favorable for desorption. Three methods applied for the desorption of adsorbates are thermal desorption, solvent extraction, and pH variation. Thermal desorption also known as desorption by steam is the process of desorption in which adsorbates are transferred from adsorbents surface into the gas phase. Desorption by both solvent extraction and pH variation involves the transfer of adsorbates into a liquid phase. Desorption solvent optimization could be done to obtain the maximum desorption efficiency (Huang et al., 2018). If the aim of desorption is the recovery of valuable substances (for example in wastewater treatment) from desorbate (the receiving gas or liquid phase), a phase separation process should be applied following the process of desorption. Adsorbates can be extracted from conventional solvents and in special cases from supercritical fluids for example from supercritical CO_2. It can be achieved by two-phase removal mechanism: initial rapid desorption followed by slower biodegradation likely coupled with the dynamic equilibrium achieved between the adsorbent and solution (Myers et al., 2018).

2.5.6.1 Factors affecting the regeneration and reactivation

The selection of an appropriate regeneration/reactivation process depends generally but not limited to a number of factors, including –

- The type of the adsorbent used.
- The character of the treated water, in particular number and nature of the accumulated adsorbates.
- Further treatment objectives, additional to the restoration of the adsorbent capacity (e.g. recovery of valuable substances).
- Economic efficiency (Vukelic et al., 2018) etc.

2.6 ADSORPTION EQUILIBRIUM

Development of methods for treatment of water or wastewater using adsorption technique requires deep understanding and knowledge of adsorption equilibrium and its mathematical formulation. The knowledge of adsorption equilibrium data provides the basis for assessing the adsorption processes and, in particular, for adsorber design. Information about the equilibrium in a considered adsorbate-adsorbent system is necessary, for instance, to characterize the adsorbability of water pollutants, to select an appropriate adsorbent, and to design batch, flow-through, or fixed-bed adsorbers. The equilibrium position in a considered system depends on the strength of the adsorbate-adsorbent interactions and is significantly affected not only by the properties of the adsorbate and the adsorbent but also by properties of the aqueous solution, such as temperature (Sajid et al., 2018), pH value (Ahmaruzzaman, 2011), and occurrence of competing (Anastopoulos et al., 2018) adsorbates.

Mathematical formulation of adsorption equilibrium can be done by considering the single-solute adsorption first and then generalizing the same for multisolute adsorption because some general aspects of adsorption processes can be explained more clearly for the simple case where only one adsorbate has to be considered. For example the simple case of adsorption thermal energy storage by (Schreiber et al., 2018) to providing a validated dynamic model could be considered. Practically single solute adsorption is very rare but to develop a mathematical relation among variables concerned, a deep understanding of single solute adsorption is necessary because characterization of single solute adsorption is sufficient for the determination of adsorption capacities and comparison of adsorbabilities of individual adsorbents.

Last but not the least, the models for mathematical description or prediction of multisolute adsorption equilibria are typically based on single-solute adsorption isotherms. So, in the next section mathematical aspect of single-solute adsorption equilibrium is discussed and the equilibrium of multisolute adsorption is discussed in the sections following that.

2.6.1 Single-Solute Adsorption Equilibrium

Adsorption equilibrium depends on the following factors –

a) Variable adsorbate concentration,
b) Adsorbed amount (also referred to as adsorbent loading), and
c) Temperature.

Since, the amount adsorbed depends on the concentration of adsorbate and temperature of the system, for a single-solute adsorption, equilibrium in terms of above factors can be described as –

$$q_{eq} = f\left(C_{eq}, T\right) \tag{2.21}$$

Where q_{eq} is the adsorbed amount (adsorbent loading) at equilibrium, C_{eq} is the concentration of adsorbate at equilibrium and T is the temperature.

It is inconvenient to express the equilibrium at varying temperature. So, the adsorption equilibriums are expressed at constant temperatures in the form of adsorption isotherms as shown in Fig. 2.5. For a single-solute, adsorption equilibrium at constant temperature will be –

$$q_{eq} = f\left(C_{eq}\right) \qquad T = constant \tag{2.22}$$

Mathematical equation for the dependence of adsorbed amount at equilibrium (q_{eq}) on equilibrium concentration (C_{eq}) is determined at constant temperature. From the equation obtained for the curve shown in Fig. 2.5, q_{eq} at a given C_{eq} can be determined (Shirtcliffe, 2008).

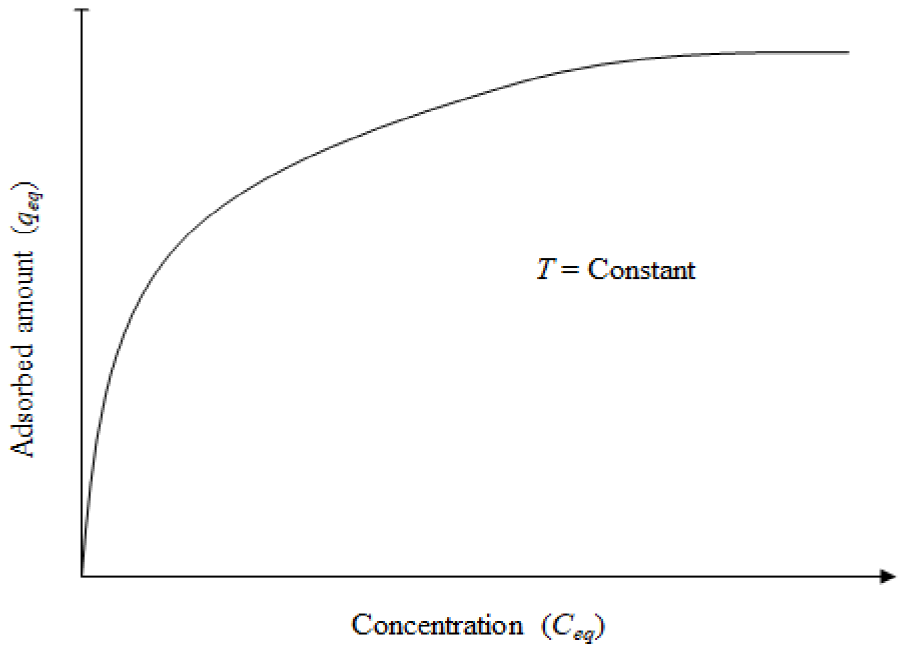


Fig. 2.5 Adsorption isotherm for single-solute equilibrium

2.6.1.1 Experimental determination of data at equilibrium

Adsorption tests are carried out to determine the values of q_{eq} and C_{eq}. If the initial concentration of adsorbate is C_0 in a given volume of experimental container V_L and the mass of adsorbent used is m_A then at equilibrium by mass balance equation –

Decrease in the mass of adsorbate = Increase in the mass of adsorbent (2.23)

i. e. $$m_0^l - m_{eq}^l = m_{eq}^a - m_A \quad (2.24)$$

Where m_0^l is the initial mass of adsorbate in the liquid, m_{eq}^l is the mass of adsorbate in the liquid at equilibrium, m_{eq}^a is the mass of adsorbent at equilibrium and m_A is initial mass of the adsorbent. Eq. 2.24 can be in the form of C_{eq} and q_{eq} as follows –

$$V_L\left(C_0 - C_{eq}\right) = m_A q_{eq} \quad (2.25)$$

i. e. $$q_{eq} = \frac{V_L}{m_A}\left(C_0 - C_{eq}\right) \quad (2.26)$$

2.6.1.2 Mathematical equation for isotherms

One parameter, two parameter, three parameter and more than three parameter equations can be fitted for single-solute adsorption as done by (Syafiuddin et al., 2018) for reliability and validity of isotherm models. Quality of data fitting increases with increasing number of parameters but complexity also increases with increasing number of parameters, making the isotherm unsuitable for adsorber models.

Therefore, the number of parameters should be as low as possible. One parameter model was of no significance and fitting three or more than three parameter model was not possible due to experimental limitations so, two parameter models based on the assumptions of Langmuir and Freundlich are discussed in the context of this study.

Two parameter Langmuir isotherm is written as –

$$q = \frac{q_m bc}{1+bc} \tag{2.27}$$

Where q_{eq} and C_{eq} are simply replaced by q and c because in Langmuir isotherm only equilibrium concentration and adsorbed amount are used. The two parameter used in Eq. 2.27 are q_m and b. Parameter q_m is measured in mg/kg and the unit of b is L/mg.

2.6.2 Multisolute Adsorption Equilibrium

In a multisolute adsorption (Wan Ngah and Hanafiah, 2008) competition effect also influences the amount of adsorption because in this case adsorbates present in the solution compete with each other for the available adsorption sites. So, the amount of adsorption at equilibrium, $q_{eq,i}$, of an adsorbate under consideration depends not only on the concentration of adsorbate itself, $C_{eq,i}$, but also on the equilibrium concentrations of remaining adsorbates. Therefore, if a solution contains N-adsorbates, its equilibrium can be represented by the following set of equations:

$$\begin{aligned} q_{eq,1} &= f(C_{eq,1}, C_{eq,2}, C_{eq,3}, \dots, C_{eq,N}) \\ q_{eq,2} &= f(C_{eq,1}, C_{eq,2}, C_{eq,3}, \dots, C_{eq,N}) \\ q_{eq,3} &= f\left(C_{eq,1}, C_{eq,2}, C_{eq,3}, \dots, C_{eq,N}\right) \\ &\vdots \\ q_{eq,N} &= f\left(C_{eq,1}, C_{eq,2}, C_{eq,3}, \dots, C_{eq,N}\right) \end{aligned} \tag{2.28}$$

Thermodynamic models and multicomponent isotherms (Gholitabar and Tahermansouri, 2017) are used to represent the multisolute adsorption. Thermodynamic models are preferred over multicomponent isotherm equations for representation of multisolute adsorption because these models possess more general characteristics and have broader application. Ideal Adsorbed Solution Theory (IAST) is used for prediction of multisolute adsorption from single-solute isotherm parameters so it has a dominant positon under the thermodynamic models. IAST is also considered as standard method for prediction of multisolute adsorption. Boundary conditions for these models are derived from the fundamental equations of the IAST.

2.6.2.1 Experimental determination of data at equilibrium

Since, multisolute adsorption involves N numbers of single-solute adsorption, experimental data for multisolute adsorption at equilibrium can be determined in the same way it was done for single-solute adsorption. So, the balance equations for the partial as well as total adsorbent loading can be written analogously to Eq. 2.26 as –

$$q_{eq,i} = \frac{V_L}{m_A}\left(C_{0,i} - C_{eq,i}\right) \qquad i = 1, 2, 3, \ldots\ldots, N \tag{2.29}$$

$$q_{eq,t} = \sum_{i=1}^{N} q_{eq,i} = \frac{V_L}{m_A}\left(\sum_{i=1}^{N} C_{0,i} - \sum_{i=1}^{N} C_{eq,i}\right) = \frac{V_L}{m_A}\left(C_{0,t} - C_{eq,t}\right) \tag{2.30}$$

Where $C_{0,i}$, $C_{eq,i}$ and $q_{eq,t}$ are the initial concentration of i'th solute, equilibrium concentration of the i'th solute and total adsorbent loading respectively of a multisolute adsorption system. In this study two solute (Cu^{2+} and Zn^{2+}) adsorption was studied and adsorption isotherms were drawn together representing single solute.

2.6.2.2 Mathematical equation for isotherms

Butler and Ockrent (1930) developed the extended form of Langmuir isotherm to describe the multisolute adsorption isotherm. In the extended form the partial component i in an N-solute adsorbate solution can be represented as –

$$q_i = \frac{q_m b_i c_i}{1 + \sum_{i=1}^{N} b_i c_i} \tag{2.31}$$

The parameters q_m and b have similar meaning as it was for the single-solute adsorption. However, solution for Eq. 2.31 exists only if the value of maximum loading of all components is equal. This is a sufficient but not a necessary condition so the extended Langmuir isotherm can be used even if this condition is not met, but then it will have an empirical character (Ayawei et al., 2017). The isotherms drawn in this study were also of empirical character but their applicability and practical significance cannot be avoided as they were drawn for a naturally and abundantly available LCA.

2.7 ERROR REDUCTION IN ISOTHERM DETERMINATION

Determination of isotherms could prove to be erroneous if utmost care has not taken while determining the experimental data (Coles and Yong, 2006). To reduce the experimental errors (Gholitabar and Tahermansouri, 2017; Hor et al., 2016) in isotherm determination, the following recommendations should be considered.

- A representative adsorbent sample should be taken.

- The adsorbent should be washed prior to use with ultrapure water to remove fine particles.
- After that, the adsorbent has to be dried at 110˚C because, by definition, the adsorbed amount is related to the dry mass of adsorbent. Alternatively, the exact moisture content has to be known.
- The dried adsorbent should be stored in a closed vessel or in a desiccator to avoid the uptake of water vapor.
- Taking into account the unavoidable analytical error in concentration measurement, the adsorbent dose should be chosen in such a way that the difference between the initial and equilibrium concentrations is not too small; otherwise the error in the calculated adsorbed amount may become very high.
- The applied adsorbent mass should not be too small to reduce errors resulting from particle loss or from heterogeneities in the adsorbent composition (e.g. residuals from the production process). If necessary, the volume has to be increased in parallel to the adsorbent mass to realize a designated adsorbent dose.
- After equilibration, the adsorbent particles have to be removed from the solution by filtration or centrifugation.

2.8 CHOOSING AN APPROPRIATE EQUILIBRIUM TIME

Choosing an appropriate equilibrium time is of greater significance in determination of adsorption isotherms. At a constant temperature the equilibrium time depends on the ratio C_{eq}/q_0, the particle radius, and the specific coefficients for the rate-limiting mass transfer. The minimum time required for adsorption to reach equilibrium is given by the following equations.

$$t_{min} = \frac{T_{B,min} r_p^2}{D_S} \tag{2.32}$$

$$t_{min} = \frac{T_{B,min} r_p^2 \rho_p q_{eq}}{D_p C_0} \tag{2.33}$$

Where r_p is the adsorbent particle radius, D_S is the surface diffusion coefficient, D_p is the pore diffusion coefficient, ρ_p is the particle density, q_{eq} is the adsorbent loading in equilibrium with initial concentration C_0, and $T_{B,min}$ is the minimum dimensionless time needed for approaching equilibrium.

2.9 PREDICTION OF ISOTHERMS

The easiest way to determine the isotherms experimentally is by batch isotherm tests. But, the batch isotherm test are less efficient method of isotherm determination and are time consuming. So, to avoid these time-consuming experiments, a number of studies have been carried out to find a model approach that allows predicting isotherms or isotherm parameters. In most practical cases, the isotherms of different adsorbates can be described satisfactorily by the following equation.

$$\log_e V_{ads} = \log_e \left(\frac{q}{\rho}\right) = A\left(\frac{\gamma}{N}\right)^B + \log_e V_0 \tag{2.34}$$

Where V_{ads} is the adsorbed volume, q is the adsorbent loading (mass/mass), ρ is the adsorbate density, γ is the adsorption potential, V_0 is the maximum volume available for the adsorbate, N is a normalizing factor, and A and B are empirical parameters. Since the adsorbate density in the adsorbed state (Ayawei et al., 2017) is unknown, the adsorbate density under normal conditions has to be used to calculate the adsorbed volume. The latter is based on the postulate that liquid and solid solutes will separate out as liquid-like or solid-like adsorbates.

But often it happens that some isotherms do not fall exactly on one single characteristic curve. Frequently, better correlations can be found if only compounds of the same substance class are considered. While the correlations within the substance groups are acceptable, clear differences exist between the class-specific characteristic curves. Certain deviations of experimental data from the characteristic curve within the same substance group may also exist.

2.10 APPLICATIONS OF ADSORPTION

The process of adsorption is very important as it has many applications in domestic as well as in industrial processes (Ayawei et al., 2017). Some of them are as follows –

1. **In heterogeneous catalysis:** Surface active materials are widely used as catalysts mostly due to adsorption processes. If the surface active materials (adsorbents) have a different phase from that of substrates, then the catalysis is called heterogeneous catalysis. A system where both the catalyst and the substrate are in same phase is called homogeneous catalysis.
2. **In removal of colouring material:** Many coloured materials or impurities are removed through adsorption by suitable surface active materials like charcoal. Activated charcoal has been extensively used for this purpose.
3. **In ion exchange resins:** Several polymeric materials are used for the separation of ionic substances in chromatography through ion-exchange.
4. **In adsorption indicators:** Several dyes like eosin and fluoresein are used as indicators in the titrations of Cl^- Br^- etc., against Ag^+ (Fajan's method).
5. **In gas masks:** Activated charcoal is used to remove toxic gases in gas masks.

6. **In dyeing of cloth:** Many substances work as mordants for dyeing of cloths. Several metal cyanogen complexes and alums work as efficient mordants in dyeing cloths.
7. **In de-humidifiers:** Many substances, when they adsorb water, change their colour. Silica and alumina gels are used as adsorbents for removing moisture. Silica is colourless but after adsorbing water becomes blue.
8. Application of adsorption also includes chromatographic separation, removal of colouring matter, curing diseases (e.g. extracorporeal blood purification and hemodialysis), and Froth flotation process.
9. **Purification:** Adsorption is most widely used in water industry because of its ability to capture multiple pollutants simultaneously. Generally, contaminated water contains several pollutants so adsorption is used as a purification technique.

2.11 ADSORPTION ISOTHERMS

Adsorption isotherm is a curve that expresses the variation in the amount of adsorbate adsorbed by the adsorbent with concentration at constant temperature. It may be defined as a relation between the amount of adsorbate adsorbed on a given surface at constant temperature and the equilibrium concentration of the substrate in contact with the adsorbent. The adsorption isotherms characterize the adsorbent. It depicts the nature of adsorption-desorption process (Rogala et al., 2017) occurring on the surface and also reveals the pore structure of the adsorbent. Often the isotherms for liquid-solid interface are expressed as amount adsorbed as a function of concentration at constant temperature.

2.11.1 Presentation of Primary Data

The quantity of adsorbate adsorbed is measured in any convenient units, but for the presentation of the data, it is recommended that the amount adsorbed should be expressed in mg/g of freshly prepared adsorbent for a liquid-solid interface adsorption. If possible, the composition of the adsorbent should be specified and its surface characterized. For instance, (Cegłowski et al., 2018) characterized the material obtained and tested their adsorption. To facilitate the comparison of adsorption data, it is recommended that adsorption isotherms are displayed in graphical form with the amount adsorbed plotted against the equilibrium concentration (Largitte and Pasquier, 2016).

2.11.2 Classification of Physisorption Isotherms

In the year 1985 IUPAC classified a new set of physisorption isotherms that were grouped into six types (IUPAC, 1985). Over the past 30 years various new characteristic types of isotherms have been identified and shown to be closely related to particular pore structures. But, in this study it was considered expedient to present the original IUPAC classifications of physisorption isotherms and associated hysteresis loops. The phenomena involved in the process of adsorption that should be considered in an adsorption model or determination of adsorption isotherms are –

a) Initial monomolecular adsorption: at low and high coverage,
b) Multilayer adsorption,
c) Chemisorption, and
d) Capillary condensation.

Considering the above mentioned phenomena adsorption isotherms can have very different shapes depending on the type of adsorbent, the type of adsorbate, and intermolecular interactions between the adsorbate and the solid surface (IUPAC, 1994). Although, isotherms of varying shapes have been observed in the literatures, the first systematic attempt to interpret adsorption isotherms for gas-solid equilibria was introduced by Brunauer, Deming, Deming, and Teller (BDDT) in 1940. These authors classified isotherms into five types. The BDDT classification has become the core of the modern IUPAC classification of adsorption isotherms. The BDDT isotherms and an additional one introduced much later by Sing, completes the IUPAC classification are illustrated in Fig. 2.6. So, IUPAC has classified the adsorption isotherms into six, as shown in the Fig. 2.6 below.

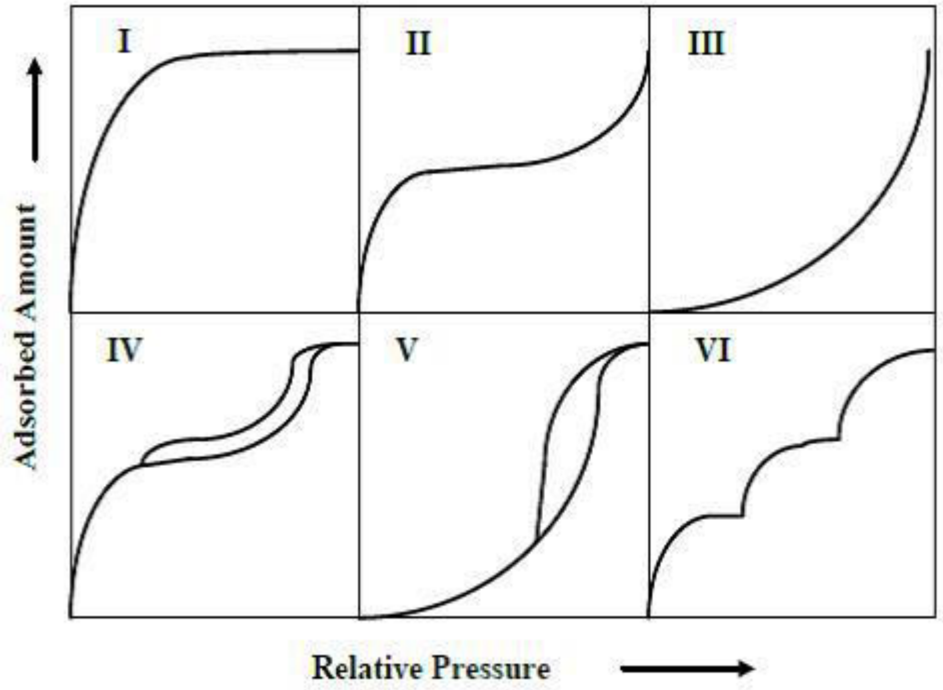


Fig. 2.6 IUPAC classification of adsorption isotherms

(Source: www.researchgate.net)

2.12 ADSORPTION HYSTERESIS

Reproducible, permanent hysteresis loops, which are located in the multilayer range of physisorption isotherms, are generally associated with capillary condensation (IUPAC, 1985). This form of hysteresis can be attributed to adsorption metastability and/or network effects. In an open-ended pore (e.g., of cylindrical geometry), delayed condensation is the result of metastability of the adsorbed multilayer. It follows that in an assembly of such pores the adsorption branch of the hysteresis loop is not in thermodynamic equilibrium (Pandiarajan et al., 2018). Since evaporation does not involve nucleation, the desorption stage is equivalent to a reversible liquid‑vapour transition. Therefore, if the pores are filled with liquid-like condensate (IUPAC, 1994), thermodynamic equilibration is established on the desorption branch.

2.12.1 Origin of Hysteresis

In more complex pore structures, the desorption path is often dependent on network effects and various forms of pore blocking. These phenomena occur if wide pores have access to the external surface only through narrow necks (e.g., ink-bottle pore shape). The wide pores are filled as before and remain filled during desorption until the narrow necks empty at lower vapour pressures. In a pore network, the desorption vapour pressures are dependent on the size and spatial distribution of the necks. If the neck diameters are not too small, the network may empty at a relative pressure corresponding to a characteristic percolation threshold. Then, useful information concerning the neck size can be obtained from the desorption branch of the isotherm.

Theoretical and experimental studies have revealed that if the neck diameter is smaller than a critical size (estimated to be 5‑6 nm for nitrogen at 77 K), the mechanism of desorption (Romero-Flores et al., 2018) from the larger pores involves cavitation (i.e., the spontaneous nucleation and growth of gas bubbles in the metastable condensed fluid). Cavitation controlled evaporation has been found for instance with certain micro-mesoporous silicas, mesoporous zeolites, clays, and also some activated carbons. Contrary to the situation of pore blocking/percolation controlled evaporation no quantitative information about the neck size and neck size distribution can be obtained in the case of cavitation.

With the development of the study at this stage it become pertinent to mention that the theories used to explain the process of adsorption of Cu^{2+} and Zn^{2+} from aqueous solution on compost are based on the original theories developed to study adsorption of gases on solids or in liquids. That is why it may appear at some places in the text that these are the explanations for adsorption of gas which is true.

But based on the review of literature evidence have been provided (where ever necessary) that with slight modification the original theory of adsorption on gas-solid or gas-liquid interface can be applied to the adsorption on liquid-solid interface and the required modifications have been incorporated too. In this study, purification of water using physisorption was studied so the conceptual background presented in this study are application mostly to physisorption but not restricted to it only.

2.12.2 Types of Hysteresis Loops

Many different shapes of hysteresis loops have been reported, but the main types are shown in Fig. 2.7. Types H1, H2 (a), H3 and H4 were identified in the original IUPAC classification of 1985 (IUPAC, 1985), which is now extended in the light of more recent findings. Each of these six characteristic types is fairly closely related to particular features of the pore structure and underlying adsorption mechanism.

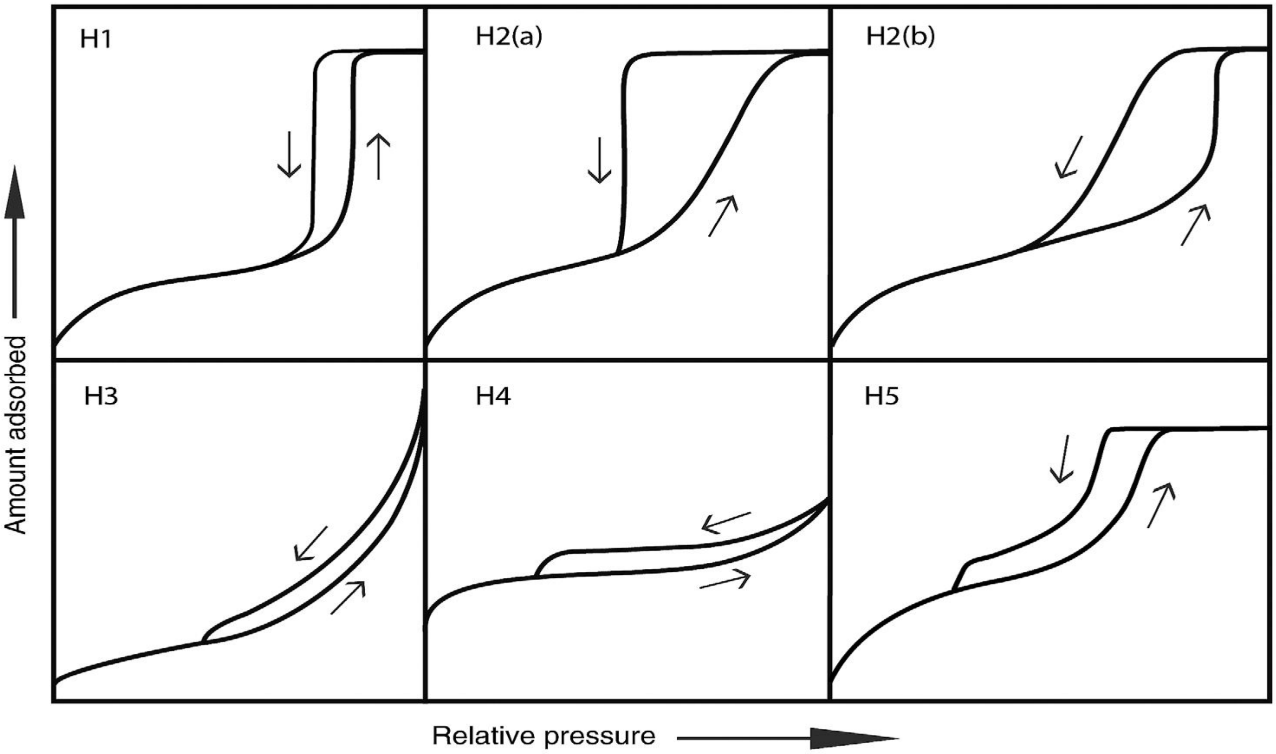


Fig. 2.7 Types of hysteresis loops found in the adsorption process
(Source: www.researchgate.net)

2.13 PORE SIZE DISTRIBUTION AND CAPILLARY CONDENSATION

The two important terms used above to explain the type of adsorption isotherms and hysteresis loops found in the isotherms are porous adsorbents and capillary condensation. Porous adsorbents are classified based on their pore size distribution presented in section 2.5.4 of this chapter. IUPAC recommended pore size distribution is presented there and it was used as a supplementary concept to the theoretical background of the study. Capillary condensation is a phenomenon whereby a gas condenses to a liquid-like phase in a pore at a pressure (*p*) less than saturation pressure (p_0) of the bulk liquid (IUPAC, 1985). Since, adsorption is reversible in nature, hysteresis loops occur in the adsorption isotherms and capillary condensation is one of the reasons for it. As the adsorption progresses, isotherm passes through points A, B, C, D, E, and F shown in Fig. 2.8. Point A represents a monolayer formation, point B represents multilayer adsorption, point C shows a situation when critical film thickness is reached, D is the point where capillary condensation occurs, point E occur corresponding to pore evaporation, and point F on the curve shows multilayer film after adsorption in the Fig. 2.8.

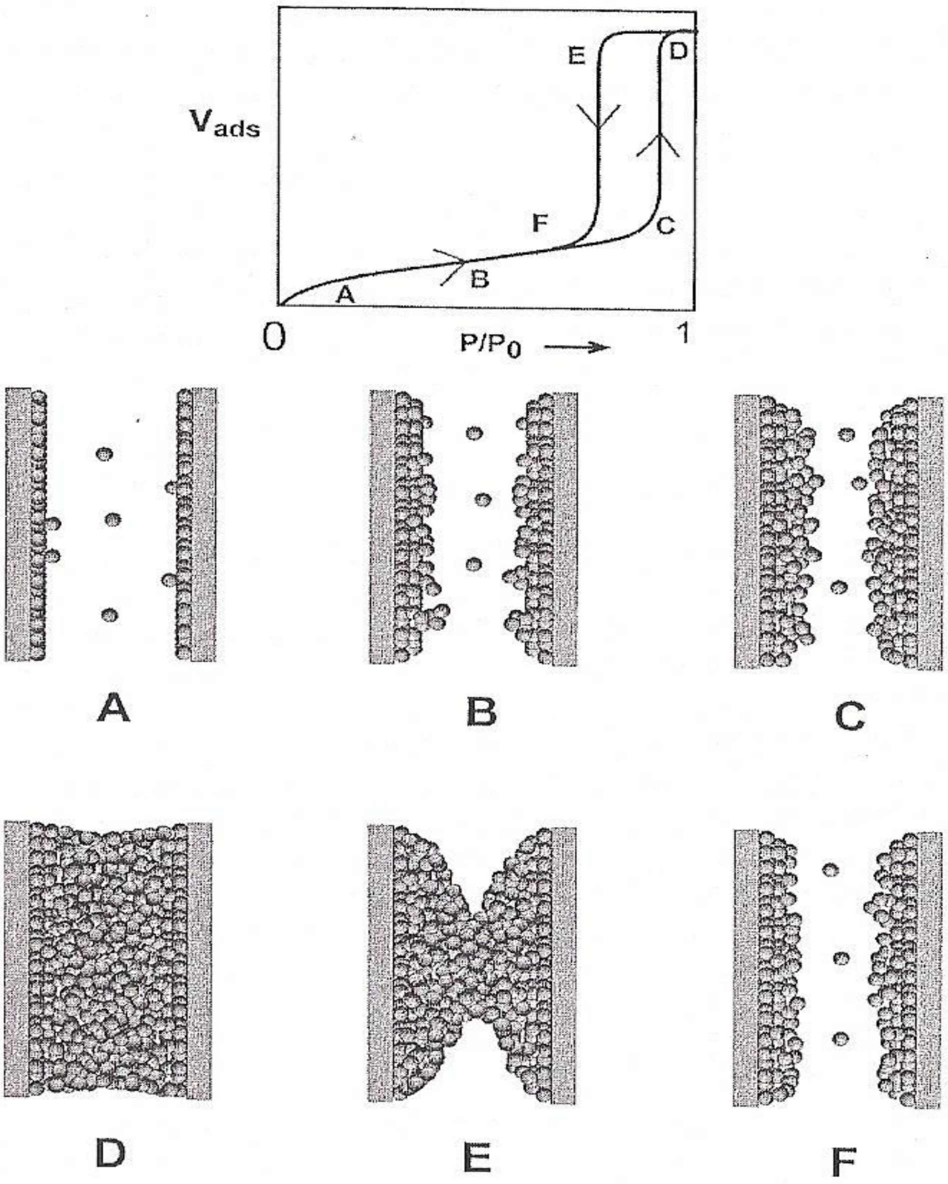
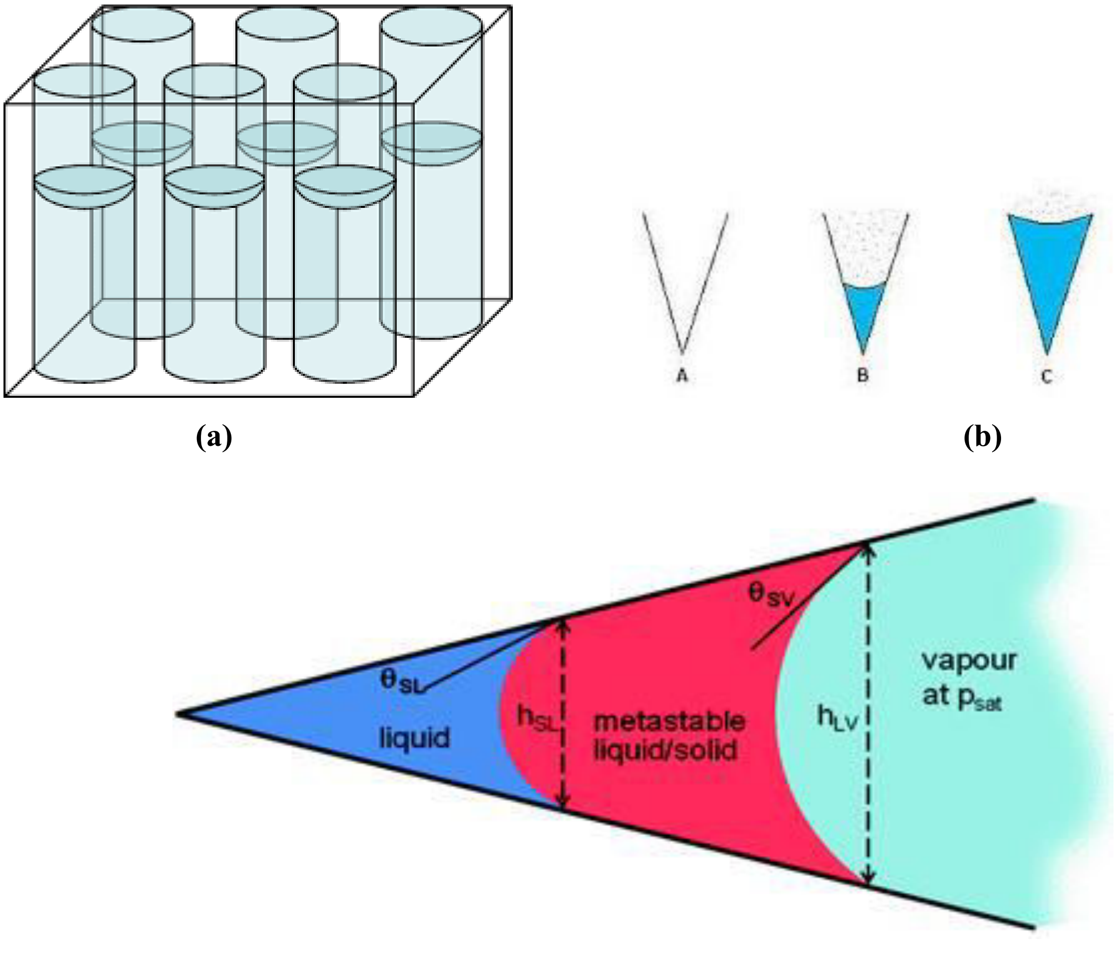


Fig. 2.8 Phenomena of capillary condensation

(Source: www.fhi-berlin.mpg.de/acnew)

Once condensation has occurred, a meniscus immediately forms at the liquid-vapor interface which allows equilibrium to occur below saturation vapor pressure. Fig. 2.9 (a) shows the capillaries found in porous adsorbents, fig. 2.9 (b) denotes the development of meniscus below saturation pressure of liquid, and fig. 2.9 (c) symbolizes the variable require to determine the dimensions of the meniscus. The variables that are needed at metastable liquid-solid interface (Shirtcliffe, 2008) are the contact angle (θ_{SL}) and height of the curvature of meniscus (h_{SL}). Similarly, the contact angle at solid-vapour interface (θ_{SV}) in upper part of the capillary and height of curvature of the upper meniscus (h_{LV}) at liquid-vapor interface are the variables required to determine the dimensions of upper meniscus. Although, phenomena of capillary condensation mostly occurs during adsorption of gasses on solids, it is imperative to explain it here because the theories developed for adsorption of substances from liquid onto the solid are based on the concept of adsorption of gases on solids and it also helps in replacing the corresponding variable like surface energy used in adsorption of gases by surface tension in adsorption from liquids on solids.



(a) **(b)**

(c)

Fig. 2.9 Formation of meniscus during capillary condensation

(Source: www.keresearchgroup.com/uploads)

2.14 MODELS FOR FITTING OF ADSORPTION ISOTHERMS

Since, error reduction in determination of adsorption isotherms and prediction of isotherms are already discussed in section 2.7 and section 2.9 respectively in this chapter, to strengthen the theoretical background needed to develop this study, model for fitting of adsorption isotherms is discussed in this section with the basic concepts of adsorption isotherms discussed above. Knowledge of nature of adsorbents helps in deciding what type of isotherm will be obtained. Once the type of isotherm is known, model of fit for it can be chosen with the help of Table 2.3. Table 2.3 summarizes the type of adsorption isotherms, general model of fit for it and nature of adsorbent for which a particular type of isotherm is obtained.

Table 2.3 Type of isotherms their mathematical forms and nature of adsorbents

Isotherm	Form of Adsorption	Nature of Adsorbent
Type I	Langmuir model	Porous material with small pores (Generally microporous material)
Type II	Sigmoid curve	Non-porous material
Type III	Hyperbolic	Porous material with cohesive force between adsorbate particles greater than the adhesive force between adsorbate particles and adsorbent
Type IV	Sharp approach to the line C_0 S-Curve	Mesoporous adsorbents with pores radius range of approximately 15-1000 Angstroms (Å)
Type V	Elongated S-Curve	Porous materials with cohesive force between adsorbate particle and adsorbent being greater than that between adsorbate particles
Type VI	Sigmoid curve in intervals for steps	Uniform non-porous material

2.14.1 Adsorption Isotherms in Solid-Liquid Systems

Interaction between adsorbent and adsorbate may fall into two categories –

1. Weak and reversible physical adsorption, or
2. Stronger, irreversible or chemisorption

The isotherm can be classified into four fundamental isotherm shapes based on the form at low concentrations as shown in Fig. 2.10. Since, physisorption at low concentration (Shirtcliffe, 2008) was studied during the course of this study, it become imperative to discuss the shapes of isotherms observed for adsorption in solid-liquid system while discussing the fitting of isotherms.

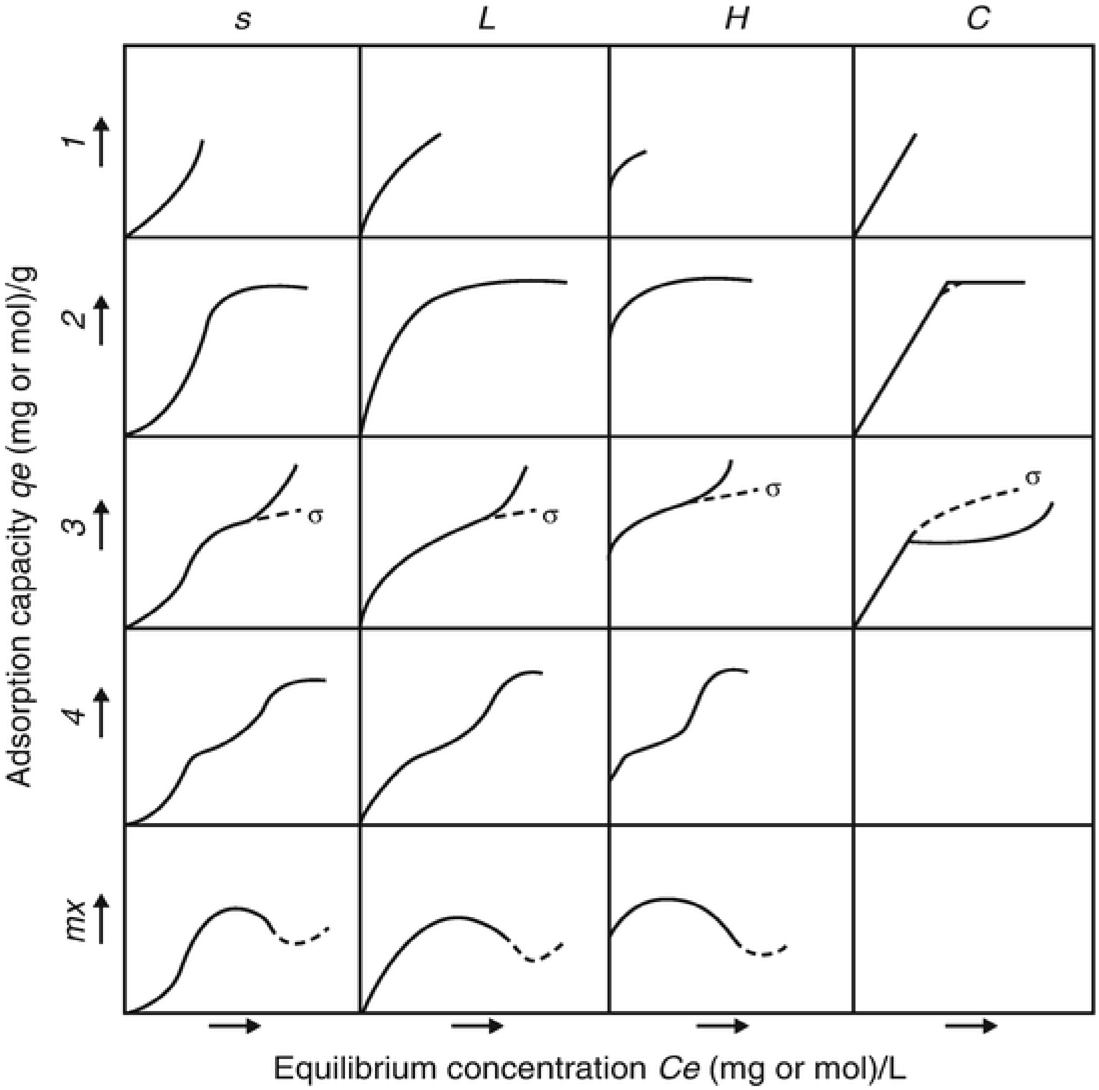


Fig. 2.10 Shape of isotherms for solid-liquid system

(Source: www.researchgate.net)

S-class: Initial slope of S-class is convex to the concentration axis. S1, and then S2 →S4 shown in Fig. 2.10 are happen to be Type III and/or Type V isotherms.

L-class: Also called Langmuir isotherm is identified by having its initial region concave to the concentration axis. As concentration of adsorbate increases, it reaches a plateau (L2) and then L3, and L4. L-class shown in Fig. 2.10 are normally Type I, Type II or Type IV isotherms.

H-class: Also known as high affinity class are observed for a very strong adsorption at low adsorbate concentrations. The isotherm has a positive intercept on the ordinate.

C-class: This class exhibits an initial linear portion of isotherm, indicating a constant partitioning of the adsorbate between the solution and the solid. C-class shapes occur in solid with microporous structure, but not for homogeneous solid surfaces (IUPAC, 1994).

2.14.2 Equations for Adsorption Isotherms

Equations for some popular adsorption models used to fit isotherms and to explain the process of adsorption are given in Table 2.4.

Table 2.4 Linear forms of two parameter isotherm models

Isotherm models	Linear form	Plot
Hill-Deboer isotherm	$\ln\frac{C_e(1-\theta)}{\theta}-\frac{\theta}{1-\theta}=-ln\,K_1-\frac{K_2\theta}{RT}$	$\ln\frac{C_e(1-\theta)}{\theta}-\frac{\theta}{1-\theta}$ versus θ
Fowler-Guggenheim isotherm	$\ln\frac{C_e(1-\theta)}{\theta}=-ln\,K_{FG}+\frac{2\omega\theta}{RT}$	$\ln\frac{C_e(1-\theta)}{\theta}$ versus θ
Langmuir isotherm	$\frac{C_e}{Q_e}=\frac{1}{Q_{max}K_L}+\frac{C_e}{Q_{max}}$	$\frac{C_e}{Q_e}$ versus C_e
Freundlich isotherm	$lnQ_e=ln\,K_f+\frac{1}{n}lnC_e$	lnQ_e versus lnC_e
Dubinin Radushkevitch isotherm	$lnQ_e=lnQ_{max}-\beta\varepsilon^2$	lnQ_e versus ε^2
Temkin isotherm	$Q_e=B_TlnK_T+B_TlnC_e$	Q_e versus lnC_e
Flory-Huggins isotherm	$\ln\frac{\theta}{C_0}=ln\,K_{FH}+n\,ln(1-\theta)$	$\ln\frac{\theta}{C_0}$ versus $ln(1-\theta)$
Hill isotherm	$\ln\frac{Q_e}{Q_H-Q_e}=n_Hln\,C_e-ln\,K_D$	$\ln\frac{Q_e}{Q_H-Q_e}$ versus lnC_e
Halsey isotherm	$lnQ_e=\frac{1}{n_H}ln\,K_H+\frac{1}{n_H}lnC_e$	lnQ_e versus lnC_e
Harkin-Jura isotherm	$\frac{1}{{Q_e}^2}=\frac{B}{A}-\frac{1}{A}logC_e$	$\frac{1}{{Q_e}^2}$ versus $logC_e$
Jovanovic isotherm	$lnQ_e=lnQ_{max}-K_1C_e$	lnQ_e versus C_e
Elovich isotherm	$ln\frac{Q_e}{C_e}=ln(K_eQ_{max})-\frac{1}{Q_{max}}Q_e$	$ln\frac{Q_e}{C_e}$ versus Q_e
Kiselev isotherm	$\frac{1}{C_e(1-\theta)}=\frac{K_i}{\theta}+K_iK_n$	$\frac{1}{C_e(1-\theta)}$ versus $\frac{1}{\theta}$

All the models presented in Table 2.4 are two parameter models. Over the years several models have been developed but the models given in Table 2.4 covers almost all aspects of adsorption process. Although, higher parameter models have been developed (Ayawei et al., 2017), to given limit the models given in Table 2.4 are applicable in every stage of adsorption (Komárek et al., 2018). The symbols used in the models given in Table 2.4 have their usual meaning. To cover the aspects of this study, meaning of some symbols are explained while development of model for this study.

2.15 APPLICATIONS OF ADSORPTION ISOTHERMS

Adsorption isotherms in a solid-liquid system are used for describing the adsorption mechanism and behaviour of adsorbents. Some common applications of adsorption isotherms are listed below.

1. To assess the spontaneity and exothermicity of a system.
2. Percentage removal of adsorbate could also be evaluated with the help of isotherms.
3. Langmuir parameters helps in determining maximum adsorption uptake and affinity between adsorbent and adsorbate.
4. Freundlich parameters could well be used to estimate the adsorption capacity of adsorbents.
5. Dubinin Radushkevitch (D-R) parameters are helpful in explaining the adsorption mechanism.
6. Temkin parameters are used to study the adsorbate-adsorbent interactions.

2.16 STRENGTH OF CONTEMPORARY RESEARCH

Review of the reported literature and the background of the study shows that following strengths of contemporary research can be cited:

- Many international research journals (Bhattacharya et al., 2006; Krstić et al., 2018) have published and given significant importance and thrust to the research on ‘The removal of PTEs from water using LCAs’. Many research articles have also discussed issues concerned with the removal of heavy metals using adsorption as a technique. Adsorption is used in the tertiary (3^0) treatment of polluted water in water industries. These journals and articles have been referred for the literature review and are indicated in the References section. Such publications provide a major boost to the research in the area of water and wastewater treatment.
- Recent technological advances for removal of PTEs from contaminated water using LCAs have led to the sudden and sustained scope of improvement in developing LCAs from agricultural waste and industrial waste. This has drawn attention of the researchers studying technical as well as commercial issues affecting use of LCAs in water and wastewater treatment.
- Water industry has now recognized the significance of effective adoption of adsorption technique involving LCAs for removal of PTEs from contaminated water for reducing the cost of treatment significantly. Research work and publications provide a base for researchers in this area to do further research and share their research findings and also to improve the quality of adsorbents and technical developments in this area. Publication dealing with the use of LCAs for adsorption of PTEs are referred in the literature and are indicated in the References section.

- As discussed in various section of this chapter that toxicity of PTEs cannot be compromised, removal of it from contaminated water is very necessary at the same time cost of removal should also be minimized so the use of LCAs for removal of PTEs with the advancements should be reinvigorated.

2.17 GAPS IN EXISTING KNOWLEDGE AND IDENTIFICATION OF RESEARCH AREAS

It is evident from the reported literatures in the study that water quality is degrading due to continuous pollution of water sources which has been a matter of concern for civic bodies. In the recent past civic body administrations have spent a lot on improving the water quality. Despite their hard fought efforts to improve the water quality using expensive PTEs removal technologies, they could not find a cost effective solution to this long persisting problem. So, alternative treatment methods using LCAs were used to improve the conventional treatment processes so that the process of purification could become cost effective. A wide range of LCAs were used to achieve the desired water quality.

The source of LCAs used for wastewater treatment could be agricultural waste, seafood waste, food waste, industrial by-product or soil. These adsorbents could be considered as better alternatives because there are easily and readily available in huge amount. Moreover, these are the waste products of the respective sources. These LCAs provide an alternative cost effective treatment because these could be used directly or with a small pretreatment which is inexpensive and not very complicated to do. Use of LCAs have been reported widely in the studies conducted in the recent past but its efficiency in removing metal ions from aqueous solution or wastewater has been the matter of concern for researcher. In this study, the LCAs used fall under agricultural and domestic waste category. The LCAs used were the compost collected from waste processing plants in Hungary.

To minimize the gaps in the existing knowledge, factors affecting the maximum adsorption capacity, efficiency and performance of adsorbents were studied in detail in this study. Comparisons of the different fractions of adsorbents obtained from different source were also done to make the selection of available adsorbents easier. LCAs used in this study were found to be the good adsorbents excluding some which shown the sign of weaknesses. To counter this, SWOT (strength, weakness, opportunities, threat) analysis was also conducted on the fractions of samples used in this study. SWOT analysis helped in countering the weaknesses encountered by the use of compost as LCAs. Advantages of using low-cost material as adsorbents were also identified using SWOT analysis. Application of SWOT analysis in the identified research area helped in identifying the quality of low-cost materials which could be used in water and wastewater treatment.

Chapter 3

METHODOLOGY

3.1 STUDY AREA

Once the study variables were selected, hypothesis was formulated, precursors for LCAs to be used in the study were decided and processing methods for the development of LCAs to be used in this study was decided, it was the time for deciding the study area for sample collection. For carrying out the study, sample were collected from seven waste management plants of Hungary as shown in Fig. 3.1. Hungary, situated in the heart of central Europe is a member of OECD, NATO, EU and the Schengen Convention (Hungarian Geographical Bulletin, 2009). Administratively, Hungary is divided into 19 counties with the capital city of Budapest being independent of any county government. Hungary is one of the 25 most popular tourist destinations in the world with a capital regarded as one of the most beautiful cities. Despite its relatively small size, the country is home to numerous World Heritage Sites, UNESCO Biosphere Reserves, the second largest thermal lake in the world (Lake Hévíz), the largest lake in Central Europe (Lake Balaton), and the largest natural grassland in Europe (Hortobágy).

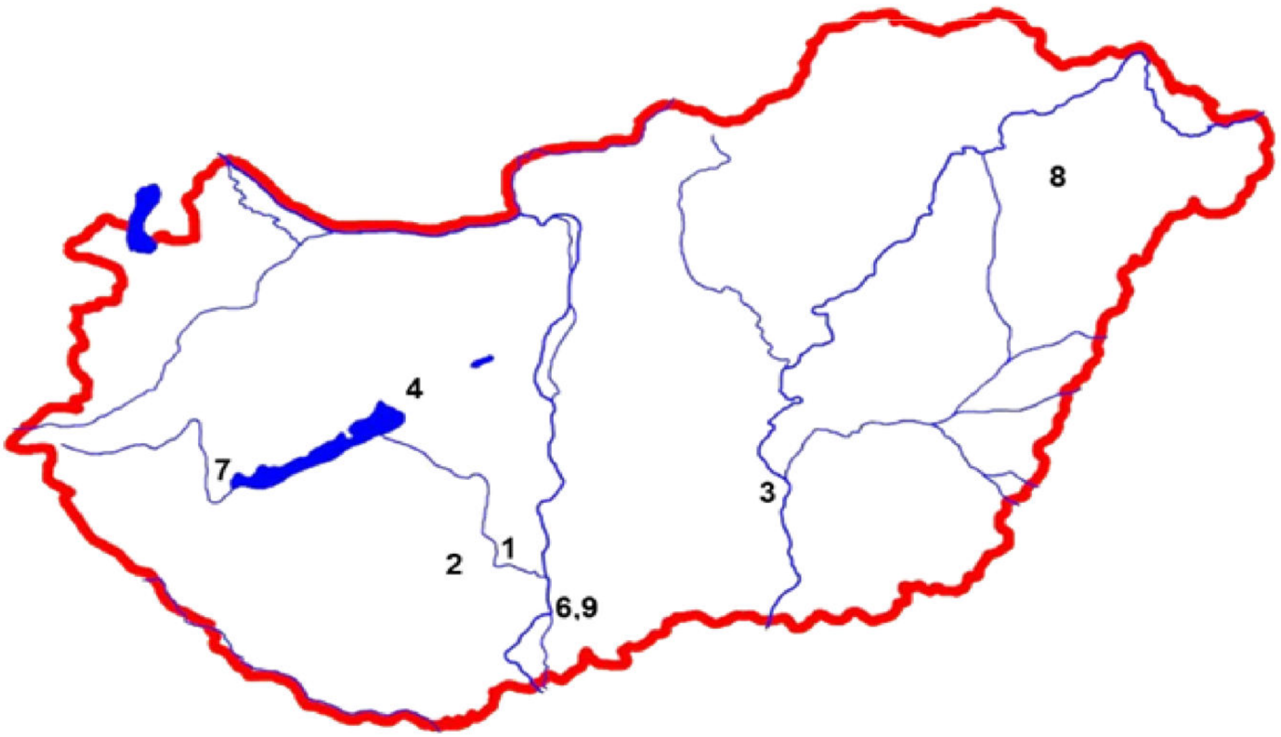


Fig. 3.1 Sampling locations in the map of Hungary
(Source: https://upload.wikimedia.org/wikipedia/hu/4/4f/Magyarorsz%C3%A1g.png)

Hungary is a landlocked country, situated in the Carpathian Basin at Longitude: 19° 30' 20.71" E and Latitude: 47° 09' 40.18" N. Spanning 35,920 square mi in the Carpathian Basin, it borders Slovakia to the north, Ukraine to the northeast, Austria to the northwest, Romania to the east, Serbia to the south, Croatia to the southwest, and Slovenia to the west. Its two longest rivers called Danube and Tisza divide Hungary into three parts: Transdanubia (to the west of the Danube), the plain between the Rivers Danube and Tisza, and the Trans-Tisza region (to the east of the Tisza). Hungary's 'mountains' are actually hills, which seldom exceed an elevation of 1,000 meters. Two-thirds of Hungary's geographic area is less than 200 meters above sea level. Protected from extreme weather conditions by the surrounding mountain ranges, the Alps and the Carpathians, Hungary is in the temperate zone and has a relatively dry continental climate (Hungarian Geographical Bulletin, 2009). There are big differences in temperature between the four seasons: summers are hot, while winters are cold. Average temperatures range from -1 °C in January to 21 °C in July.

For municipal solid waste (MSW) collection, Hungary is divided into seven regions as shown in Fig. 3.2. The population of most regions is around 1.0-1.5 million, while it is higher in the central region around Budapest in the Közép-Magyarország (Central Hungary) (Herczeg, 2013). The population of the Közép-Magyarország region, is approximately 3.0 million (Hungarian Geographical Bulletin, 2009) with a MSW generation of 1.5 million tonnes, nearly three times the average of other regions. So. Central Hungary is responsible for more than a third of the municipal waste generated in the country. The Közép-Magyarország region is also where the country's only municipal waste incinerator is operating (Herczeg, 2013), other parts of the country have lower population density, making transportation costs a more significant factor of waste management.

Fig. 3.2 MSW collection regions in Hungary
(Source: Herczeg, 2013)

The Republic of Hungary with its population nearly 10 million and geographical area of 93,030 square kilometers (Hungarian Geographical Bulletin, 2009) generates approximately 4.1 million tonnes of MSW (Herczeg, 2013). From this amount, around 62 % is household waste and the rest is similar waste generated by institutions, service providers, and businesses. Approximately 85% of the MSW generated is used for landfills. But, according to the EU Landfill Directive, it is a general requirement that Member States have to reduce the amount of biodegradable municipal waste (BMW) landfills by 2006, 2009 and 2016. The targets are related to generated amount of BMW in 1995, in which year Hungary generated close to 2 million tonnes of BMW, consisting of 1.17 million tonnes of bio-waste and 765 000 tonnes of paper waste (Herczeg, 2013). So, to meet the EU Landfill Directive, Hungary started processing the MSW into reusable products like compost. As a result of that several MSW processing plants were built in Hungary. The Quality of compost produced at these plants is as good as it can be used as LCA instead of using material like modified fly ash, clay and chitosan etc. because the carbon content of these samples was higher than the fly ash, clay and chitosan, providing the samples higher adsorption capacity.

3.1.1 Sample Collection

Fig. 3.1 shows the location of seven plant (6 and 9 are showing one location) from where samples were collected for this study. The number 1 in the Fig. 3.1 is showing Sióagárd, 2 Bonyhád, 3 Felgyő, 4 Polgárdi, 7 Keszthely, 8 Nyíregyháza, and 6 and 9 are showing Baja. Since, the samples collected were numbered from 1 to 9 that is why the location shown in the Fig. 3.1 are also nubered from 1 to 9. Number 5 is not shown in the Fig. 3.1 because sample 5 was the mixture of some sampmes collected that is why there was no fixed location for sample 5. Two different category of samples (Sample 6 and Sample 9) were collected from Baja that is why both 6 and 9 are showing the same location (Baja) in the Fig. 3.1.

3.2 FRAMEWORK OF THE STUDY

Research Aim and Objectives conceptualized the focus of this study, projecting factors that underpin effective adsorption of PTEs from aqueous solution using LCAs. Framework of this study was developed in two parts namely conceptual framework and methodological framework. Section 3.2.1 provides the evolution of conceptual framework of this study. Methodological framework of the study is described in detail in section 3.2.2, which presents a description of the step by step processing of data to get the results.

3.2.1 Conceptual Framework

Conceptual framework of a study helps to structure the research process into logical steps and appropriate stages. The establishment of a plan helps to guide and direct the research so that there is a clear connection between all the stages, i.e. formulation of research aim and objectives, literature review, data collection and analysis and the findings and conclusions identified in the course of the analysis. Fig. 3.3 provides the conceptual framework of the study that encompasses the research processes, which were applied and were suitable for this study.

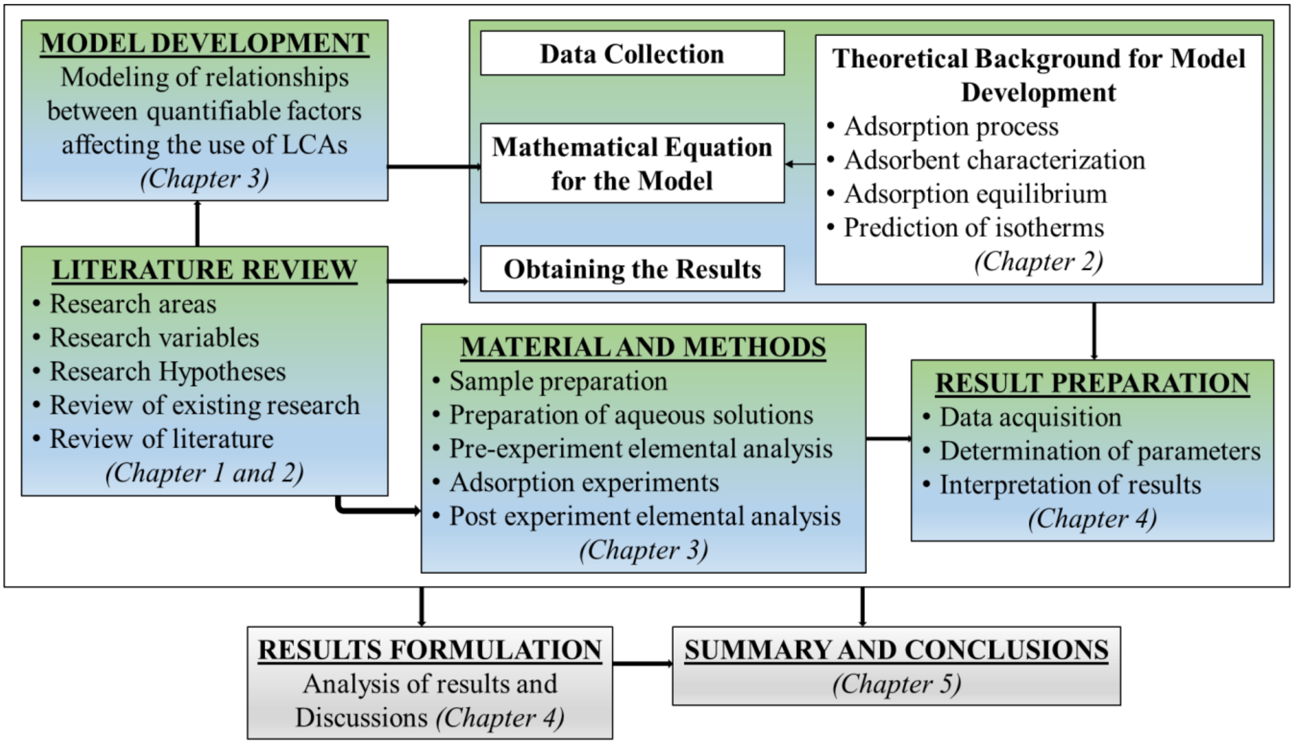


Fig. 3.3 Conceptual framework of the study

The study was supported at all stages by a detailed literature review and study of conceptual as well as empirical literature. The literature was reviewed at all stages in the research process. Review of the conceptual literature concerning the concepts and theories and the empirical literature consisting of earlier studies, which are similar to the one proposed was done first. Conclusions drawn from these reviews are presented mainly in Chapter 1 as an introduction to the study and led to the formulation of research problem and objectives. Next part of the review was conducted to study the research background in context of research objectives. This helped in identification of research variables and research areas. It validated the research objectives also. This part of the literature review is presented in Chapter 2. The third part of the literature review was related to the theoretical background needed to develop the adsorption model. This is also presented in Chapter 2. Review of literature for development of methodology and research design of the study was conducted in part four of the literature review. It was an important part of literature study as only by using appropriate methodologies and methods of research, applied with rigor, can the body of knowledge for a working technique be established and advanced with confidence. This part led to the formulation of methodology and finalization of research design. This part of the literature review is presented in later parts of Chapter 2 and subsequently cited in related chapters.

3.2.2 Methodological Framework

Methodological framework of the study was designed to achieve the research objectives by way of including effective data collection and analysis. The study required an understanding of the adsorption of PTEs from aqueous medium using LCA, measurement of identified factors affecting adsorption of PTEs and relationships between these factors. Some of the identified factors could be measured quantitatively, but some factors like precursors, economic feasibility and technical feasibility required qualitative assessment. Thus, the methodology divided the research into quantitative and qualitative research. Quantitative analysis was conducted through empirical analysis of data using the model developed and parameters required were determined. Sample of adsorbents were analyzed through SWOT analysis forming the qualitative component of the study. Methodological framework of a study paves the way to begin from the very first idea of the study to the finalizing of the study. A detailed methodological framework of the study is given in Fig. 3.4.

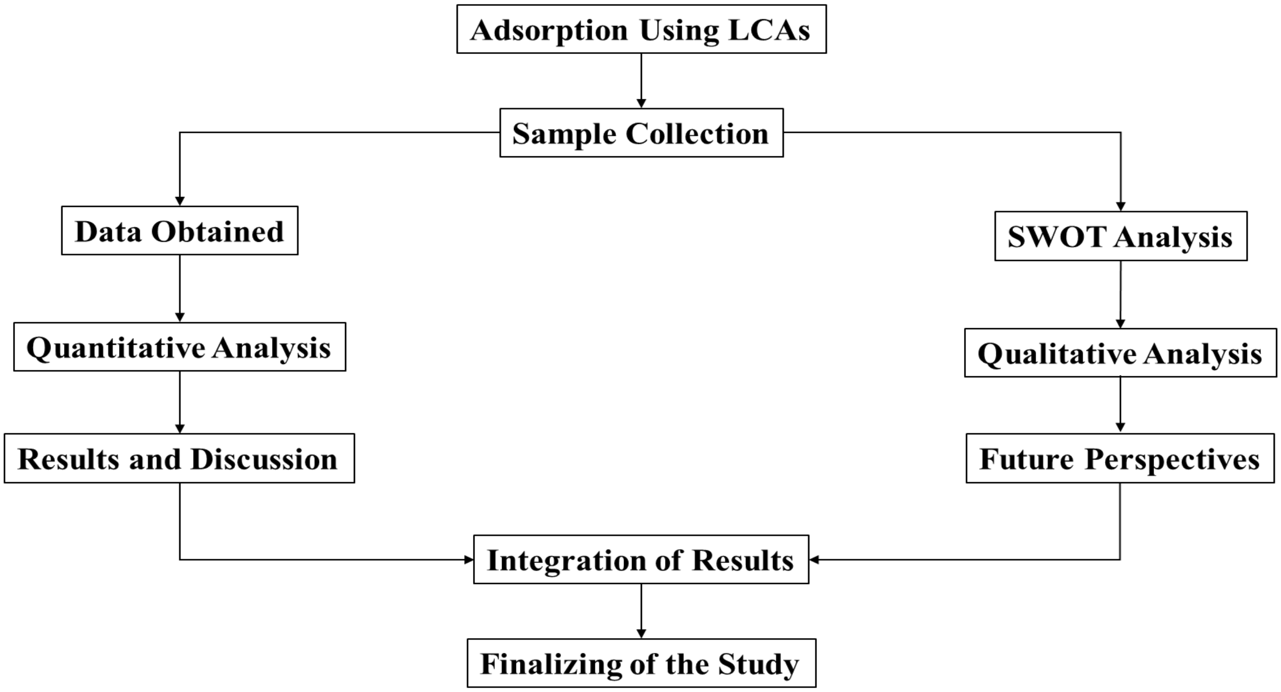


Fig. 3.4 Methodological framework of the study

3.3 JUSTIFICATION OF THE METHODOLOGY

Attempts were made to leverage opportunities available to make research practical by blending quantitative and qualitative study. Quantitative data helped in understanding the relationship among key study variables after empirical testing. Qualitative study was used as a supplementary study to support the quantitative study by filling up gaps of this study. Thus the methodology is rich in both quantitative as well as qualitative analysis. The methodology is supposed to provide valuable practical insights and ideas that can be used in developing and implementing methods for enhancing effective adsorption of PTEs from contaminated water using LCAs. The synthesis of quantitative and qualitative studies was done by taking into consideration the differences and the similarities of the conclusions of both the studies. This has helped in proposing the validated conceptual as well as methodological framework for implementation.

3.4 DEVELOPMENT OF MODEL FOR THIS STUDY

Isotherm models developed by Langmuir and Freundlich were primarily used to describe the phenomena of adsorption on gas-solid interface (adsorption of gases on solids) (Largitte and Pasquier, 2016; Schwaab et al., 2017; Syafiuddin et al., 2018). Langmuir model describes the phenomena of unimolecular adsorption with assumptions of number of active sites proportional to the surface area (Qu et al., 2018; Tian et al., 2018), monolayer surface coverage, independent and homogeneous sorption surface and energy etc. and better explains the process of chemisorption.

Freundlich isotherm model is an empirical model used to describe multilayer adsorption on heterogeneous surfaces with non-uniform distribution of heat of adsorption (Contreras et al., 2017; Pandiarajan et al., 2018). Since, physical adsorption is a multilayer sorption phenomena, Freundlich isotherm is generally used to describe physisorption. However, applicability of the two models is not restricted to original assumptions only, these models are used to describe adsorption at solid-liquid interface also. Linear forms of Langmuir and Freundlich adsorption isotherm models are represented by eq. 3.1 and eq. 3.2 respectively.

$$C_e/Q_e = 1/(Q_{max}K_L) + C_e/Q_{max} \tag{3.1}$$

$$\ln Q_e = (1/n)\cdot lnCe + \ln K_F \tag{3.2}$$

Amount of adsorption at equilibrium Q_e was calculated as follows –

$$Q_e = (C_i - C_e)V/w \tag{3.3}$$

Where, Q_e (mg/g) is the amount of adsorbed heavy metals per unit weight of fraction of compost sample at equilibrium, C_i (mg/L) is the initial heavy metal concentration in the solution, C_e (mg/L) is the equilibrium concentration, V is the volume of solution, and w is the weight of fraction of compost sample used for adsorption. The Langmuir parameters K_L (L/mol) is related to the adsorption rate and Q_{max} (mg/g) is the adsorption capacity (maximum adsorption). Heterogeneity and non-linearity of the adsorption is represented by (n) and K_F ($mg^{1-1/n}g^{-1}L^{1/n}$) is the Freundlich constant.

Since, Langmuir and Freundlich models were originally developed for gas-solid interface, applying them on liquid-solid interface may sometimes lead to erroneous results (Komárek et al., 2018; Rogala et al., 2017; Romero-Flores et al., 2018; Schreiber et al., 2018; Sharipova et al., 2017) because assumptions made during the development of models were for gas-solid interface. These errors may occur due to nature of adsorption, type of adsorption curves, and surface heterogeneity (Sharipova et al., 2017). Some commonly noticeable short-coming of Langmuir and Freundlich models are the large variation of isotherm (Largitte and Pasquier, 2016) parameters with varying initial concentration of the solute, huge increase in adsorption capacity with increase in initial concentration, and some other mechanism for example precipitation (Bharathi and Ramesh, 2013; Komárek et al., 2018) may also play an important role at higher concentrations. As a result of this adsorption capacity may be estimated wrongly or over estimation of same can happen. To overcome these shortcomings, both linear and non-linear zones of Langmuir and Freundlich models were segregated into one and a segregated polynomial model to obtain the isotherms in this study was derived. The polynomial model used in this study was derived as follows –

The rate of change of concentration at time t is given by –

$$\frac{dC}{dt_{ads}} = -K_{ads}C_t^{n1} + K_{des}Q_t^{n2} \tag{3.4}$$

Where C_t is the concentration of adsorbate at time t, K_{ads} is the adsorption constant, K_{des} is the desorption constant, and Q_t is the amount of adsorption at time t. Minus sign in the first term of right hand side of the eq. 3.4 indicates that during adsorption concentration of adsorbate decreases and once the desorption starts, concentration of adsorbate starts increasing that is why the plus sign with K_{des}. In eq. 3.4 it was assumed that the rate of change of concentration at time t depends on $n1$th power of concentration at time t and $n2$th power of amount of adsorption at time t.

But, at equilibrium –

$$\frac{dC}{dt_{ads}} = -K_{ads}C_e^{n1} + K_{des}Q_e^{n2} = 0 \tag{3.5}$$

i. e. $$Q_e = K_e C_e^n \tag{3.6}$$

or $$Q_e = a_i C_{ei}^i \quad i = 0, 1, 2, \dots., n \tag{3.7}$$

Where K_e equals to K_{asd}/K_{des} and n equals to *n1/n2* and both indicate the relative adsorption capacity and adsorption intensity, respectively as in Freundlich model. So, eq. 3.7 shows that amount of adsorption at equilibrium is an *n*th degree polynomial of concentration of adsorbate at equilibrium and a_i's are constants. In this study adsorption isotherms were obtained by fitting linear model for Langmuir and Freundlich isotherms and polynomial model (quadratic and cubic) as an improvement for isotherm data. Fitting of isotherm data was done using Past 3.14 a freeware for scientific data analysis. Data may be entered via a spreadsheet-type interface, or pasted from the clipboard. It's also possible to import some files, though format support is limited (for example XLS type files are supported but XLSX type files are not supported).

3.5 MATERIAL AND METHODS

Once the type and kind of research required for the development of methods for removal of PTEs from contaminated water (the ultimate aim of the study) was identified, material and methods needed to carry out the study were selected and prepared to obtain the data.

3.5.1 Materials Used in the Study

Materials needed to achieve the aim of the study were the LCAs sample and contaminated water. The contaminated water used in this study was aqueous solution prepared from the standard solutions of the PTEs needed to be studied. Since, removal of two elements Cu^{2+} and Zn^{2+} was needed to be studied for the development of the study, so the aqueous solutions of only two elements Cu^{2+} and Zn^{2+} were used in the study.

3.5.1.1 LCA samples

The LCAs selected for removal of PTEs from contaminated water in this study were composts of different compositions. Nine compost samples of different origin were collected from seven waste management plants in Hungary. To make the study more comprehensive and experiment with the samples easily identifiable, collected sample were numbered 1 to 9 and were divided into three categories namely green compost, mushroom compost and sewage sludge compost. Nine compost samples collected for the study are given with their category and serial numbers below.

1. Green compost from Sióagárd

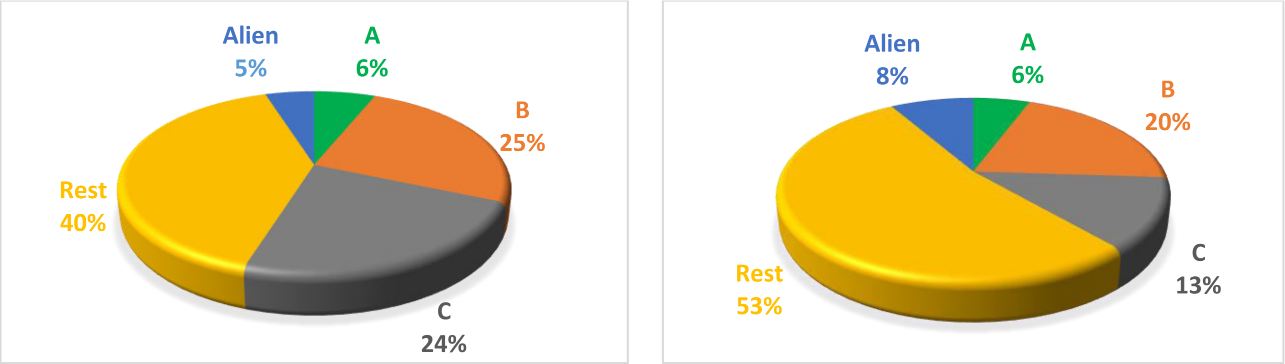
2. Green compost from Bonyhád
3. Green compost from Felgyő
4. Green compost from Polgárdi
5. Mushroom compost
6. Green compost from Baja
7. Green compost from Keszthely
8. Sewage sludge compost from Nyíregyháza
9. Sewage sludge compost from Baja

Sample preparation: Sample preparation started with the pre-treatment of samples which was initiated with drying of samples at room temperature and removal of "alien" materials (glass, plastic, rock, metals etc.) by hand sorting (Quek et al., 1998) preceded by size partitioning using sieves.

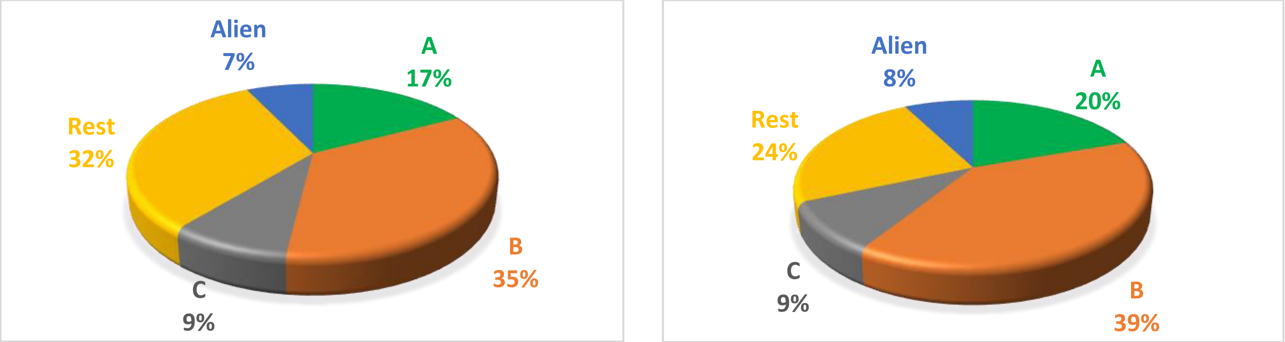
Particle size fractionation: Particle size partitioning of samples were done in five different fractions of particle size. Particle size fractionation was done by sieving the samples. Five fractions from each sample were labeled –

A (FPS ≤ 0.32 mm),
B (0.32 mm < FPS ≤ 1.00 mm),
C (1.00 mm < FPS ≤ 1.40 mm),
Rest (FPS > 1.40 mm) and
Alien (Materials which did not belong to the original compost)

There was no size limit for the fraction **Alien** because aliens were the material which did not belong to the original compost material. After fractionation, weight of each fraction was measured and weight by weight percentage of each fraction from every sample were calculated to have an idea of basic physics of the samples. Percentage particle size distribution of fractions of samples were also calculated to know the effect of particle size of fraction on the way samples were handled and to be ranked as LCA. Weight by weight percentage and particle size distribution of fraction of samples are shown in fig. 3.5 and fig. 3.6. Particle size distribution of fractions of Green compost from Sióagárd, Bonyhád, Felgyő and Polgárdi, Mushroom compost, Green compost from Baja and Keszthely, and Sewage sludge compost from Nyíregyháza and Baja are shown in Fig. 3.5 and Fig. 3.6 respectively. Followed by calculating the weight by weight percentage of each fractions of the samples, weight of a given volume of fractions were measured to have the knowledge of bulk density of the fractions. Bulk density is important to know the porosity of the samples which is very important for controlling the speed of filtration.



(Sample 1) (Sample 2)



(Sample 3) (Sample 4)

Fig. 3.5 Percentage particle size distribution of Sample 1 to Sample 4

3.5.1.2 Aqueous solution

Aqueous solutions of different concentration (wherever needed in a required concentration) used in the study were prepared from standard solutions containing 1000 mg/L Cu^{2+} (Merck 1.19786.0100) and Zn^{2+} (Merck 1.19806.0100), respectively using purified water obtained from Milli-Q Direct 16 water purification system (ZR0Q016WW). Standard solutions and water purification system both were purchased from Merck Ltd., an affiliate of Merck KGaA, Darmstadt, Germany. The standard solutions used in the study were NIST (National Institute of Standard Technology, United States of America) recommended solutions. The concentrations of Cu^{2+} and Zn^{2+} in the diluted solution were also measured to avoid any possible error during dilution.

3.5.2 Methods Applied in the Study

The equipment, instruments and methods applied on the prepared samples to obtain the data for the study are explained in the following sub-sections.

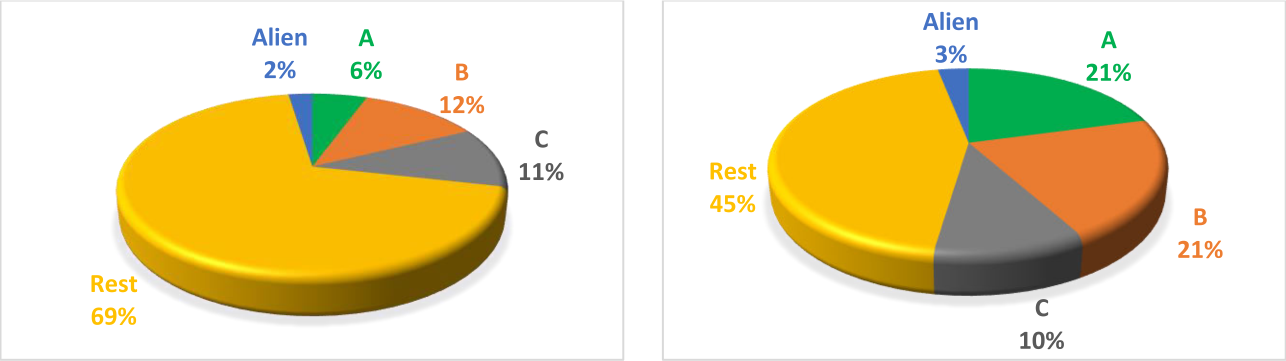
3.5.2.1 Calculation of bulk density

Bulk density (BD) of a granular solid can be calculated as dry BD or wet BD depending on need of the study. BDs of the fractions of samples used in this study were calculated using following formulae.

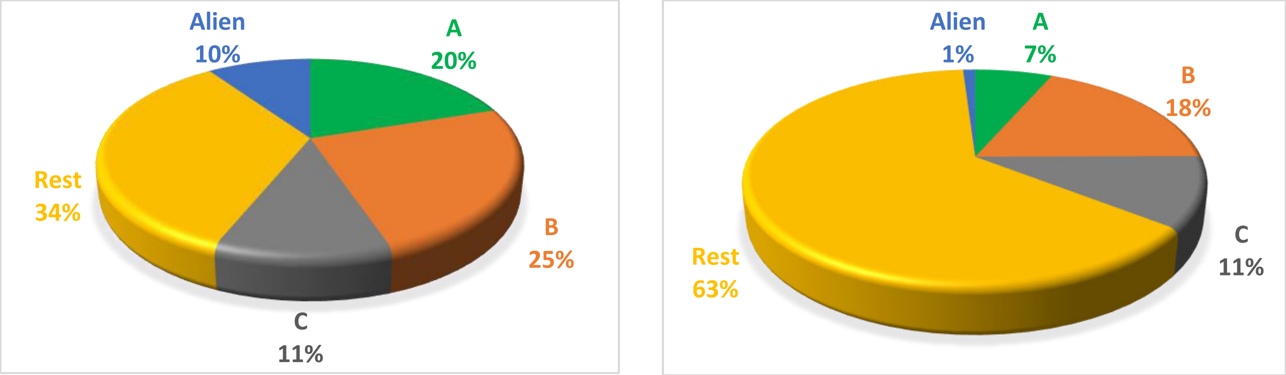
$$\text{Dry BD } \rho_d = \frac{M_s}{V_p + V_v + V_i} \tag{3.8}$$

$$\text{Wet BD } \rho_w = \frac{M_s + M_l}{V_t} \tag{3.9}$$

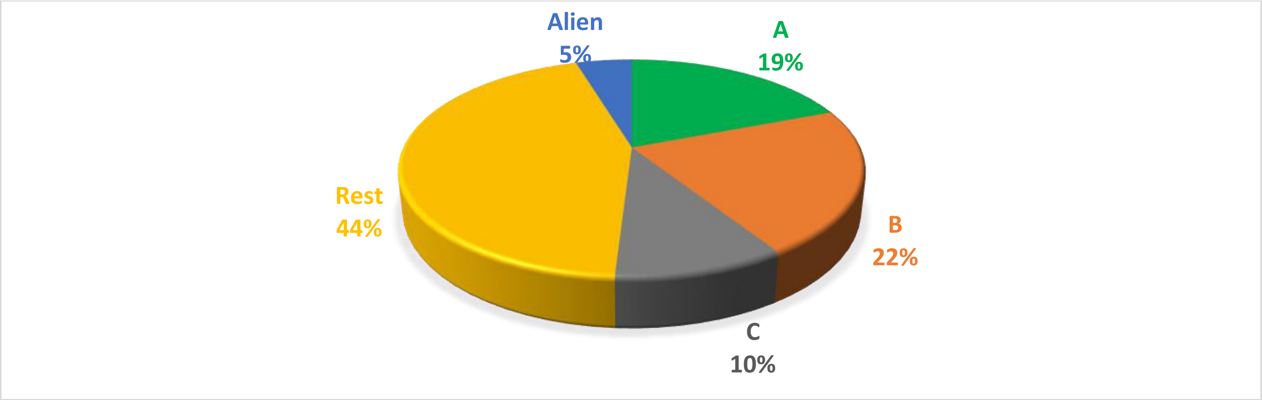
Where M_s is the mass of solid, M_l is mass of liquid, V_p, V_v and V_i are the particle volume, inter-particle void volume, and internal pore volume respectively. V_t in eq. 3.9 is the total volume (volume of particles plus volume of liquid) because in this case liquid will occupy all the voids and pores. In this study dry BD of each fraction of samples were calculated without any compaction or consolidation.



(Sample 5) (Sample 6)



(Sample 7) (Sample 8)



(Sample 9)

Fig. 3.6 Percentage particle size distribution of Sample 5 to Sample 9

3.5.2.2 Microwave digestion

Microwave assisted acid digestion was done by Microwave Accelerated Reaction System (CEM MARS5) to prepare the fractions of samples for determination of pseudo-total elemental content. Digestion in CEM MARS5 is done in control vessels housed in support modules. The control vessel consists of vessel lid with pressure release check valve and pressure transducer attached, glass thermal well with compression fitting and fibre optic temperature sensor, Teflon reaction vessel, Kevlar explosion proof sleeve, and pressure transducer. Separated rotors were used for the vessels in the system applied for this study. MSZ 21470-50:2006 Hungarian standard methodology was used for the digestion. Digestion was done by adding 5 ml 65 *m/m*% HNO_3 and 2 ml 30 *m/m*% H_2O_2 to a known small quantity in the range (0.2000-0.4000 g) of fractions of samples in the reaction vessel ("liner"). To wash the walls of the Teflon reaction vessel and to make the volume in the vessel up to 10 ml (minimum measurable volume in the vessel was 10 ml), high purity (HPLC) water was added. For digestion, CEM MARS5 was programmed as follows:

20 min RAMP time (to 190°C, and/or 450 PSi)
18 min HOLD time (with 800W, on 190°C, and/or 450 PSi)
5 min STILL time with 0 W
5 min HOLD time (with 800W, on 190°C, and/or 450 PSi)
Cooling down (to 35-40°C)

Fig. 3.7 Digestion of samples using CEM MARS5

After digestion reaction vessels were open in exhaust box and digested fractions were filtered using MN 389 type filter paper. High purity water was added in filtered fractions to make the volume of each sample 25 ml and that 25 ml of fractions were transferred to Falcon tube for elemental analysis using ICP-OES. In house modules of CEM MARS5 for digestion are shown in Fig. 3.7 above.

3.5.2.3 Elemental analysis

Experiment started from analyzing the fractions of compost samples for its initial (pre-filtration) elemental content. Elemental analysis of the fractions were done using HORIBA Jobin Yvon ACTIVA-M, ICP-OES with imaging charged coupled device (CCD) detection. NIST recommended Yttrium internal standard (1 mg/L) solution was used for elemental analysis using ICP-OES. Internal standard was used to reduce the matrix effect, to improve the efficiency of nebulization and to get the correct values of concentrations. Cu and Zn were detected at 324.754 nm and 213.857 nm wavelengths respectively in the analysis. Quality control was done using QC solutions (CPAchem D73122, 8236.1.2N.L1.1 for Cu, Zn, and Y with 1 mg/L concentrations in 2% HNO_3). Elemental analysis and recording of data on console are shown in Fig. 3.8. Mass by volume (mg/L) elemental concentration of 9 elements (Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Zn) of the fractions of samples were determined using ICP-OES, and mass by mass (mg/kg) concentration of the samples were calculated.

Fig. 3.8 Analysis using ICP-OES

3.5.2.4 Construction of adsorbent columns

Adsorbent columns were constructed by constructing contaminated water (aqueous solution) columns and compost columns. Aqueous solution column was constructed by filling the aqueous solution into a burette equipped with a valve and compost column was constructed by filling a fixed amount of the selected fraction of compost samples in a dry Conical Bottom Tube (CBT) with a drilled hole in the bottom. A thin layer of cotton was provided at the mouth of the hole from inside to stop the free falling of compost from CBT under gravity.

The water column and the compost column were clipped in two stands and were arranged vertically in a line with the help of stands as shown in Fig. 3.9 and aqueous solution containing Cu^{2+} and Zn^{2+} was allowed to flow through the CBT from top of the tube. The vertical flow of artificial contaminated water (aqueous solution) through compost column was controlled with help of valve. Aqueous solution flowing through CBT under controlled conditions was collected in graduated tubes placed under compost columns and analyzed using ICP-OES.

Fig. 3.9 Adsorption column used for preliminary tests

3.5.2.5 Performance evaluation

Performance of the fractions of samples were evaluated using following formula-

Percentage adsorption $A = \frac{M_a - M_f}{M_a} \times 100$ (3.10)

Where M_a is the mass of adsorbate allowed to be adsorbed and M_f is the mass of adsorbate in filtrate.

3.5.2.6 Study of adsorption behaviour

Adsorption columns discussed in section 3.5.2.4 were used to perform the preliminary adsorption tests. Preliminary continuous flow adsorption test was performed to study the adsorption behaviour. The main aim of the preliminary test was to determine the W/V of adsorbent (compost) and aqueous solution. Four preliminary tests were performed in this study. Test 1 was performed using 5.00 g of fractions of Sample 1 in the CBT, and 50 ml of aqueous solution containing 10 mg/L Cu^{2+} and Zn^{2+} together in the aqueous solution column. For test 2, 2.00 g of fractions of Sample 2 were used in the CBT and 100 ml of aqueous solution containing 10 mg/L Cu^{2+} and Zn^{2+} together was used in the aqueous solution column. Test 3 was conducted using 1.00 g of fractions of Sample 3 in the compost column and 200 ml of aqueous solution containing 10 mg/L Cu^{2+} and Zn^{2+} together in the aqueous solution column. Test 4 was different of all the other preliminary tests in terms of quantity of compost used in the CBT and volume of aqueous solution used in aqueous solution column.

Test 4 was conducted to observe the extreme adsorption behaviour that is why huge quantities of adsorbent and aqueous solution were used in adsorption column. For test 4, 25.00 g of fraction 3A and 1000 ml of aqueous solution containing 50 mg/L Cu^{2+} and Zn^{2+} were used in the CBT and aqueous solution column respectively. Solution flowing through CBT was collected in graduated tubes in 10 fractions of 5 ml for test 1, 10 fractions of 10 ml for test 2, 10 fractions of 20 ml for test 3, and 20 fractions of 50 ml for test 4. Concentrations of Cu^{2+} and Zn^{2+} in the filtrates were determined by ICP-OES. W/V obtained from preliminary test was used to perform steady state adsorption experiments and data obtained from steady state adsorption experiments were used to study adsorption isotherms.

The details of continuous flow adsorption tests (preliminary tests) conducted are given in Table 3.1. Only fractions A, B, and C of the samples were used both in preliminary tests as well as in steady state adsorption tests because FPS of fraction Rest was too large to be used in the preliminary test and fraction Alien was used only to decide the degree of sorting needed if a certain amount of a sample is prepared for the preliminary test.

Table 3.1 Specification of preliminary tests

Fraction	Amount used in compost column (g)	Filtered Volume (ml)	Fraction Volume (ml)
1A, 1B, 1C	5	50	5
2A, 2B, 2C	2	100	10
3A, 3B, 3C	1	200	20
3A	25	1000	50

3.5.2.7 Study of adsorption isotherms

Mono and binary adsorption studies for adsorption of Cu^{2+} and Zn^{2+} were carried out and adsorption isotherms were plotted for both mono and binary adsorption of heavy metals separately. Adsorption isotherms were plotted using the data obtained by adding 0.5 ± 0.0010 g of compost in 100 ml mono and binary aqueous solutions of Cu^{2+} and Zn^{2+}. Solutions were prepared in five concentrations of 1.25 mg/L, 2.5 mg/L, 5 mg/L, 10mg/L, and 20 mg/L. After adding 0.5 g of compost to 100 ml solutions of Cu^{2+} and Zn^{2+} in five different concentrations, 15 suspensions (5 each for mono solutions of heavy metals and 5 for binary solution) of aqueous solution and compost were obtained. Suspensions ready for steady state adsorption tests are shown in Fig. 3.10. Five suspensions were shaken together in the experiment that is why Fig. 3.10 shows only five suspensions in it.

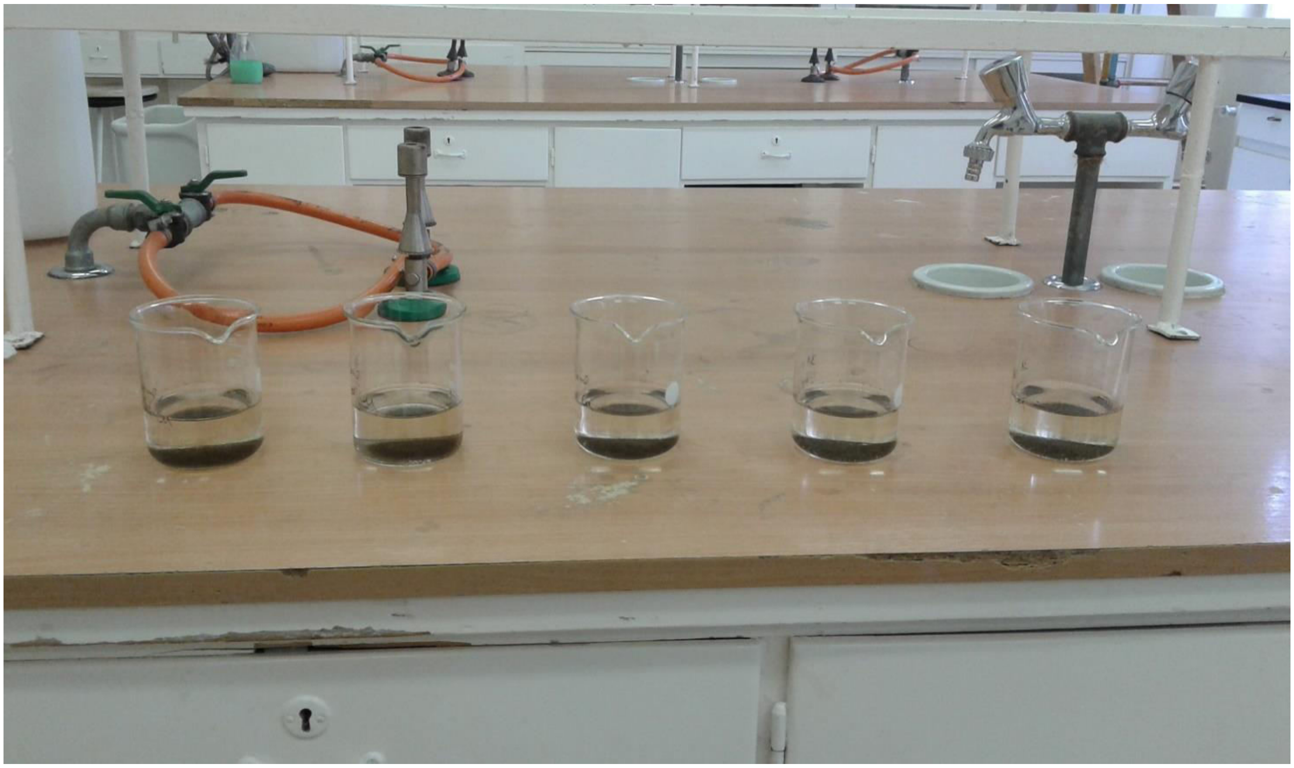


Fig. 3.10 Suspensions used in the steady state adsorption test

Each suspension was shaken well for 10 hour and pH of every suspension was recorded at an interval of 2 hours. Finally, 50 ml of solutions from suspensions were filtered using 0.45 µm polyvinylidene fluoride (PVDF) membrane syringe filters (diameter 25 mm and hydrophilic wettability) for ICP-OES analysis. Filtration using PVDF membrane is shown in Fig. 3.11. PVDF filters were used after the adsorption not only to stop any compost particle from entering into solution going to be used for ICP-OES analysis but also to avoid any hindrance in the process of nebulization during determination of concentration using ICP-OES.

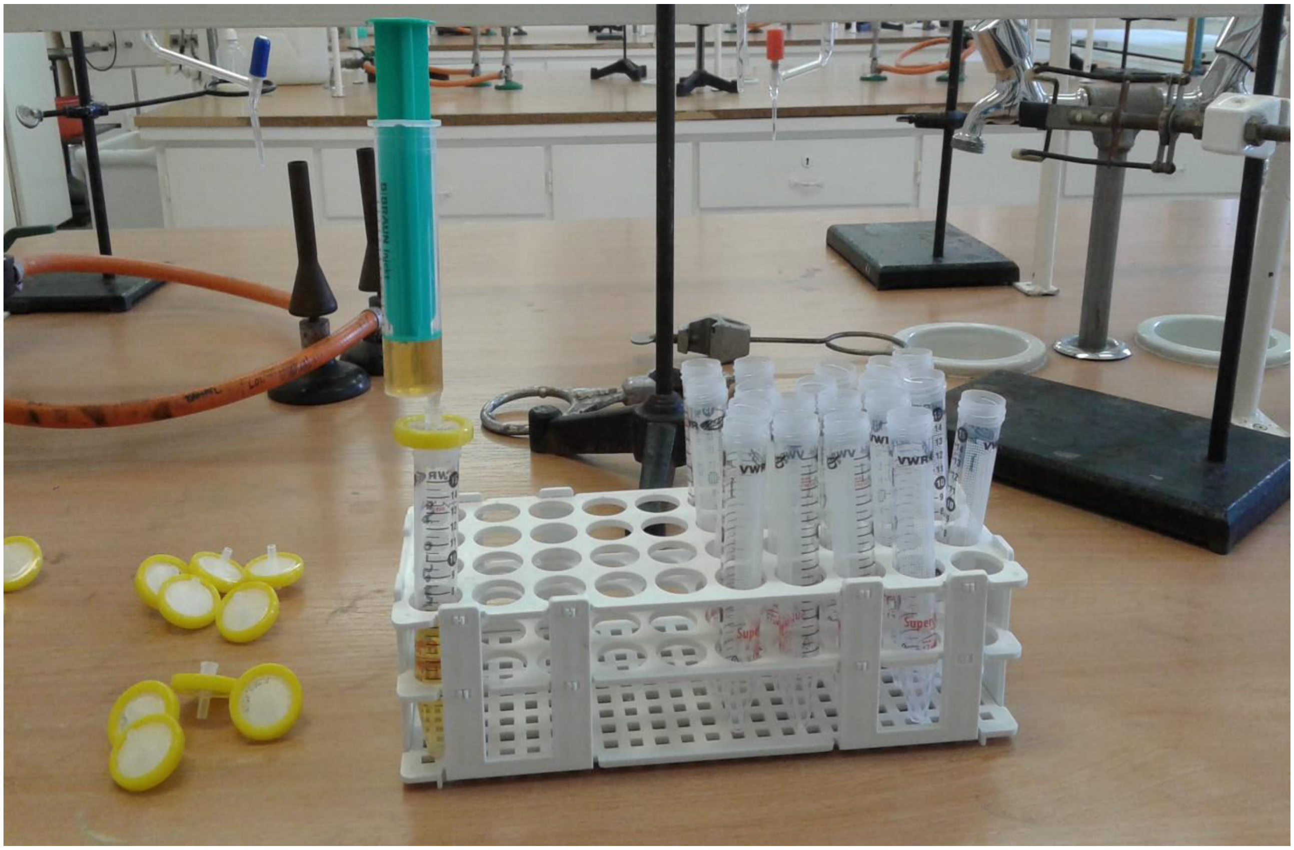


Fig. 3.11 Filtration of suspension for ICP-OES analysis using PVDF

3.5.2.8 Observation of pH variation

Using the results of preliminary studies it was observed that equilibrium could be reached after 10 hour. To observe the effect of pH on equilibrium, changes in pH was recorded after every two hours. We recorded the pH of solutions first and pH of suspensions were recorded following that. Time to reach the equilibrium was divided into interval of 2 hours so that we have enough values of pH measurements to confirm the point of equilibrium. In case, if pH could not confirm the equilibrium point, it was confirmed by slope of the polynomial model (given in section 3.4) developed to determine the parameters of adsorption isotherms.

3.5.2.9 Plant experiment

Safe disposal of adsorbents after the process of adsorption is needed to mitigate the environmental risk that might be caused by adsorbents if the concentration of PTEs become too high in the adsorbents. Plant experiments are carried out for the uptake of PTEs from adsorbent's surface so that the concentrations of PTEs could be brought down to a level safe for it's disposal or reuse. Since, the reusability is a crucial issue to be considered for adsorbent development, to check the reusability and to evaluate the environmental risk of the compost samples used as adsorbent in this study, plant experiment was carried out using 0.5000 ± 0.0050 g of original sample and sample after adsorption. Original and used sample after experiment were put in small pots and the pots were seeded with seven seeds of mustard. The plant experiment in this study was carried out for 21 day to get enough mass of grown plants for elemental analysis. During the period of 21 days plants were watered and checked if they start dying. At the end of 21 days plants were uprooted and dried up. The dried plants were digested in microwave digester and elemental analysis of digested plants was done using ICP-OES.

3.6 DATA COLLECTION AND ANALYSIS APPROACH

Data collection, data analysis, development and verification of relationships, and conclusions are very much interrelated and interactive set of processes. The analysis starts right from the beginning of collection of data, and it goes past till the analysis finishes. Data collection and analysis can be conducted through quantitative approach, qualitative approach or mixed methods approach. The former approach involves generation of data in the quantitative form, which can be subjected to rigorous quantitative analysis for e.g. using a model or other data processing methods. The later approaches helps in using different methods for different purpose in the study. In this research, study of the identified research variables requires use of quantitative as well as qualitative methods. Thus, this research focuses on collecting and analyzing both quantitative and qualitative data in a sequential manner (*sequential mixed methods).*

To develop a balanced check mechanism, the research involves both quantitative and qualitative methods. The purpose of studies is to verify their results by collecting the data for an identified study area. The purpose of this study is to start with quantitative results obtained from 45 fractions of 9 samples to analyze the research variables, and to probe explore and validate the results in more depth. In this study, primary data were used for determination of parameters involved in the model developed for this study. The primary data needed for the development of methods for removal of PTEs from contaminate water using LCAs were collected from a set of experiment performed in the laboratory.

Technical and economic feasibility of the samples were verified by the source of samples, literature review and primary data obtained from the experiments.

3.6.1 Data Preparation

Data preparation is the process of assembling and organizing the collected and analyzed data so that it could be used into the model formulation of the study to get the results and to achieve aim and objectives the study. Three types of primary data were used for the preparation of this study. The type of data used to achieve the aim and objectives of this study were –

a) **Raw Data:** It was the data obtained directly from the sample preparation. Physical composition of samples, FPS, percentage particle size distribution, and pre-adsorption elemental analysis were the raw data used in this study. Preparation of raw data helped in calculating the bulk densities and ranking of the fractions of samples.

b) **Preliminary Data:** The post-adsorption data obtained from preliminary study were grouped as preliminary data. Important variable like W/V was obtained from the preparation of preliminary data. Determination of W/V from the data obtained from preliminary continuous flow adsorption tests helped in calculating the amount of compost and volume of aqueous solution required for performing the steady state adsorption test.

c) **Key Data:** It was also obtained post-adsorption. The data obtained from steady state adsorption test were grouped as key data because these were considered as the backbone of this study. Preparation of key data helped in deciding the parameters needed and development of the model for the study.

In this study collected and prepared data are organized in a way so that it can be used in the model formulation of the study.

Chapter 4

ANALYSIS, RESULTS AND DISCUSSION

4.1 RESEARCH AT A GLANCE

The research reported in this thesis concerns the investigation of issues related to the adsorption of PTEs from aqueous solution using LCAs. Research was carried out with the objectives specified in Chapter 1 and as per the Methodology specified in Chapter 3. The research process included a sequence of activities performed for achieving the objectives. This chapter synthesizes the results of these research activities leading to the 'Development of Methods for the Treatment of Water Containing PTEs using LCAs.

4.2 SAMPLE ANALYSIS

Three types of data (given in section 3.6.1) required for this study consists of 45 fractions of 9 compost samples which were collected from 7 waste management plants in Hungary. Although, compost samples were divided in 45 fractions but 36 of them were studied and analyzed because 9 fractions (Alien) from each sample were not of interest of this study. Analysis of samples led to the categorization of samples into three namely Green compost, Mushroom compost, and Sewage sludge compost. Data obtained from analysis of sample before adsorption tests were particle size distribution, bulk density, and elemental content analysis. Based on these data ranking of samples and selection of the prima optimal adsorbents were done.

4.3 RESULTS AND DISCUSSION OF RAW DATA

4.3.1 Particle Size Distribution

Particle size distribution of all the fractions of samples (Spl) are given in the Table 4.1. The distribution shows the percentage of each fraction of samples naturally present after sorting and sieving a given weight of the samples. The value for fraction 1A is 6.16% which means Green compost from Sióagárd was having 6.16% of the fraction with FPS ≤ 0.32 mm. Similarly, Sample 5 had 69.04% of the fraction with FPS > 1.40 mm. Fraction 5Rest was the highest percentage of any fraction present in any sample. That gave Sample 5 an upper hand because smaller size particle could easily be prepared by simply grinding the larger particles. Amount of fraction 8Rest is the second highest with 63.40%. Samples were alienated into fractions of varying particle size to know the even or uneven distribution of particles in the sample. The more the even distribution of particles, easier was the sample to handle. So, the sample with higher amount of evenly distributed particle got higher rank based on particle size fractionation. For example, fraction 1B of Sample 1 got higher rank than fractions of Sample 8 while Sample 8 had the second highest percentage of fraction Rest.

Table 4.1 Percentage particle size distribution of fractions

Fraction	Spl 1 (%)	Spl 2 (%)	Spl 3 (%)	Spl 4 (%)	Spl 5 (%)	Spl 6 (%)	Spl 7 (%)	Spl 8 (%)	Spl 9 (%)
A	6.16	5.70	17.29	19.61	5.54	20.73	19.92	6.53	19.16
B	25.28	20.30	34.64	39.31	12.17	21.19	24.87	18.37	21.77
C	23.41	12.62	9.00	9.54	10.84	10.42	11.36	10.67	10.03
Rest	40.24	53.00	31.96	23.94	**69.04**	44.61	34.26	63.40	44.37
Alien	4.92	8.37	7.11	7.60	2.41	3.05	9.58	**1.02**	4.67

4.3.2 Bulk Density

Bulk density of the fraction of samples (Spl) used in this study was calculated using eq. 3.8 by measuring the mass of 38 cm^3 volume of each fraction of samples. Calculated bulk densities are given in the Table 4.2. Bulk density of fraction Alien is not given here because alien materials present in the sample did not have any role to play in the study other than in percentage particle size distribution of samples so it was not calculated. We can see the decrease in bulk densities as we move from fractions A to C in the Table 4.2. It was obvious because with increasing FPS mass of material decreases in a given volume and smaller particles consolidate faster too. In some cases bulk densities of fraction Rest were found a little higher than the corresponding fraction C because the larger particles of fraction Rest were having some high density material in it. That was also one of the reasons for exclusion of fraction Rest from most part of the study.

Bulk densities in the range (0.5-0.7) were found more suitable for the study because in this range surface area of contact in the process of adsorption was found considerable for maintaining the speed of filtration of contaminated water. Some of the values slightly above or below this range were also found outstanding. For example, the bulk density of fraction 5B was 0.44 g/cm^3 but it was ranked 2. Exceptionally, some of the values belonging to the range (0.5-0.7) did not performed well. For example, the bulk densities of the fractions 6C and 7C were 0.53 g/cm^3 and 0.52 g/cm^3 respectively but these were ranked 23 and 24. Reason for these exceptional performance of the fractions were the properties of samples like presence of clay in the compost, percentage fraction particle size distribution and elemental content. Particle size distribution affected the ranking of the most fractions because with increasing particle size voids and porosity increases resulting in reduced contact surface area available for adsorption. That is why fraction Rest of almost all the sample got the bottom rank with the exception of 8C and 9C. Reason for 8C and 9C coming in the bottom was both Sample 8 and Sample 9 were sewage sludge compost with alot of hard material present in the original composition of these samples which might hinder the process of adsorption using these samples.

Table 4.2 Bulk densities of fractions of samples

Fraction	Spl 1 g/cm^3	Spl 2 g/cm^3	Spl 3 g/cm^3	Spl 4 g/cm^3	Spl 5 g/cm^3	Spl 6 g/cm^3	Spl 7 g/cm^3	Spl 8 g/cm^3	Spl 9 g/cm^3
A	0.78	0.71	0.90	0.64	0.63	0.85	0.69	0.75	0.72
B	0.63	0.57	0.70	0.53	0.44	0.63	0.56	0.65	0.55
C	0.50	0.51	0.52	0.29	0.37	0.53	0.52	0.59	0.49
Rest	0.56	0.56	0.50	0.25	0.44	0.54	0.47	0.62	0.53

4.3.3 Elemental Content Analysis

Concentrations of four elements Cr, Cu, Ni and Pb having major impact on the ranking of fractions of samples are given in the Fig. 4.1. Effect of elemental content on ranking of fractions is explained using concentrations in fraction A Fig. 4.1 and fraction C Fig. 4.2. Copper was present in deciding amount (as shown in Fig. 4.1 and Fig. 4.2 for fractions A and C) in all the fractions of samples. Both Fig. 4.1 and Fig. 4.2 shows minimum values of copper in Sample 5 with 31.63 mg/kg for fraction A and 41.79 mg/kg for fraction C so the fractions of Sample 5 rightly got the highest rank.

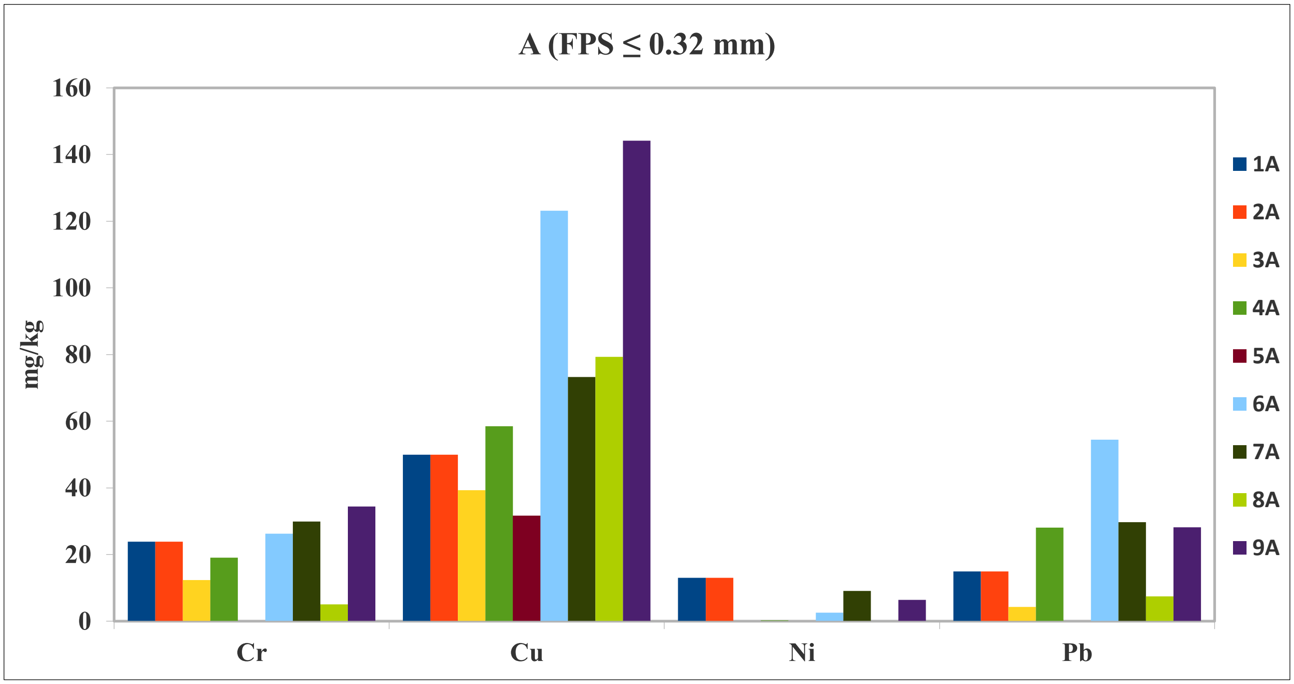


Fig. 4.1 Concentration of Cr, Cu, Ni and Pb in fraction A of all the samples

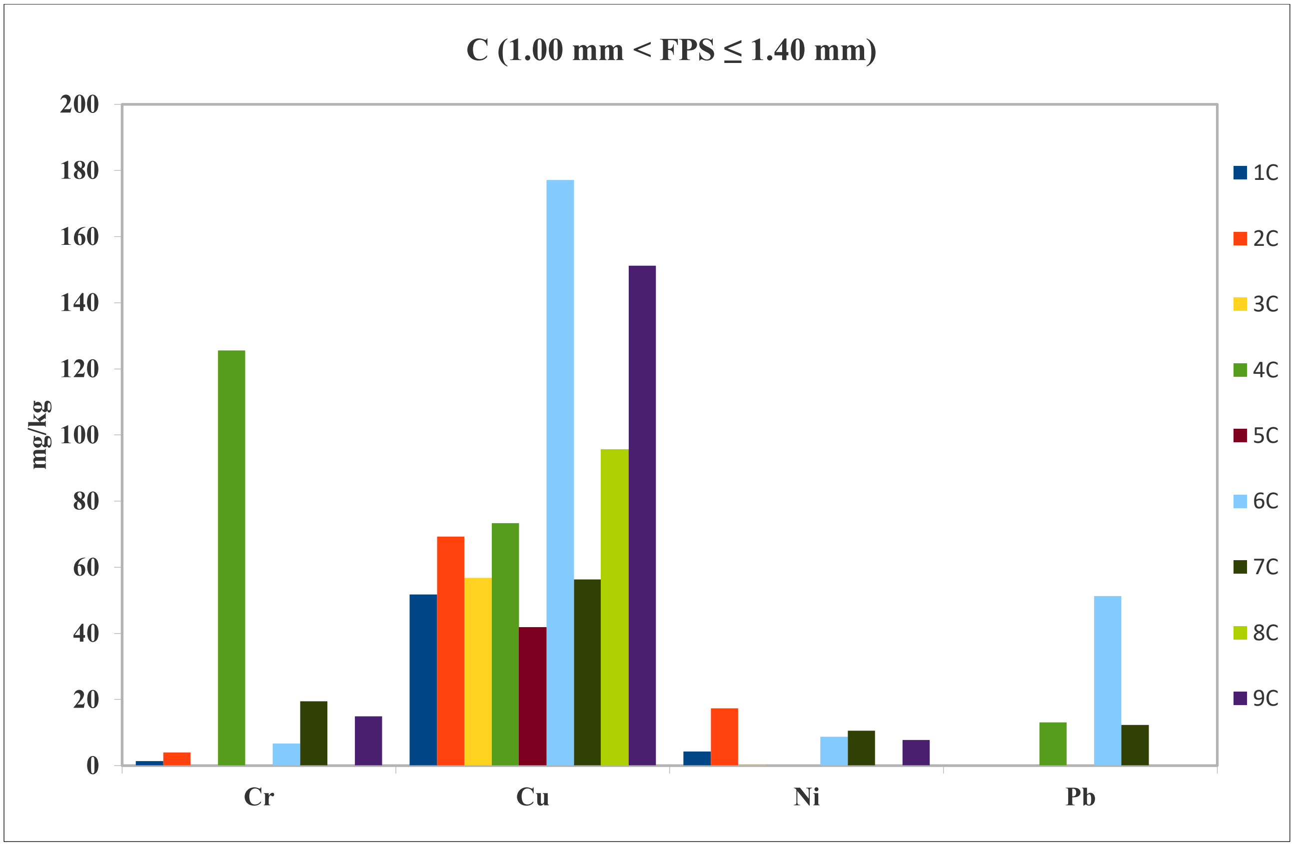


Fig. 4.2 Concentration of Cr, Cu, Ni and Pb in fraction C of all the samples

Presence of all other elements were uneven in the fractions but the element which affected the ranking the most was Cr. It was not present in both the fractions A and C of Sample 5 which again justify the ranking. Cr was present in very little amount (3.94 mg/kg) in fraction 2C which is also in accordance with the ranking. Similarly effect of other elements on fractions of samples were studied and fractions were ranked as shown in Table 4.3.

4.3.4 Selection of the prima optimal adsorbents

All the fractions of samples studied were ranked as LCAs from best to worst based on their FPS, BD and concentration of elements (mg/kg) of the fraction weight. Table 4.3 shows ranking of all the fractions. Based on the ranking in Table 4.3, fractions of samples can easily be selected for adsorption of PTEs from contaminated water. Overall effect of all three parameters considered for the selection of prima optimal LCA shows that fraction 5A might be considered as a prima optimal LCA. Analysis of these parameters ranked fraction 5B as the second best LCA out of the fractions studied because concentration of most of the elements in fractions 5A and 5B were found to be very low. Constraint analysis of the fraction particle size, bulk density and concentration of elements ranked fraction 9Rest as the worst LCA. It was mostly because of the bigger particle size of this fraction.

Table 4.3 Ranking of fractions of samples

Rank	Fraction	Rank	Fraction	Rank	Fraction	Rank	Fraction
1	5A	10	1A	19	4A	28	2 Rest
2	5B	11	3C	20	6A	29	3 Rest
3	1B	12	2A	21	9A	30	4 Rest
4	2B	13	8B	22	4C	31	8C
5	5C	14	3A	23	6C	32	6 Rest
6	3B	15	8A	24	7C	33	9C
7	4B	16	7B	25	7A	34	7 Rest
8	2C	17	6B	26	5 Rest	35	8 Rest
9	1C	18	9B	27	1 Rest	36	9Rest

4.4 RESULTS AND DISCUSSION OF PRELIMINARY DATA

4.4.1 Continuous Flow Adsorption Test

Latter half of the study was carried out using fractions A, B, and C of Sample 1, Sample 2 and Sample 3 even fractions 5A and 5B got the top ranks. Sample 1, Sample 2, and Sample 3 were selected for the latter half of the study because these samples belong to the green compost category and were easier to handle. Since these samples were green compost, they were more environmental friendly and readily available as compare to the other samples. Only fractions A, B, and C were used for the continuous flow adsorption tests because FPS of fraction Rest was too large to be used in adsorption columns and fraction Alien was of no use.

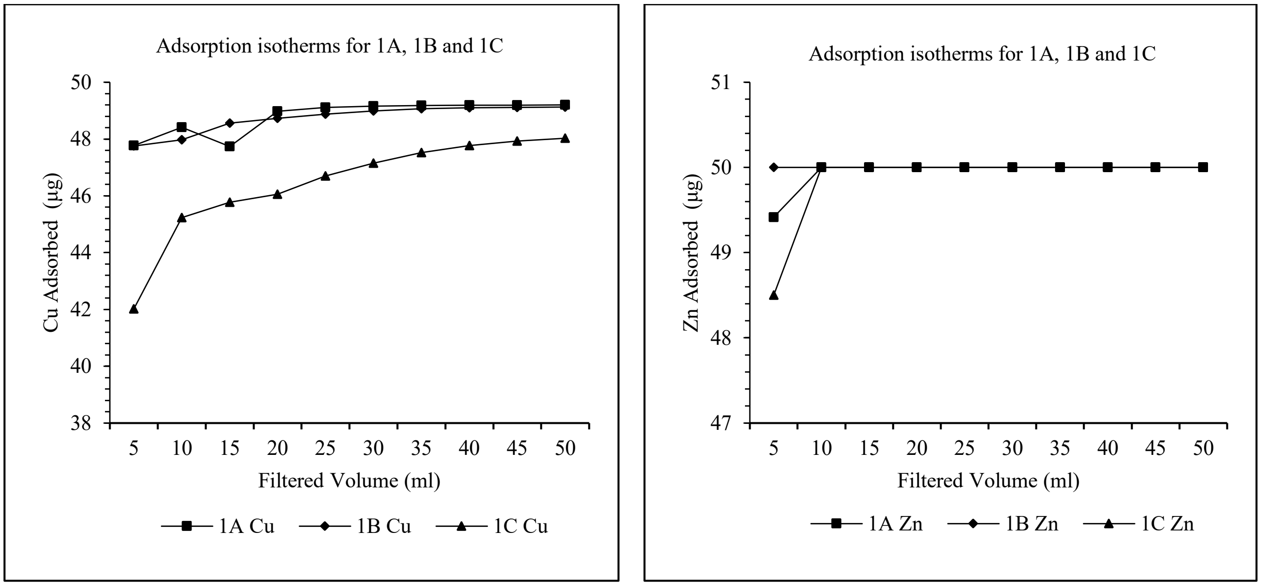
Bulk densities given in Table 4.2 were calculated to have a control over the speed of filtration in continuous flow adsorption test. With the given bulk densities, rate of filtration was highest for fraction 3C and was minimum for fraction 1A. Pre-filtration elemental analysis is useful for calculating amount of adsorption using fractions of samples and post-filtration elemental analysis of fractions also. But in this study amount of adsorption was calculated by determining the concentration of elements in the filtrate. So, the elemental content discussed in section 4.3.3 might be used for verifying or cross checking the adsorption by fraction of samples.

4.4.1.1 Adsorption using fractions of Sample 1

Adsorption isotherms of Cu and Zn for fractions of Sample 1 are given in Fig. 4.3 (a) and Fig. 4.3 (b) respectively. These adsorption isotherms were drawn by filtering 50 ml of aqueous solution with adsorbent columns containing 5 g of fractions of Sample 1. Filtrate was collected in fractions of 5 ml in 10 graduated tubes and elemental content in μg was determined for each fraction of filtrate. Adsorption per fraction of filtrate was plotted against fraction volume and the dots in the curves of Fig. 4.3 are showing the same. Adsorption by 1A and 1B was very similar that is why the curves corresponding to these fraction overlapped while reaching towards saturation. With the weight to volume ratio of 1/10, percentage adsorption of Cu^{2+} by 1A, 1B, and 1C were calculated as 97.58%, 97.45% and 92.83% respectively which are high percentage of adsorption but it was time taking.

The two main parameters that needed to be optimised in the study were weight to volume ratio and amount of adsorption. So, with the weight to volume ratio of 1/10 adsorption by fractions of Sample 1 was considerably high with optimal value of 97.58% obtained for fraction 1A. The value in absolute terms are given in Table 4.4. Percentage adsorption by fractions of sample can be verified by the mean concentration of Cu^{2+} and Zn^{2+} in the whole filtered volume by a fraction which were 9.758 mg/L, 9.745 mg/L and 9.283 mg/L.

The average concentrations of Cu^{2+} and Zn^{2+} in the whole filtered volume by a fraction were 1/10 of the percentage value because the original concentrations of Cu^{2+} and Zn^{2+} in the aqueous solution was 10 mg/L hence the calculated percentage adsorption were correct. Although, the calculated adsorption are (w/w) percentage, it can be verified by the concentration of elements in the filtrate because the adsorption can be calculated both by measuring the quantity of elements in filtered volume as well as in adsorbent used in the adsorbent column. The adsorption of Zn^{2+} was also calculated and verified in the same way and the values are given in Table 4.4.

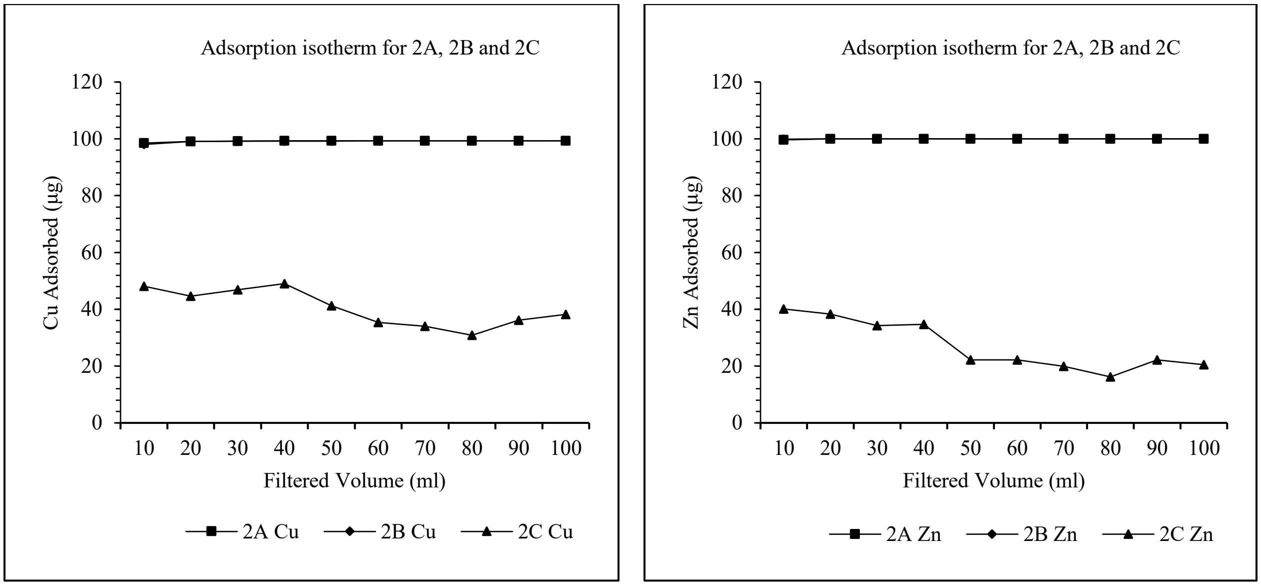


(a) Adsorption of Cu **(b) Adsorption of Zn**

Fig. 4.3 Adsorption of Cu and Zn by fractions of Sample 1

4.4.1.2 Adsorption using fractions of Sample 2

Weight to volume ratio used for adsorption of Cu^{2+} and Zn^{2+} by fractions of Sample 2 was 1/50. That is 100 ml of aqueous solution was filtered using 2 g of 2A, 2B, and 2C in the adsorbent columns. The filtered volume was collected in fractions of 10 ml and the adsorption per fraction was calculated as shown in Fig. 4.4 (a) for Cu^{2+} and Fig. 4.4 (b) for Zn^{2+}. The ordered pair of values of percentage adsorption of Cu^{2+} and Zn^{2+} by fractions of Sample 2 (2A, 2B, and 2C) were (99.19%, 99.96%), (99.13%, 99.99%) and (40.45%, 27.06%) respectively. The values in the first two ordered pairs show that adsorption of Cu^{2+} by 2A and 2B was very high and better than that of fractions of Sample 1. Adsorption of Zn^{2+} by 2A and 2B was also very high and was similar to that of fractions of Sample 1 but the adsorption of both Cu^{2+} and Zn^{2+} by 2C was very low. So, fraction 2C could not be used for adsorption of both Cu^{2+} and Zn^{2+}. All the values calculated were verified the same way it was done for fractions of Sample 1. More details are given in Table 4.4.

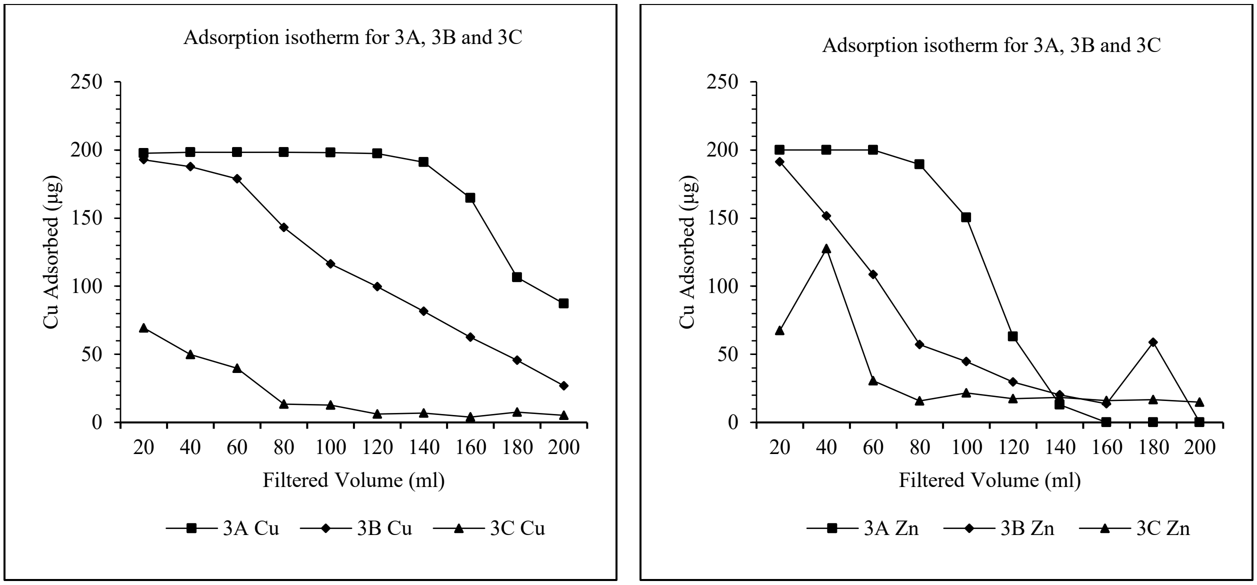


(a) Adsorption of Cu **(b) Adsorption of Zn**

Fig. 4.4 Adsorption of Cu and Zn by fractions of Sample 2

4.4.1.3 Adsorption using fractions of Sample 3

To minimize the time of filtration, weight to volume ratio was reduced to 1:200 for adsorption of Cu^{2+} and Zn^{2+} by 3A, 3B, and 3C. Filtered volume was again collected in ten fractions but 20 ml each. All filtered fraction were analysed for adsorption of Cu^{2+} and Zn^{2+} and the values obtained are shown in Fig. 4.5 (a) and Fig. 4.5 (b) respectively for Cu^{2+} and Zn^{2+}. Curves in Fig. 4.5 indicate that it didn't take long for the process of adsorption to reach the saturation value. Percentage adsorption calculated for Cu^{2+} by 3A, 3B, and 3C were 86.85%, 56.74% and 10.74% and those for Zn^{2+} were 50.79%, 33.78% and 17.33% respectively. Percentage adsorption as low as 10.74% and 17.33% were obtained by 3C for Cu^{2+} and Zn^{2+} respectively. The only considerable value obtained was adsorption of Cu^{2+} by 3A which was 86.85%. The results show that weight to volume ratio of 1:200 is not considerable because by increasing the weight to volume ratio contact time can be increased and so as the amount of adsorption. Improvement is possible especially in fraction 3B which performed relatively well with adsorption percentage of 56.74% for Cu^{2+} and 50.79% for Zn^{2+}. Adsorption behaviour [as shown in Fig. 4.5 (a) and 4.5 (b)] of 3B and 3C was so uneven and the amount adsorbed was so low for Zn^{2+} that it could not be used as LCA even with possible improvements.



(a) Adsorption of Cu **(b) Adsorption of Zn**

Fig. 4.5 Adsorption of Cu and Zn by fractions of Sample 3

4.4.1.4 Preliminary adsorption test 4

Although, in the previous experiment W/V used was decreased to 1:200 to achieve the adsorption sooner, W/V ratio used for this test was 1:40 for adsorption of Cu^{2+} and Zn^{2+} from aqueous solution. Though, the W/V used was 1:40, 1000 ml of aqueous solution containing 50 mg/L of Cu^{2+} and Zn^{2+} was filtered using 25 g of 3A in the adsorption column. Percentage adsorption observed during this test was 95.05% and 24.38% for Cu^{2+} and Zn^{2+} respectively. Adsorption behaviour for this test is shown in Fig. 4.6. Huge increase in the weight of compost and volume of aqueous solution was done to see the effective changes in the amount of adsorption. But, the changes observed mainly in the amount of adsorption was not so different and most of the results of this study confirmed that the adsorbent has more affinity for adsorption of Cu^{2+} than Zn^{2+} except in first preliminary test where adsorption of Cu^{2+} 0.215 mg/g was less than the adsorption of Zn^{2+} 1.016 mg/g.

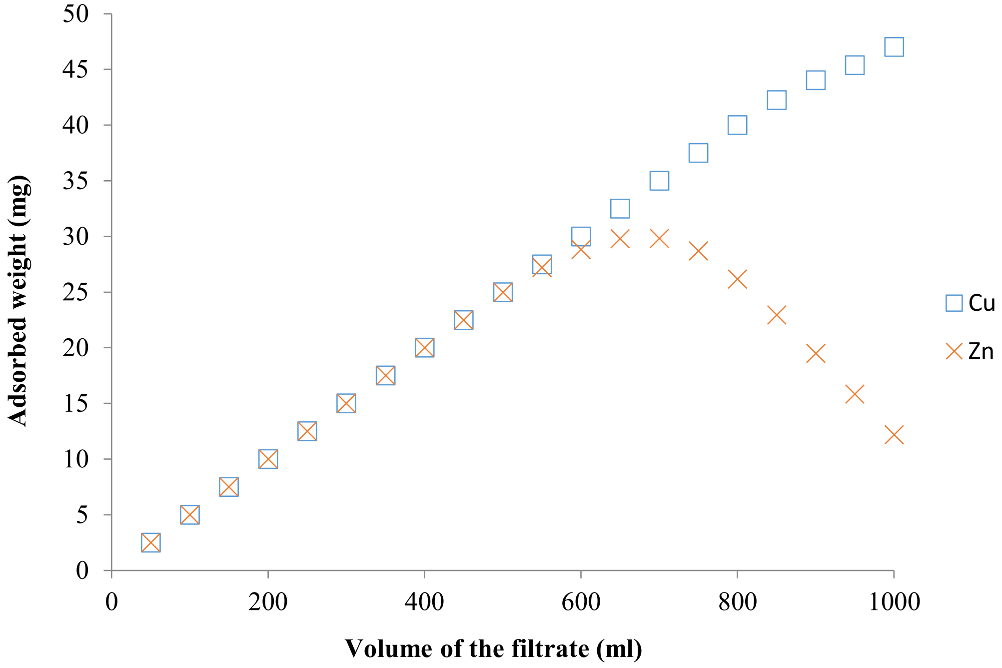


Fig. 4.6 Adsorption of Cu and Zn using 3A

4.4.2 Comparison and Feasibility Study

Mean concentration and quantity of elements per filtered fraction (FF) of aqueous solution, total adsorption and percentage adsorption (calculated using eq. 3.10) by the fractions of samples studied are given in Table 4.4. To get the optimal value of adsorption, three different weight to volume ratios were used for the fractions of three samples used in the study. For fractions of Sample 1 the ratio used was 1:10 but with this ratio rate of filtration was very slow. It took 8 hours for 1A, 6.5 hours for 1B and 3.5 hours for 1C to filter 50 ml of aqueous solution using 5 g of each in the adsorbent columns. The weight to volume ratios used for fractions of Sample 2 and Sample 3 were 1:50 and 1:200 respectively. The amount of time taken to filter 100 ml of aqueous solution using 2 g of 2A, 2B, and 2C in the adsorbent columns were 3.25 hours, 2.5 hours and 1.5 hours. With the weight to volume ratio of 1:200, 3A, 3B, and 3C took 2.17 hours, 1.17 hours and 0.25 hours respectively to filter 200 ml of aqueous solution using 1 g of each separately in the adsorbent columns. The amount of time taken by 3C to filter 200 ml of aqueous solution using 2 g of it was only 15 minutes which means time of contact of aqueous solution with 3C was very less that is why performance of 3C was very poor. It was 10.74% for adsorption of Cu^{2+} and 17.33% for adsorption of Zn^{2+}. There was no Zn^{2+} detected in the filtrate filtered by 1B so its percentage adsorption was 100% for 50 ml filtered volume in 6.5 hours. But, the optimal parameters for adsorption of Zn^{2+} were 99.99% adsorption in 2.5 hours with 1:50 weight to volume ratio by 2B. Optimal parameters for adsorption of Cu^{2+} were 99.19%

adsorption in 3.25 hours by 2A with weight to volume ratio of 1:50. Since, fractions of Sample 2 gave the optimal values for adsorption of both Cu^{2+} and Zn^{2+} therefore 2A for adsorption of Cu^{2+} and 2B for adsorption Zn^{2+} were most feasible both technically and economically. Other fractions were also technically and economically feasible for example 1A, 1B, 1C, 2C and 3A were also performed very well and all the samples studied were easily and cheaply available. Depending upon the availability of time 3B and 3C could also prove to be useful by modifying the weight to volume ratio.

Table 4.4 Adsorption details of fractions of samples

Fraction	Element	Mean conc. per FF (µg/ml)	Mean qty. per FF (µg)	Mean adsorption per FF (µg)	Total adsorption (µg)	(%) Adsorption
1A	Cu	0.2416	1.21	48.79	487.9	97.58
1B		0.2547	1.27	48.73	487.2	97.45
1C		0.7164	3.58	46.42	464.2	92.83
1A	Zn	0.0117	0.06	49.94	499.4	99.88
1B		0.0000	0.00	50.00	500.0	100.0
1C		0.0300	0.15	49.85	498.5	99.70
2A	Cu	0.0806	0.81	99.19	991.9	99.19
2B		0.0866	0.87	99.13	991.3	99.13
2C		5.9550	59.55	40.45	404.5	40.45
2A	Zn	0.0037	0.04	99.96	999.6	99.96
2B		0.0011	0.01	99.99	999.9	99.99
2C		7.2943	72.94	27.06	270.6	27.06
3A	Cu	1.3147	26.29	173.7	1737	86.85
3B		4.3257	86.51	113.5	1135	56.74
3C		8.9257	178.5	21.49	214.9	10.74
3A	Zn	5.5353	54.88	145.1	1016	50.79
3B		6.6331	124.9	75.06	675.6	33.78
3C		8.2671	165.3	34.66	346.6	17.33

4.5 RESULTS AND DISCUSSION OF KEY DATA

Since, it was decided to carry out the latter part of the research using green compost samples, one more continuous flow adsorption test using 3A was performed. Preliminary adsorption tests helped in deciding as to what W/V should be used for steady state adsorption test to determine the adsorption capacity of the green compost used as LCA in this study. Amount of adsorptions for Cu^{2+} and Zn^{2+} determined by first preliminary test were 0.215 mg/g and 1.016 mg/g respectively. The values of amount of adsorption determined by fourth preliminary adsorption test were 1.881 mg/g and 0.488 mg/g for adsorption of Cu^{2+} and Zn^{2+} respectively. As mentioned in adsorption test three (section 4.4.1.3) that W/V of 1:200 is not considerable especially for smaller amount of LCAs because it did not provide the enough contact time for fraction 3C. But, at the same W/V of 1:200 was found considerable for fraction 3A with the improved rate of filtration and preliminary test 4 (section 4.4.1.4) also did not indicate any significant improvement in the adsorption behaviour with higher quantities. It was also detected that the pH measurement was more effective with W/V equals to 1:200. Since, the process of adsorption is highly concentration dependent so getting slightly better result with higher concentration W/V (in the fourth preliminary test concentration of Cu^{2+} and Zn^{2+} used was 50 mg/L) was possible but reaching the equilibrium with higher concentration W/V was not smooth and process of adsorption was also very slow. So, to maintain the effectiveness of pH measurement and to make the process of adsorption smooth and quick, we used a W/V ratio of 1:200 in five concentrations of 1.25 mg/L, 2.5 mg/L, 5 mg/L, 10 mg/L, and 20 mg/L in this study.

4.5.1 Effect of pH on Adsorption

Since the aqueous solutions used in this study were prepared from standard solutions containing 1000 mg/L Zn^{2+} and Cu^{2+} respectively in 2% HNO_3, solutions prepared were acidic in nature. Higher the concentration of solution, more was the acidity because less water was needed for dilution. As the solution for binary adsorption of Cu^{2+} and Zn^{2+} was prepared from two standard solutions, it was more acidic than the solution prepared for mono adsorption. It was observed that the effect of solution pH on mono and binary adsorption of Cu^{2+} and Zn^{2+} was similar under similar conditions. During experiment it was also detected that pH of solutions was approaching neutral pH as process of adsorption was reaching towards equilibrium. Exception in the adsorption behaviour of mono Cu^{2+} was observed as it did not reach the equilibrium even after 10 hour and pH value of 7.15 so its equilibrium was predicted by polynomial model of the study. Since, the binary solution of Cu^{2+} and Zn^{2+} was highly acidic (average pH 2.60), it reached the equilibrium at an average pH value of 5.59 within 10 hour.

4.5.2 Model and Isotherms Analysis

Parameters of the experimental data fitted by Langmuir and Freundlich model are given in Table 4.5. The K_L values for binary adsorption of Cu^{2+} and Zn^{2+} both are negative which means Langmuir model is not a fit for the experimental data obtained for binary adsorption of Cu^{2+} and Zn^{2+} in this study because K_L is a physical quantity which cannot be negative. The only considerable value obtained by

Langmuir model was the R^2 value for mono adsorption of Zn which was 0.998 but the reason for it was that at lower concentrations amount of adsorption was of similar extent. The considerable difference in the amount of adsorption was observed at concentration of 20 mg/L that is why the Langmuir model got a better fit but that too was not the case for other adsorptions so Langmuir model was not a fit for this experiment. Similarly, the R^2 values for Freundlich model were also very low and the value as low as 0.215 for binary adsorption of Cu^{2+} was obtained. So, Freundlich model was also not a good fit for the experimental data obtained in this study.

Table 4.5 Langmuir and Freundlich model parameters

Type of adsorption	**Langmuir Model**			**Freundlich Model**		
	Q_{max}	K_L	R^2	n	K_F	R^2
Mono Cu	6.623	27.366	0.675	1.214	2.643	0.879
Mono Zn	1.585	12.990	0.998	3.135	0.975	0.732
Binary Cu	0.829	-ve	no fit	5.525	0.770	0.215
Binary Zn	0.581	-ve	no fit	6.803	0.582	0.445

The adsorption isotherms for adsorption of PTEs from solutions with one and two metals are shown if Fig. 4.7, Fig. 4.8 and Fig. 4.9. Mono adsorption of Cu^{2+} and Zn^{2+} are shown in Fig. 4.7 and Fig. 4.8 respectively whereas binary adsorption isotherms for Cu^{2+} and Zn^{2+} are shown in Fig. 4.9. The isotherms were obtained by fitting quadratic and cubic polynomials and the values of parameter are given in Table 4.6. Higher degree polynomials were not fit for the data because the degree of fit started decreasing. The best fit for mono adsorption of Cu^{2+}, mono adsorption of Zn^{2+}, and binary adsorption of Cu^{2+} was quadratic polynomial with R^2 values of 1.0, 0.997, and 0.971 respectively. Adsorption isotherm for binary adsorption of Zn^{2+} was best represented by cubic polynomial with R^2 value of 0.996 so the polynomial model developed was proved to be a good fit for the experimental data obtained in this study.

Fig. 4.7. shows that the mono adsorption of Cu^{2+} could not reach the equilibrium in 10 hours of experiment so its equilibrium value was predicted from the polynomial model and it was found that if the experiment was carried out under similar condition, it would have reach the equilibrium provided the initial concentration used was needed to be 79.81 mg/L and the value of maximum adsorption at that concentration would be 8.247 mg/g. Since, other adsorption isotherms reach the equilibrium so their maximum adsorption and concentration at that point was determined by differentiating the isotherms.

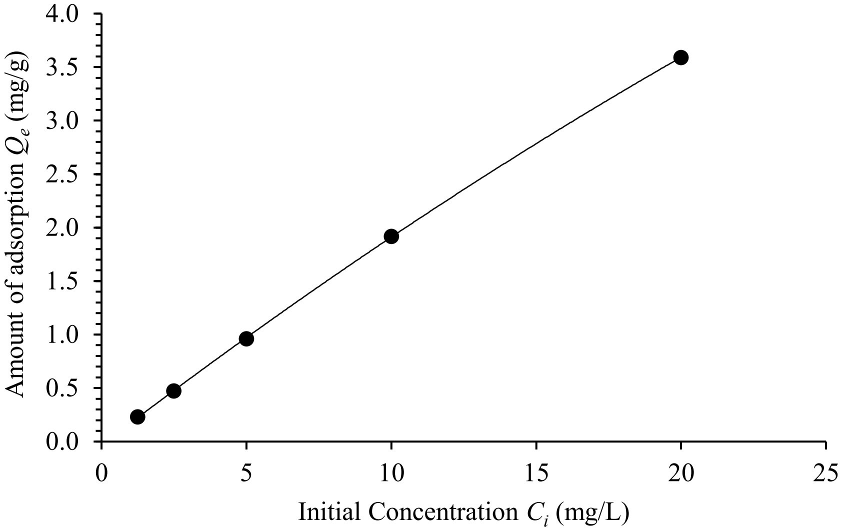


Fig. 4.7 Isotherm for Mono adsorption of Cu^{2+}

The adsorption capacities of green compost for mono adsorption of Zn^{2+}, binary adsorption of Cu^{2+}, and binary adsorption of Zn^{2+} were found at concentration of 14.46 mg/L, 11.92 mg/L, and 6.17 mg/L respectively and the corresponding values are given in Table 4.6. Binary adsorption of Zn^{2+} was very low and it reached the equilibrium at the end 6 hours with maximum adsorption of 0.875 mg/g and desorption of Zn^{2+} started at concentration 14.5 mg/L as shown in Fig. 4.9.

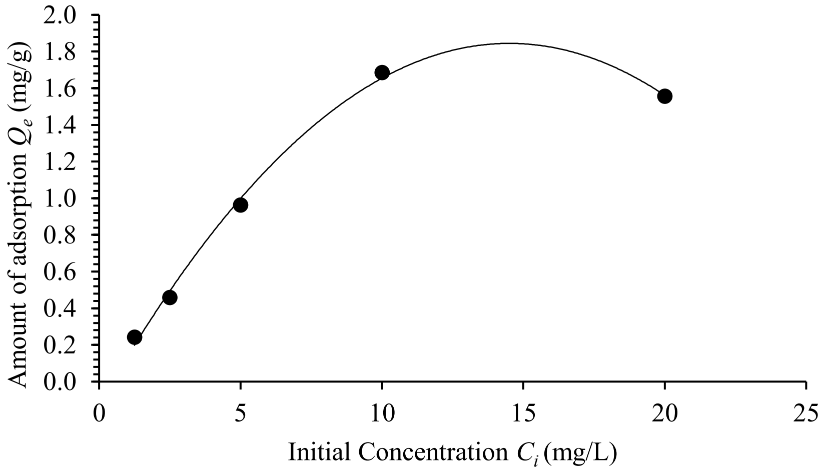


Fig. 4.8 Isotherm for Mono adsorption of Zn^{2+}

A key result retrievable from the adsorption isotherms shown in Fig. 4.7, Fig. 4.8, and Fig. 4.9 was that Cu^{2+} ion was adsorbed more than the Zn^{2+} ion. So, it was confirmed from the result that the green compost adsorbent had the major affinity for Cu^{2+} ions and a lower affinity for Zn^{2+} ions. In broad spectrum, the adsorption behaviour of the green compost used as LCA in this study for single-element or multi-element adsorption can be explained by the physicochemical properties of it as adsorbent.

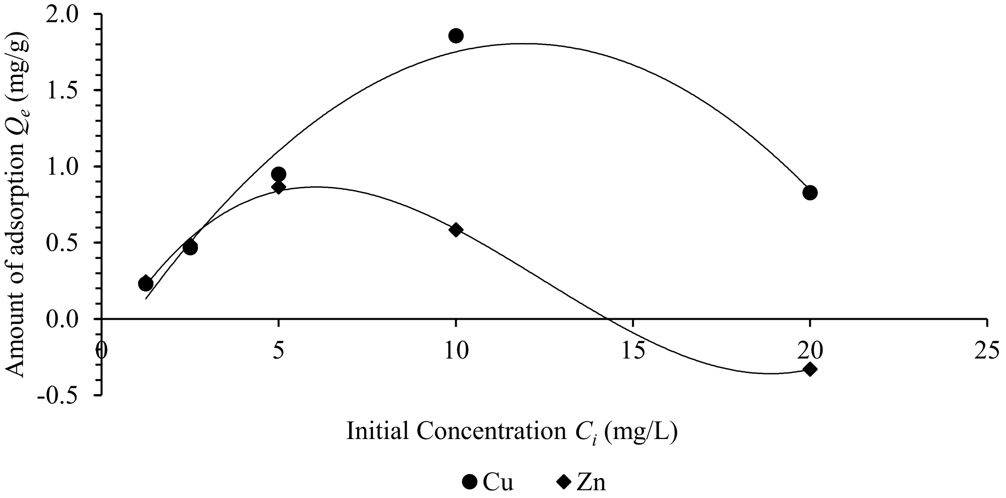


Fig. 4.9 Isotherm for Binary adsorption of Cu^{2+} and Zn^{2+}

But, adsorption also depends on the solution parameters (i.e. solution chemistry, pH etc.). The effect of pH is explained in section 4.5.1, concentration variation was other aspect which was corroborated to study the adsorption behaviour and optimisation of the model parameters. It is a common observation that with varying particle size specific surface area also varies (decrease in particle size increases the specific surface area and vice versa). So, parameter optimisation is suggested by using finer particles of the green compost.

Table 4.6 Polynomial model parameters and values

Type of adsorption	Parameters				Values	
	a_0	a_1	a_2	a_3	Q_{max}	R^2
Mono Cu	-0.033	0.208	-0.001	-----	8.247	1.000
Mono Zn	-0.127	0.272	-0.009	-----	1.838	0.997
Binary Cu	-0.263	0.350	-0.015	-----	1.805	0.971
Binary Zn	-0.213	0.398	-0.043	0.001	0.875	0.996

4.5.3 Plant Experiment Analysis

Plant experiment was performed using green compost obtained from preliminary test after adsorption because preliminary experiments were used as environmental risk evaluation test and steady state adsorption experiment was used as capacity determination test. Dry weight of plants uprooted from original sample (green compost before adsorption test) was 0.0186 g and it was 0.0245 g for the compost used after adsorption. Amount of uptakes for original green compost used for plant experiment were 0.0696 mg/g and 0.0297 mg/g for Cu^{2+} and Zn^{2+} respectively.

Amount of PTEs uptaken by mustard plant uprooted from the green compost with adsorbed heavy metal on it were 0.8209 mg/g and 0.3886 mg/g (as shown in Table 4.7) for Cu^{2+} and Zn^{2+} respectively. Since, mustard plants are not the deep rooted plants so, uptake of bound Cu^{2+} and Zn^{2+} from the bulk of green compost was very-very low. The adsorbed heavy metals stays on the surface only so the uptake of adsorbed PTEs were much higher than that of bound PTEs. In the plant experiment using mustard plant for the uptake of adsorbed heavy metals, it can be assumed that all the PTEs uptaken from the adsorbent were adsorbed PTEs. Since, the water used during the plant experiment was purified water obtained from Milli-Q Direct 16 water purification system and there was no external source of nutrition (manure) provided so the only source of nutrition for the plants was the uptake of PTEs from adsorbent. So, from the values given in Table 4.7 we can say that the mustard plant can remove 0.8209 g of Cu^{2+} and 0.3886 g of Zn^{2+} per gram dry weight of plants grown in the green compost used as LCA in this study. From the results given in Table 4.6 and Table 4.7 it can be concluded that the green compost used in this study can be reused as LCA only if better and quick removal technique than plant experiment may be applied for uptake of PTEs from green compost's surface because the uptake of PTEs from green compost surface by plant experiment was much lower and slower so it will take long time to prepare it for reuse.

Table 4.7 Uptake of PTEs in plant experiment

Sample Name	Uptake of Cu^{2+} (mg/g)	Uptake of Zn^{2+} (mg/g)
Original compost	0.0696	0.0297
Compost after adsorption	0.8209	0.3886

4.5.4 Adsorption Capacity of Green Compost Adsorbent

A significant improvement in the adsorption capacities determined by polynomial model was found as compared to the Langmuir and Freundlich models although, Langmuir model was not found fit in some cases and Freundlich model was a poor fit for the experimental data used in this study. Overall, the experimental adsorption capacities for mono and binary removal of PTEs were found in the range 0.581 mg/g to 6.623 mg/g for old models and it was in the range 0.875 mg/g to 8.247 mg/g for the polynomial model. Finally, both mono and binary adsorption processes were retrieved to be mainly physisorption in nature since there was no external energy supplied to activate the green LCA particles during adsorption process. Even with the physisorption mechanism adsorption capacity as high as 8.247 mg/g was predicted by the polynomial model so it can be concluded that the LCAs used in this study could prove to a good adsorbent for adsorption of Cu^{2+} and Zn^{2+} from aqueous solution.

Chapter 5

SUMMARY AND CONCLUSIONS

5.1 OVERVIEW

This chapter summarizes and draws conclusions from the study with respect to the research objectives identified in Chapter 1. The study comprises study of related literature (Chapter 2), the theoretical background needed for the development of the study (Chapter 2), detailed discussion of research hypotheses and research methodology (Chapters 1, 3), design of research for empirical analysis of data and model development (Chapters 3), and discussion and interpretation of quantitative and qualitative data analysis leading to the development of methods for the treatment of water containing PTEs using LCAs (Chapter 4). This chapter highlights the significant research contributions this study makes to the field of water and wastewater treatment. Limitations of the study are identified and the future research scope emerging from the study is also discussed.

5.2 SUMMARY OF RESEARCH FINDINGS AND CONCLUSIONS

The research focused on collecting and analyzing both quantitative and qualitative data in the study in a sequential manner (*sequential mixed methods).* The collected data were grouped into three as: Raw data, Preliminary data, and Key data. Based on the grouping of data, analysis of collected data was also done separately for each group. Analysis of Raw data was mostly the qualitative analysis based on the properties of the material like particle size fractionation, distribution of particle size, porosity, and bulk density. Analysis of Raw data helped in ranking of fractions of samples studied and selection of prima optimal adsorbents. Preliminary data were obtained from experiments (preliminary continuous flow adsorption tests) so analysis of preliminary data was quantitative analysis and it helped in quantifying as to what W/V of varying concentrations should be used for steady state adsorption test. Analysis of Key data was also quantitative analysis because Key data used in the study were all experimental data obtained from steady state adsorption test. Analysis of Key data with the developed polynomial model helped in stablishing the adsorption equilibrium and quantifying the adsorption capacities of the compost samples used as LCAs in this study.

The findings of the study are synthesized with respect to the research objectives and summary of the findings reflecting upon the achievement of the research objectives is presented here. The following sections present the research objectives for reference and conclusions of the research study with respect to these research objectives.

5.2.1 Research Objective 1

> First, objective of the study was the construction of a test system for study of the cleaning process of contaminated water samples using LCA.

To achieve the first objective, four material properties, particle size fractionation, distribution of particle size, porosity and bulk density were analyzed. To improve the efficiency of results, elemental content analysis was also done using ICP-OES. Based on the analysis of four material properties and elemental content of the LCAs, LCAs were ranked and selected as prima optimal adsorbents. The selected prima optimal adsorbents were used to construct the adsorbent columns which were used as a test system for study of the cleaning process of contaminated water samples.

5.2.2 Research Objective 2

> Second, objective of the study was the analysis of compost and polluted water by ICP-OES for PTEs content before and after treatment.

As mentioned in the first objective, elemental content analysis of compost samples used as LCAs in this study was done using ICP-OES before treatment, the same was not needed after the treatment because amount of adsorption was calculated using elemental content analysis of the filtrate obtained from the adsorbent columns. Elemental content analysis of the filtrate was also done using ICP-OES. Since, contaminated water used in this study was the aqueous solution of different concentrations prepared from standard solutions so the elemental content analysis before the adsorption test was not needed but the same done after the treatment. Second objective was more the precautionary measure than experimental so it was achieved easily.

5.2.3 Research Objective 3

> Third, objective of the study was the study of the adsorption behaviour of several PTEs on various composts e.g. their fractions of different particle size.

Adsorption behaviour of PTEs for adsorption on LCAs were studied form the data obtained from continuous flow adsorptions tests. Adsorption behaviour of Cu^{2+} and Zn^{2+} were studied using fractions of Sample 1 (1A, 1B, and 1C), fraction of Sample 2 (2A, 2B, and 2C), fractions of Sample 3 (3A, 3B, and 3C) and a special test using fraction 3A in the adsorption columns. Third objective of the study was completely experimental and time taking but the backbone of the study and was achieved successfully. The value of W/V obtained from this objective was used to carry out the steady state adsorption test which gave the values of adsorption capacities of the LCAs.

5.2.4 Research Objective 4

> Fourth, objective of the study was the optimization of the parameters in the cleaning process in order to elaborate a functional system.

Data obtained from the steady state adsorption test were used to optimize the values of amount of adsorption determined from continuous flow adsorption tests. Though, continuous flow adsorption tests are used to develop a functional system, it is very hard to determine the maximum adsorption using this test. So, maximum adsorption was obtained using steady state adsorption test and optimal parameters to elaborate a functional system were obtained from data analysis of steady state adsorption test using the developed model.

5.3 SIGNIFICANT RESEARCH CONTRIBUTIONS

All the fractions of samples analyzed and used for continuous flow adsorption tests were found to be the good adsorbents for adsorption of Cu^{2+} and Zn^{2+} except fraction 3C. Analysis of data obtained from continuous flow adsorption tests revealed that fraction 2A and 2B were best of them all for adsorption Cu^{2+} and Zn^{2+} and fraction 3C was the poorest adsorber. Since, the adsorbents used in this are easily and cheaply available so using these LCAs in a larger functional system can reduce the cost of treatment significantly. Removal of PTEs form contaminated water using the method developed in this study is not only cost effective but environment friendly too because specific goals of the study (section 1.4.1) covers every aspect of the environmental risk evaluation and mitigation. Despite, the above mentioned advantages of this study, it is believed that this study could make the following research contributions to water and wastewater industry.

a) As per the literature review findings, till now a few such studies using compost as LCAs have been conducted and when it comes to the wastewater industry, it is neglected. Thus, this study provides a direction for research using compost as LCA in the water and wastewater industry.
b) Development of method shows that the model formulation is as important as effective implementation of same for optimization of parameters.
c) The rapid increase in costs associated with wastewater treatment, means that use of LCAs has acquired special relevance in decreasing the cost of removal of harmful pollutants like PTEs from water and wastewater.
d) From cost perspective, the results of this study should be of use to both managers of water and wastewater facilities and responsible administration, as the cost effective treatment allows the curbing of water pollution at lower possible costs.

During the preparation of this study, it was realized that the application of LCAs in water treatment is boon for the environmental scientists and Government authorities. It is due to their inexpensiveness and free availability. Their applications are important for developing and under developed countries. It can be concluded from the critical evaluation of this study that the discussed LCAs could efficiently remove Cu^{2+} and Zn^{2+} from contaminated water. Of course, many research are available on this subject but adsorption is not developed fully especially at pilot and industrial scales. Therefore, there is a great need of the removal of PTEs from water by using LCAs at pilot and industrial scales.

5.4 LIMITATIONS OF THE STUDY

Any study or research cannot said to be complete in itself and this study is also not an exception. In the methodological framework analysis, following limitations were felt due to the research time limitations which deserve further investigation in future research.

a) The features of compost samples used as LCAs in this study were not characterized by FTIR (Fourier Transform Infrared Spectroscopy) or some other technique.
b) Column studies were not accompanied with batch studies for better understanding of adsorption mechanism as well as for understating the interaction of adsorbents with an adsorbates.
c) Number of continuous flow adsorption tests performed were less and no pilot study was carried out hence no functional system was tested.

5.5 FUTURE PERSPECTIVES OF LCAs

Conventional water treatment systems have changed drastically with the introduction of LCAs in the water treatment systems. By reducing the cost of treatment significantly, LCAs have provided a better and cost effective approach of water management. SWOT (strength, weakness, opportunities and threats) analysis is a tool used for identifying the strengths, weaknesses, opportunities and threats emanating by the use of LCAs in the water treatment system. The weaknesses and threats identified by SWOT analysis should be changed to strength and opportunities to provide a sustainable wastewater management. Since, by using SWOT analysis, life span of LCAs can be increased so SWOT analysis ultimately helps in determining the future perspective of LCAs. To better understand the future perspectives of LCAs it is necessary to understand the four elements (strength, weakness, opportunities and threats) of SWOT analysis clearly. So, in the following sections strength, weakness, opportunities and threats of LCAs or discussed in detail. Detail analysis of these four elements helps in identifying the relevance of SWOT in determining the future perspective of LCAs.

5.5.1 Strength of LCAs

As it is already included (low-cost) in the name, LCAs are inexpensive and affordable in terms of cost. The strengths of LCAs identified by SWOT analysis include its lower cost, easy availability in the environment, and presence in ample amount because LCAs are mostly the waste or by products of industrial, households or agricultural sectors. The low-cost materials used in this study for the development of methods for treatment of water containing PTEs were the waste products of households and agricultural sectors. The LCAs used in this study were the processed compost sample obtained from various waste processing plants in Hungary which were easily and readily available. One of the strengths of LCAs (used in this study) identified by SWOT analysis also include the waste management for the sector from which LCAs were obtained because if these waste products are not utilized as LCAs, they may cause unhygienic problems for humans. So, use of compost samples as LCAs to conduct PTEs adsorption in this study, will help to solve the water pollution problems. Moreover, it will increase the waste management practices without any significant cost involved.

Since, the LCAs used in this study were prepared from agricultural waste, it is pertinent to mention about other by-products from agricultural production which can be used as LCAs without composting. These products include rice husk, rice bran, rice straw, palm oil husk, nut shell, apricot stone, fruit peelings, sugar cane baggases and coconut husk which are easily available. Apart from available abundantly these products are good adsorbents for PTEs. The best thing with the use of these products as adsorbents is the absence of extra sludge which gets generated from removal of PTEs using chemicals. Strong adsorption ability of LCAs make them a bonus in water treatment system (Osita et al., 2014). Above all, reactivation and regeneration ability of LCAs has presented them as novel alternative for water management. Not only this, regeneration and reactivation of LCAs also promotes sustainability in water and wastewater treatment products.

5.5.2 Opportunities of LCAs

Opportunities of LCAs for removal of PTE from contaminated water could also be identified using SWOT analysis. With the known fact that LCAs are cost effective, many studies including this one have found that LCAs are time efficient too. These two opportunities of LCAs identified by SWOT analysis could help in reducing the cost and time consumed by the treatment methods. Efficiency of LCAs could be improved by small modifications or by pretreatment (De Gisi et al., 2016). Improved efficiency, less time consumption, and low-cost of LCAs make them a value added product management system and the sectors from which low-cost material for LCAs were obtained.

5.5.3 Weakness of LCAs

SWOT analysis also help in identifying the weaknesses of LCAs as the LCAs are usually available in the form which require at least short preparation methods like shorting of alien material and particle size fractionation etc. Some other weaknesses of LCAs include its presence in the environment as raw material. This weakness requires LCAs to go through cleaning and pre-treatments before being used as adsorbents for adsorption of PTEs. Cleaning and pre-treatment also help in removing the residues of contaminants from surface of the LCAs. Some more weakness include the requirement of activation (modification and enhancement) because some LCAs are not good adsorbents in their natural forms (Kurniawan et al., 2006) found in the environment. Besides, some LCAs are metal selective and their adsorption capacities are also not universal (not same for all the PTEs).

5.5.4 Threat to LCAs

The possible threats of LCAs identified by SWOT analysis could be the over-exploitation of LCAs and in very unlikely situation the gap in demand and supply. The gap in the demand and supply may arise due to use of LCAs on very large scale which will increase the demand sharply causing shortage in supply. Regeneration of some of LCAs are not very easy which is also a threat to LCAs. It might be a threat but regeneration of LCAs promotes sustainability in water and wastewater treatment by reuse of LCAs. Table 5.1 gives a summary of the SWOT analysis for the LCA used in this study.

Table 5.1 Overview of SWOT analysis for LCAs

Strengths	**Weaknesses**
A very little or no cost	Unavailability of some LCAs in readily form
By-products or waste products from agricultural and household sectors	Some LCAs require pre-treatment and cleaning before being used.
Present in very large amount in the environment because sources of production are huge	Some LCAs require activation before being used because in natural form they are not efficient.
Good adsorption capacity and highly efficient in removal of PTEs from contaminated water	Some LCAs are PTE selective and their adsorption capacities varies for different PTEs
Opportunities	**Threats**
Reduces the cost of treatment and brings sustainability in water treatment products	Very high demand may cause gap in the demand and supply.
Reduces the time of treatment process	If needed, pH adjustment may incur extra chemical cost to provide suitable condition for maximum adsorption of PTEs (De Gisi et al., 2016; Kurniawan et al., 2006)
Value added products could be developed by modification and enhancement of LCAs	
Alternative for conventional water treatment	

5.6 RECOMMENDATIONS FOR FUTURE RESEARCH

Limitations and future perspectives of LCAs determined by SWOT analysis, of the study allows the following recommendations for future research in the concern study area.

a) Even though the adsorption process is prevalent and well established for many decades, the prospects of the design of advanced and sustainable green materials with greater selectivity and stability at lower costs are still promising and appealing to a great extent.

b) LCAs used in this study are effective for removing pollutants at mg/ml concentration. Attempts should be made to module them for working at µg/ml concentration too.

c) In this study parameter optimization was done by comparing two different experimental stages. In future research concerning this area, parameter could further be optimized using statistical techniques like data envelopment analysis or using linear programming technique.

d) The challenges stemming from the translation of research from lab scale adsorption process to pilot and industrial scale processes such as economic constraints, extensive regeneration of the adsorbents and over-utilization of chemicals must be addressed in the coming years.

e) Besides, the exploitation of LCAs and resins in other technologies such as capacitive deionization, electrode ionization processes further supports the claim of this ever growing and flourishing domain with immense potential in the years to come.

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Appendix – I

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LIST OF SYMBOLS

Å – Angstroms

β – Beta

°C – Degree Celsius

ε – Epsilon

γ – Gamma

µ – Mew

ω – Omega

% – Percentage

π – Pi

ψ – Psi

ρ – Rho

∑ – Sigma

θ – Theta

τ – Tow

Appendix – A

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Appendix – B

SOURCE OF FIGURES

Fig. 2.1: http://ygraph.com/chart/2410 (accessed on 26.12.2018).

Fig. 2.2: https://www.researchgate.net/figure/Definition-of-the-basic-terms-of-adsorption_fig3_314081363 (accessed on 26.12.2018).

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