



Hungarian University of Agriculture and Life Sciences

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Szent István University

Doctoral School of Environmental Science

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

Thesis of the PhD Dissertation

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Durg Vijay Yadav

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Name of the School: **Doctoral School of Environmental Science**

Discipline: **Environmental Science**

Head of the School: **Dr. Erika Michéli**
Professor, DSc.
MATE, Faculty of Agricultural and Environmental Sciences
Institute of Environmental Science

Supervisor: **Dr. Gábor Endre Halász**
Associate Professor
Department of Chemistry
MATE, Faculty of Agricultural and Environmental Sciences
Institute of Environmental Science

Co-Supervisor: **Dr. Márk Horváth**
Research Fellow
Department of Chemistry
MATE, Faculty of Agricultural and Environmental Sciences
Institute of Environmental Science

.....
Prof. Dr. Erika Michéli
Head of the Doctoral School

.....
Dr. Gábor Halász
Supervisor

.....
Dr. Márk Horváth
Co-supervisor

1. INTRODUCTION

1.1 BACKGROUND OF THE STUDY

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.

1.2 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.

1.2.1 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.

1.2.1.1 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.

1.2.1.2 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.

1.2.1.3 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.

2. MATERIALS AND METHODS

2.1 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. 2.1 and eq. 2.2 respectively.

$$C_e/Q_e = 1/(Q_{max}K_L) + C_e/Q_{max} \quad (2.1)$$

$$\ln Q_e = (1/n) \cdot \ln C_e + \ln K_F \quad (2.2)$$

Amount of adsorption at equilibrium Q_e was calculated as follows –

$$Q_e = (C_i - C_e)V/w \quad (2.3)$$

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 ($\text{mg}^{1-1/n} \text{g}^{-1} \text{L}^{1/n}$) 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 –

$$\frac{dc}{dt_{ads}} = -K_{ads}C_t^{n1} + K_{des}Q_t^{n2} \quad (2.4)$$

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. 2.4 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. 2.4 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 –

$$\frac{dC}{dt_{ads}} = -K_{ads}C_e^{n1} + K_{des}Q_e^{n2} = 0 \quad (2.5)$$

i. e. $Q_e = K_e C_e^n \quad (2.6)$

or $Q_e = a_i C_e^i \quad i = 0, 1, 2, \dots, n \quad (2.7)$

Where K_e equals to K_{ads}/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. 2.7 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).

2.2 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.

2.2.1 LCA samples

The LCAs selected for removal of PTEs from contaminated water in this study were composites 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 \leq 0.32 mm),
- B** (0.32 mm < FPS \leq 1.00 mm),
- C** (1.00 mm < FPS \leq 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. 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.

2.2.2 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 Cu²⁺ (Merck 1.19786.0100) and Zn²⁺ (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 Cu²⁺ and Zn²⁺ in the diluted solution were also measured to avoid any possible error during dilution.

2.3 Methods Applied in the Study

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

2.3.1 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.

$$\text{Dry BD } \rho_d = \frac{M_s}{V_p + V_v + V_i} \quad (2.8)$$

$$\text{Wet BD } \rho_w = \frac{M_s + M_l}{V_t} \quad (2.9)$$

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. 2.9 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.

2.3.2 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%* HNO₃ and 2 ml 30 *m/m%* H₂O₂ 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)

After digestion reaction vessels were open in exhaust box and digested fractions were filtered. High purity water was added in filtered fractions to make the volume of each sample 25 ml and that 25 ml of fractions were stored in volumetric flasks for elemental analysis using ICP-OES.

2.3.3 Elemental analysis

Experiment started from analysing 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% HNO₃). 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.

2.3.4 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 and aqueous solution containing Cu²⁺ and Zn²⁺ 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 analysed using ICP-OES.

2.3.5 Performance evaluation

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

$$\text{Percentage adsorption } A = \frac{M_a - M_f}{M_a} \times 100 \quad (2.10)$$

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

2.3.6 Study of adsorption behaviour

Adsorption columns discussed in section 2.3.4 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 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 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 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 was used in the adsorption column. For test 4, 25 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. The concentration of Cu^{2+} and Zn^{2+} in the filtrates was determined by ICP-OES. W/V obtained from preliminary test was used to perform the steady state adsorption experiments and the 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 2.2. 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 2.2 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

2.3.7 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. 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. 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 nebulisation during determination of concentration using ICP-OES.

2.3.8 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 2.1) developed to determine the parameters of adsorption isotherms.

2.3.9 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 0.5 ± 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.

2.4 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.

2.4.1 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.

3. RESULTS

3.1 RESULTS BASED ON RAW DATA

3.1.1 Particle Size Distribution

Particle size distribution of all the fractions of samples (Spl) are given in the Table 3.1. 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 Siógárd was having 6.16% of the fraction with $FPS \leq 0.32$ 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 3.1 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

3.1.2 Bulk Density

Bulk density of the fraction of samples (Spl) used in this study was calculated using eq. 5.1 by measuring the mass of 38 cm³ 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/cm³ 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/cm³ and 0.52 g/cm³ 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 a lot of hard material present in the original composition of these samples which might hinder the process of adsorption using these samples.

Table 3.2 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

3.1.3 Elemental Content

Concentrations of four elements Cr, Cu, Ni and Pb having major impact on the ranking of fractions of samples are given in the Fig. 3.1. Effect of elemental content on ranking of fractions is explained using concentrations in fraction A Fig. 3.1 and fraction C Fig. 3.2. Copper was present in deciding amount (as shown in Fig. 3.1 and Fig. 3.2 for fractions A and C) in all the fractions of samples. Both Fig. 3.1 and Fig. 3.2 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 (Schreiber et al., 2018; Schwaab et al., 2017; Sharipova et al., 2017; Syafiuddin et al., 2018; Tian et al., 2018; Tzabar and ter Brake, 2016; Wang et al., 2018).

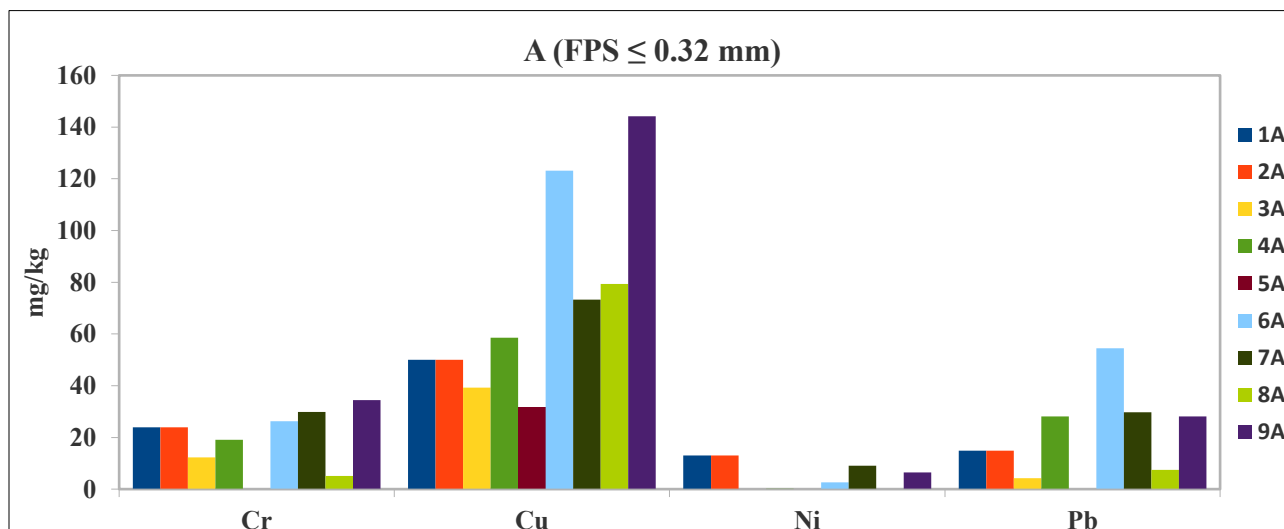


Fig. 3.1 Concentration of Cr, Cu, Ni and Pb in fraction A of all the samples

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 3.3.

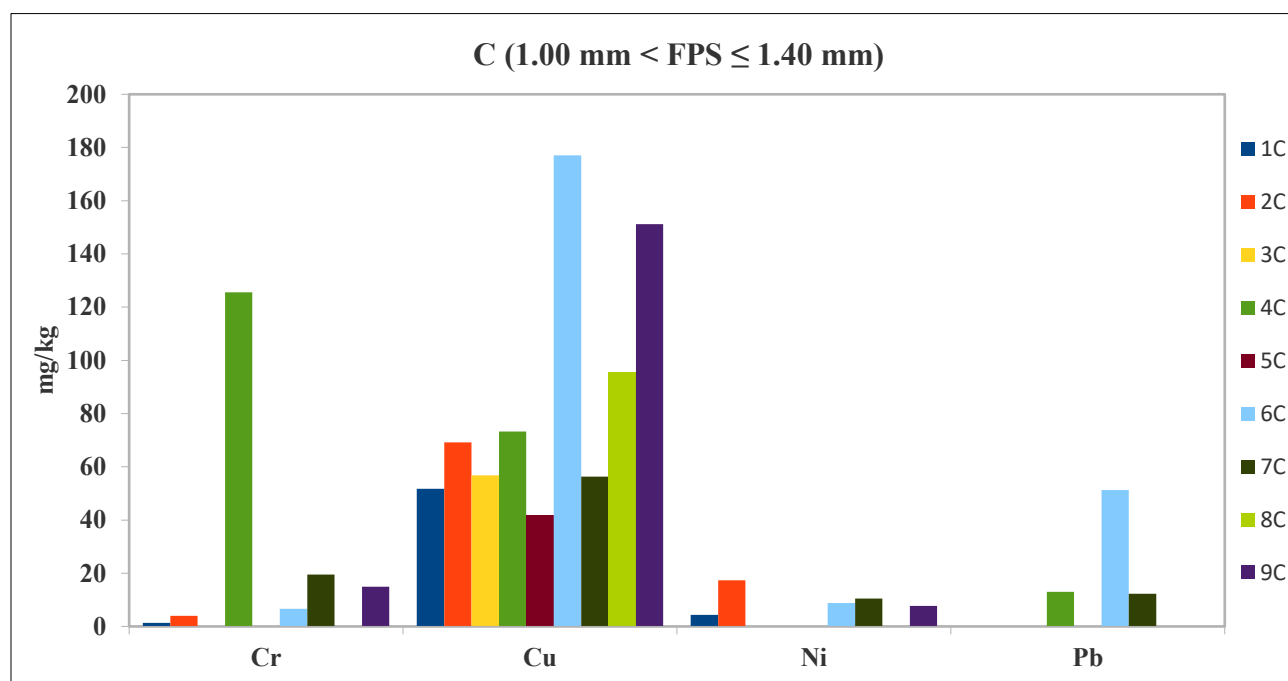


Fig. 3.2 Concentration of Cr, Cu, Ni and Pb in fraction C of all the samples

3.1.4 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 3.3 shows ranking of all the fractions. Based on the ranking in Table 3.3, fractions of samples can easily be selected for adsorption of PTEs from contaminates 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 (Komárek et al., 2018; Largitte and Pasquier, 2016; Machado Centenaro et al., 2017; Pandiarajan et al., 2018; Qu et al., 2018; Rogala et al., 2017; Romero-Flores et al., 2018).

Table 3.3 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

3.2 RESULTS BASED ON PRELIMINARY DATA

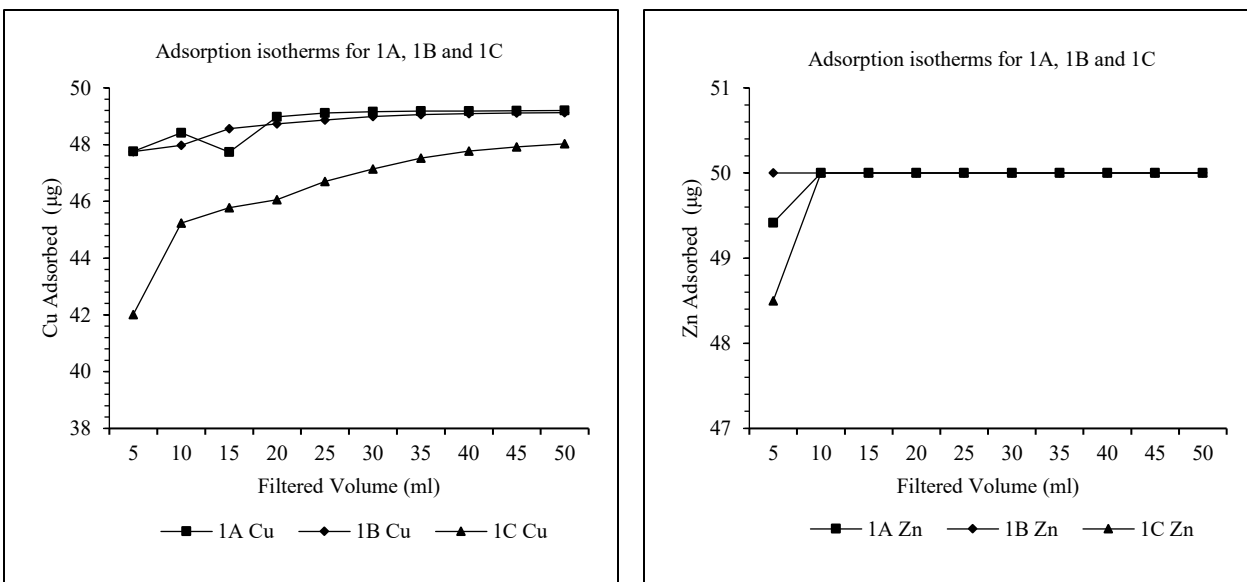
3.2.1 Continuous Flow Adsorption Test

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.

3.2.1.1 Adsorption using fractions of Sample 1

Adsorption isotherms of Cu and Zn for fractions of Sample 1 are given in Fig. 3.3 (a) and Fig. 3.3 (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. 3.3 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.



(a) Adsorption of Cu

(b) Adsorption of Zn

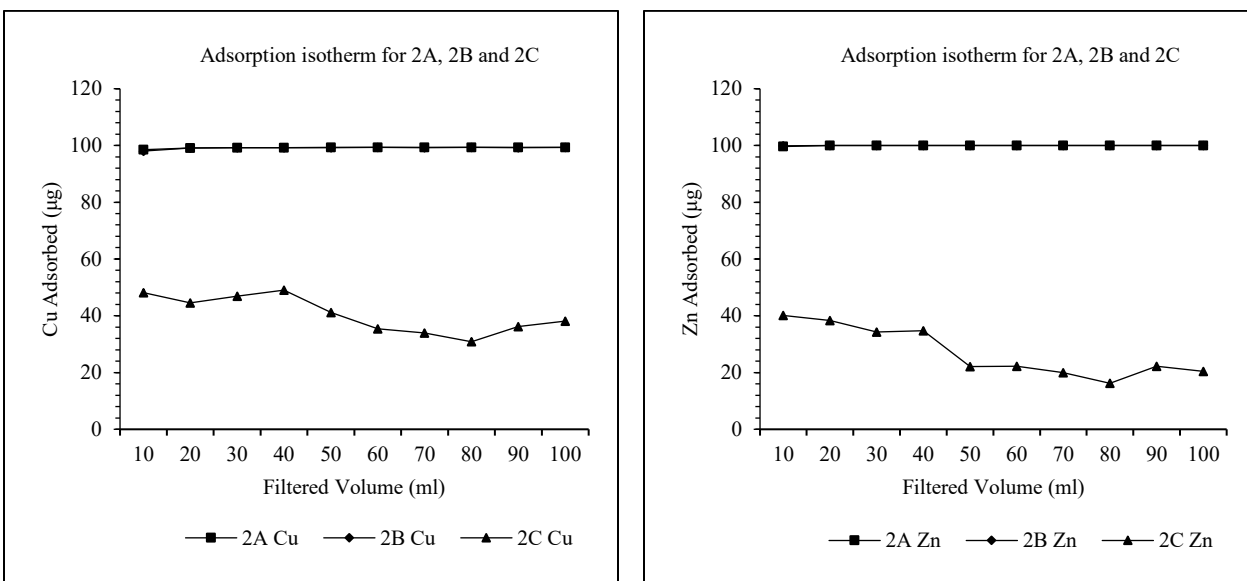
Fig. 3.3 Adsorption of Cu and Zn by fractions of Sample 1

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 3.4. 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 3.4.

3.2.1.2 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. 3.4 (a) for Cu^{2+} and Fig. 3.4 (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 3.4.



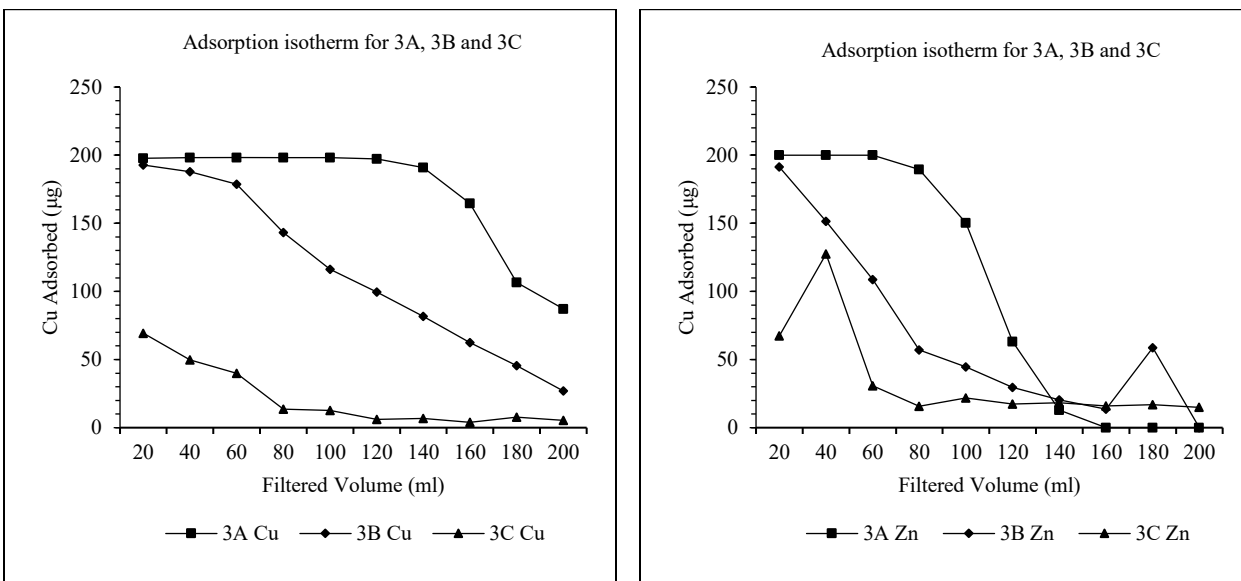
(a) Adsorption of Cu

(b) Adsorption of Zn

Fig. 3.4 Adsorption of Cu and Zn by fractions of Sample 2

3.2.1.3 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. 3.5 (a) and Fig. 3.5 (b) respectively for Cu^{2+} and Zn^{2+} . Curves in Fig. 3.5 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. 3.5 (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. 3.5 Adsorption of Cu and Zn by fractions of Sample 3

3.2.1.4 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. 3.6. 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.

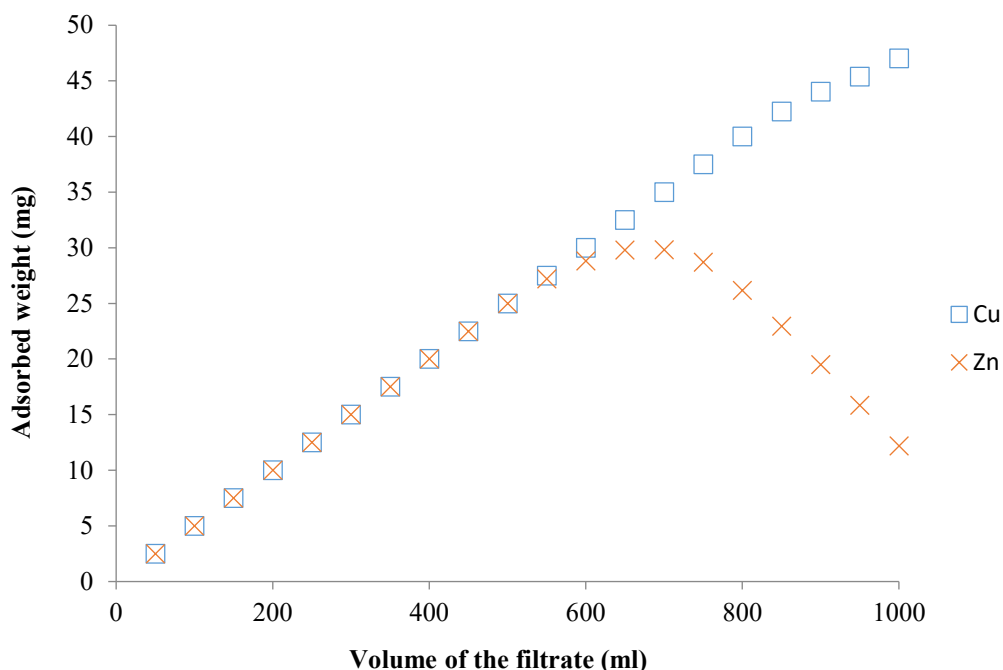


Fig. 3.6 Adsorption of Cu and Zn using 3A

3.2.2 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. 5.3) by the fractions of samples studied are given in Table 3.4. 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 3.4 Adsorption details of fractions of samples

Fraction	Element	Mean conc. per FF ($\mu\text{g/ml}$)	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

3.3 RESULTS BASED ON 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.

3.3.1 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.

3.3.2 Model and Isotherms Analysis

Parameters of the experimental data fitted by Langmuir and Freundlich model are given in Table 3.5. 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 3.5 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 in Fig. 3.7, Fig. 3.8 and Fig. 3.9. Mono adsorption of Cu^{2+} and Zn^{2+} are shown in Fig. 3.7 and Fig. 3.8 respectively whereas binary adsorption isotherms for Cu^{2+} and Zn^{2+} are shown in Fig. 3.9. The isotherms were obtained by fitting quadratic and cubic polynomials and the values of parameter are given in Table 3.6. 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. 3.7. 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.

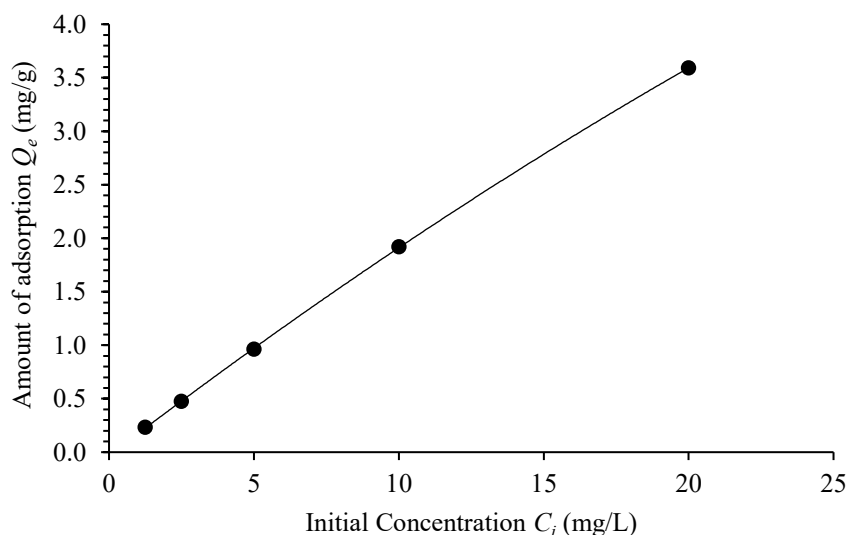


Fig. 3.7 Isotherm for Mono adsorption of Cu^{2+}

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 3.6. 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. 3.9.

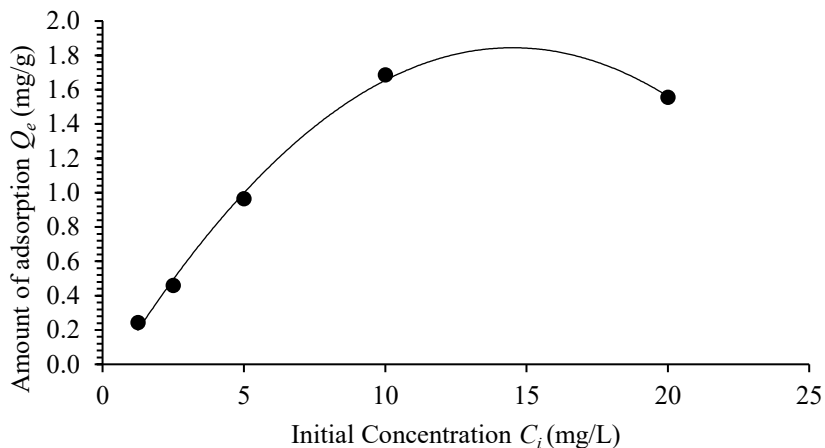


Fig. 3.8 Isotherm for Mono adsorption of Zn^{2+}

A key result retrievable from the adsorption isotherms shown in Fig. 3.7, Fig. 3.8, and Fig. 3.9 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.

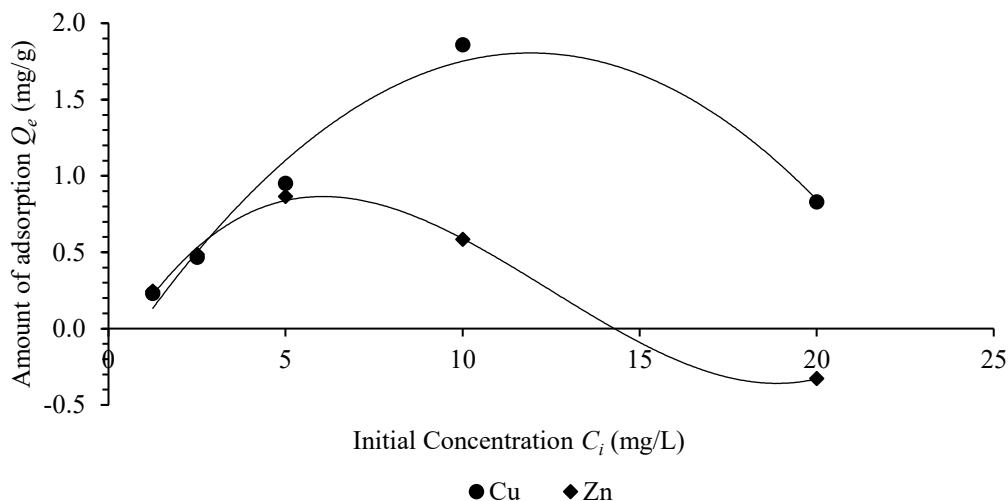


Fig. 3.9 Isotherm for Binary adsorption of Cu^{2+} and Zn^{2+}

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 3.6 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

3.3.3 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 3.7) 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 3.7 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 3.6 and Table 3.7 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 3.7 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

3.3.4 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/L to 6.623 mg/L for old models and it was in the range 0.875 mg/L to 8.247 mg/L 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 (de Abreu Domingos and da Fonseca, 2018; Fu et al., 2012; Gholitabar and Tahermansouri, 2017; Hor et al., 2016; Khandaker et al., 2018).

4. NOVEL SCIENTIFIC RESULTS

4.1 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 from 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 no 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. CONCLUSIONS AND RECOMMENDATIONS

5.1 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 base 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.

5.2 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 $\mu\text{g/ml}$ 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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7. RELATED PUBLICATIONS

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Yadav D. V., Horváth M., and Halász G., 2019 “Modeling of adsorption behaviour for removal of Cu and Zn from aqueous solutions using low-cost adsorbent” International Journal of Advances in Science Engineering and Technology, ISSN(p): 2321 -8991, ISSN(e): 2321 - 9009 Vol-6, Iss-4, Spl. Issue-2. (IF: 3.15)

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Yadav D. V., 2019 “Performance evaluation of wastewater treatment plants using DEA.” LAP LAMBERT Academic Publishing, Heinrich-Böcking-Str. 6-8, 66121 Saarbrücken, Germany www.lap-publishing.com ISBN: 978-613-9-99098-6