SZENT ISTVÁN UNIVERSITY

Doctoral School of Environmental Sciences

POLLUTED WATER TREATMENT USING COMPOST MATERIAL AS ADSORBENT: BATCH AND CONTINUES COLUMN STUDIES

Ph.D. Thesis

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INTRODUCTION

1. Introduction

Water pollution is the contamination of water bodies such as lakes, rivers, oceans, and groundwater caused by human activities, which can be harmful to organisms and plants which live in these water bodies. Water pollution by toxic heavy metals through the discharge of industrial waste is a worldwide environmental problem. The presence of heavy metals in streams, lakes, and groundwater reservoirs has been responsible for several health problems with plants, animals, and human beings (Huang et al. 2008). Copper is widely applied in the electrical wiring, selenium rectifier, plumbing, gear wheel and roofing industries for its electrical and thermal conductivity, good corrosion resistance and ease of installation and fabrication. The copper is essential and healthy to humans. However, like all heavy metals, it is potentially toxic as well. The potential sources of copper in industrial effluent are from pulp and paperboard mills, plating baths and metal cleaning, the fertilizer industry, and wood pulp production (Subbaiah et al. 2011). In recent decades, the annual global release of heavy metal reached 22,000 tons (metric tons) for cadmium, 939,000 tons for copper, 783,000 tons for lead and 1,350,000 tons for zinc (Singh et al. 2003). The excessive intake of copper results in its accumulation in the liver and produces gastrointestinal problems, kidney damage, anemia and continued inhalation of copper-containing sprays which is linked with an increase in lung cancer among exposed workers (Sunarso and Ismadji 2009). Cadmium is one such heavy metal which is added to water and soil through the effluent from battery, catalyst, paint, mining and many other industries. It affects human being adversely when injected into human bodies. It can cause both long term and short-term diseases in human beings and other aquatic life (Laniyan et al. 2011). Consequently, it became very important to remove such contaminants from industrial wastewater before they are discharged into the environment. The removals of these hazardous materials may be performed using various techniques, including precipitation, membrane filtration, ion exchange, sorptive flotation and adsorption. However, these methods are known for their high cost and ineffective when dealing with low heavy metal concentration. While a number of researchers have attempted to resolve this problem through the use of different technologies, an efficient and cost-effective approach for heavy metal removal remains a challenge. Among many methods, adsorption techniques have been found appropriate for wastewater treatment because of their cost effectiveness and uncomplicatedness. Adsorption has been recognized as an effective process in most of the industrial water and wastewater treatment (Mohammadi et al. 2005). Adsorption is the process of the attraction and accumulation of gas or liquid particles on the surface of another substance. Whereas the absorbed particles are called the adsorbate, the substance applied for adsorption is call the adsorbent. The foremost benefits of biosorption technology are its efficacy in reducing the concentration of heavy metal ions to very low levels and the use of low-cost biosorbent materials. Compost is an effective technology of retaining bio waste and generating effective fertilizer. The process of composting has also become an effective method of reducing the toxicity of heavy metals from solid waste and soils. The composts were applied to soils, which could increase the mineral nutrients and humic substances content, as well as the microbial activities (Aranda et al. 2015). Studies have found that as compost is processed, the content of dissolved heavy metals decreases, while the content of stable forms of heavy metals increases (Hanc et al. 2012). In addition, the morphological variations of heavy metals have a certain relevance to the fluctuations of organic matter and humus development throughout the composting progress. This paper evaluates the adsorption of Cd^{2+} and Cu^{2+} by using compost material as an adsorbent application. Batch experiments were carried out to examine the ability of different compost material of removing heavy metal from industrial waters. The experimental data was applied to one for the most used adsorption models, and its function fitted well. Different type of compost materials used in this research, this is to evaluate their capacity for binding heavy metals. Composting is a pacifying method to manage all forms of wastes (such as sewage sludge, municipal solid waste, tannery waste, pig manure, poultry manure etc.) which are biodegradable. The use of compost formed by above waste material to land can be used as soil fertilizer/conditioner due to presence of nitrogen, phosphorus, potassium and other nutrients. Composting is the process in which organic matter is transformed into compost by aerobic microorganisms, it comprises three major phases: mesophilic, thermophilic and cooling phase (the compost stabilization phase) (Neklyudov et al. 2008). It can reduce the solid waste volume by 40-50%, pathogens are destroyed by the metabolic heat generated by the thermophilic phase, which degrades a big number of hazardous organic pollutants and make available a final product that can be used as a soil improvement or fertilizer (Cai et al. 2007). Therefore, the fixation and adsorption of heavy metals by humus formed in the composting process is an economical and effective method of decreasing the bioavailability of heavy metals and reducing the risk of heavy metals in soils and wastewaters. Functional groups such as phenolic hydroxyl and carboxyl increase, which means that the composting process can promote humic substances and provide more adsorption sites for chelating heavy metals (Veeken et al. 2000). Adsorption is a recognized method for the removal of heavy metals from low concentration wastewater containing heavy metal. The high cost of AC limits its use in adsorption. Many varieties of low-cost adsorbents have been developed and tested to remove heavy metal ions. However, the adsorption efficiency depends on the type of adsorbents. Biosorption of heavy metals from aqueous solutions is a relatively new process that has proven very promising for the removal of heavy metal from wastewater

1.1 Research objectives

The objective of this research was to investigate heavy metal removal from industrial wastewater using various adsorbent materials in a series of batch and fixed-bed column studies under various experimental conditions. In order to achieve this objective, two different approaches conducted in laboratory studies with the following methods:

1. A batch adsorption study using different compost material was conducted to investigate the capability of removing Cu^{2+} and Cd^{2+} from industrial water.
2. A fixed bed column system adsorption study was operated using different compost material with different conditions of concentration of heavy metal, bed depth and flow rate to remove heavy metal from the aqueous solution.
3. Applying the most commonly used models for adsorption prediction.
4. Studying the compost material capacity and their chemical characteristics by relating analytical instrumental technologies.

1.2 Thesis organization

The experiments and tasks were defined, designed and are presented in this study in the following manuscript format:

Experimental

Batch study (Part I)

Laboratory examination for the part I was carried out in batch experiments. The determined concentration from 0 to 50000 μg mL^{-1} of the solution was tested with a different type of compost material. The weight of 1 g of compost material mixed with 10 mL solution concentration flask was investigated. Langmuir model was fitted to the data and its coefficient was determined.

Continuous fixed bed (Part II)

Laboratory experiments for part II were carried out to determine the efficiency of compost material in continuous adsorption mode versus different adsorption column depths, flow rate, adsorbent concentration and different time as well. The experimental work was carried out to verify the kinetic models with fixed bed columns. The investigation conducted to evaluate the compost material of removal different heavy metals which discussed in chapter 3.

Chapter 1: Introduction

The introduction part of this thesis is giving a general overview of heavy metal contamination and the work carried out.

Chapter 2: The literature review

A literature review is presented in Chapter 2 which touches on various aspects of this research. Since this research is focused on heavy metal removal from aqueous solution using adsorption, general treatment methods including adsorption were reviewed. Adsorption fundamentals, adsorption approaches and adsorbent materials for heavy metal removal were reviewed and presented.

Chapter 3: Batch and continuous fixed bed experiments

Batch experiments were implemented in a set of flasks containing 10 mL of solution to investigate the effects, biosorbent dosage (1 g), initial metal ion concentration (0 to 50000 μg mL^{-1}) and contact time (24 hours). The suspensions were then filtered and metal ion concentrations in the supernatant solutions were measured by Atomic Absorption Spectrophotometer. Series of batch experiments were conducted using Cu^{2+} and Cd^{2+}. This chapter aimed to compare different compost material and different adsorbates. The data were fitted to Langmuir isotherm and coefficient were obtained and compared. Fundamental information on the adsorption capacities of these adsorbent materials was discussed. Batch experimental was run for the removal of several heavy metals using different compost material as treatment. The fixed bed system is dedicated to kinetics study of the ability of compost material for removing copper from wastewater by Felgyő and Garé compost for removing Cu^{2+} from wastewaters and Cd^{2+} treatment by Felgyő compost is also presented. The main objective of the fixed bed column was to investigate the adsorption of heavy metals Cu^{2+} and Cd^{2+} using different flow rate and different concentration at various volume (bed depth) ratios. A laboratory bench-scale fixed-bed column study was operated in a down-flow method to evaluate low-cost adsorbents for the removal of heavy metals based on the adsorption media, which was packed at different column depths (5, 10 and 15 cm). Effluent metal concentrations were set at 20, 100 mg/L and monitored its flow into the column bed, while metal breakthroughs as a function of volumetric throughput in the columns were reported and compared to each other. The results of these fixed-bed column investigations could provide useful insights into the design of larger scale metal removal applications using these types of natural adsorbents. Metal removal efficiencies and adsorbent adsorption capacities for each of the columns was estimated to assess the suitability of these adsorption media and the preferred operating conditions for the treatment of heavy metals. From the results of this work, observations regarding the potential use of these natural adsorbents for the heavy metal removal were discussed.

Chapter 4: Recommendations and further studies

Instruments used during this study

The importance of using analytical equipment has been used by various researchers in order to give broad pictures of the mechanism of adsorption and the relationship of adsorbent-adsorbate. Amongst many techniques, the usage of the below equipment was beneficial to this study, below are the methods used and further elaborated in Chapter 1.

1. Atomic absorption spectrophotometry.
2. Energy dispersive X-ray spectroscopy (EDX)
3. Fourier transform infrared spectroscopy (FTIR)
4. Scanning electron microscopy (SEM)

2. Materials and methods

2.1 Instruments used for experimental analyses

The functional groups of the compost were characterized by a Fourier transform infrared (FTIR) spectrometer (FTIR – Mattson Research Series). The spectra of compost were measured within the range of 4,000–500 cm^{-1} wave number. Morphological analysis of the adsorbent was done by using the scanning electron microscope SEM + EDX– JEOL JSM-5600LV + EDS-2000. The acceleration voltage of the instrument was set at 5 kV, with an image point resolution of 10 μm, with x35 and x50 magnification. The metal concentration was analysed using atomic absorption spectrophotometer (AAS; model GBC 935).

2.2 Preparation of adsorbent

Adsorbents were provided by laboratory of bio combustibles from Szent István University, Gödöllő (Hungary). Each compost was ground and sieved into fractions below 2 mm. The fractions collected below mesh size of 2 mm were designated for the characterization and biosorption investigations without any pre-treatment. Felgyő compost is a green waste and sewage sludge, 2. Garé is communal sewage sludge, slurry mud and chicken manure with straw. 3. Sioagárd is green biomass/bio waste. For batch experiments, the particular weight of compost sample was one gram. 13 samples were prepared for a single set, and 3 replications were conducted to carry the test for one single metal followed by the same steps for other composts besides the heavy metals. Finally, every set of samples has 10 mL of concentrated solution per each bottle plus one gram of compost. The concentration solution ranges from 0 to 50000 $\mu g\ g^{-1}$ of one single metal and the homogeneous mixture was ready to be investigated.

2.3 Quality control

The distilled water was digested and analysed with every sample group to track any possible contamination source and obtain a baseline value. Triplicate runs for batch mode adsorption experiments were made for each adsorbent to determine the relative deviation of the experiments.

2.4 Adsorption in batch experiments

After each adsorption, the residual Cd^{2+} and Cu^{2+} were determined by digesting the filtered synthetic wastewater followed by AAS analysis as a standard method. The percentage of the adsorbed metal ions was estimated using the following equation:

$$R\ (\%) = \frac{(C_0 - C_e)}{C_0} \times 100 \quad (2.1)$$

Where C_0 and C_e are metal ions concentrations (mg L^{-1}) before and after adsorption respectively.

Adsorption capacity estimated using the bellow equation:

$$X = \frac{V(C_0 - C_e)}{M} \quad (2.2)$$

Where, V = Volume of solution (mL), M = mass of adsorbent (mg), C_0= Initial metal Concentration (µg g^{-1}), C_e = Final metal Concentration at equilibrium (µg g^{-1}), X = The adsorbate Concentration / adsorption Capacity of compost (µg g^{-1})

2.5 Preparation of synthetic wastewater

Cd and Cu added separately to distilled water in the laboratory and the value of concentration was determined in a range from 50 to 50000 µg g^{-1}. The stock solution of 1000 mg L^{-1} Cu^{2+} was prepared by dissolving $CuSO_4.5H_2O$ and $Cd(NO_3)_2.4H_2O$ in different flasks of 1.0 L deionized water and further diluted to the desired concentration with deionized water. The concentration solution was determined in a range of (0–50000 µg g^{-1}) for each metal in batch experiments and 20, 100 mg L-^{1} for bed column experiments. The chemicals used throughout this study were of analytical reagent grade provided by Reanal Ltd, Hungary. The individual metal ion concentrations in solution were analysed using an atomic absorption spectrophotometer (AAS) Varian Spectra AA-20 at the Analysis Service Unit of Szent Istvan University, Hungary.

2.6 Experimental set up for batch study

Batch adsorption experiments were carried out by shaking a series of samples containing the same amounts of different concentration solution with a mixture of 3 different composts used to sorb the heavy metal separately. The compost materials used were mixed with concentration range of (50, 100, 250, 500, 100, 250, 500, 10000, 25000, 30000, 40000, and 50000 μg g^{-1}) of Cu^{2+} and Cd^{2+}. After the composts have been collected, the product was ground and sieved to 2 mm which transferred to a small flask with a screw cap which contained 1 g compost plus 10 ml of concentrated solution, and then immerged in a shaking machine as a complete set containing 13 samples at a constant speed of 125 rpm. The shaking was run for every set of the experiment for 24 hours. All the experiments were performed in triplicate method, the adsorbate and adsorbent were separated by high speed centrifugation at 6000 rpm for 7 minutes. In this stage of the experiment the adsorbent particles were separated from the suspensions by filtration through 0.43 μm filter paper. The residual concentration of heavy metals was determined by the Atomic absorption photometer. The measured data were fitted to Langmuir function.

2.7 Fixed bed column construction

The glass columns were 30 cm long, 1.2 cm internal diameter with a porous ending at the bottom. The column packed with the desired amount of compost representing the height of the bed column with two supporting layers of glass wool at the top and the bottom. Cu^{2+} was tested on tow compost Felgyő and Garé, packed with 5, 10 and 15 g of compost with bed heights (1.1, 2 and 3.1cm), (2.4, 3.1 and 6.5cm). respectively. Cadmium was investigated by using Felgyő compost into three different bed height (1.1, 2 and 3.1cm). Columns positioned vertically and adsorption tests were performed in continuous down flow method, the experiments were conducted at room temperature. Wastewater kept in an overhead container and the only driving force of the solution through the column is the gravity and it is manually controlled for its flow operation. A flow control valve was used to adjust the flow at 4 and 8 mL min^{-1}. The initial heavy metal concentration of 20 and 100 mg L^{-1} of Cu^{2+} was prepared using analytical grade ($CuSO_4.5H_2O$) and $Cd(NO_3)_2.4H_2O$ provided by Reanal Ltd company. The solution was prepared by dissolving the individual required quantity of copper sulfate and cadmium nitrate in distilled water. It was further diluted to obtain standard solutions. 1000 mL of aqueous solution was filled on the overhead tank and then charged into fixed bed columns. The samples were collected at different time intervals to analyze Cu^{2+} and Cd^{2+} concentration using atomic absorption spectrophotometer.

3. Result and discussion

3.1 Analysis and Characterization of compost for bed column

3.1.2 Scanning electron microscopy (SEM)

SEM images are useful tools to understand the morphology of the adsorbent material. Here in this research SEM conducted before and after adsorption process. The SEM mapping before and after adsorption show how an irregular surface, which is heterogeneously shaped and cracked probably favours the sorption of Cu^{2+} and Cd^{2+} on different parts of the adsorbent; making it a propitious adsorption technique. SEM images are indicating that the compost had good characteristics to be used as an adsorbent for metal ion uptake due to its heterogeneous distribution and particle sizes which perhaps favour the adsorption mechanisms. The composition of Felgyő and Garé was very similar despite the large differences in the morphology (Garé compost containing much larger particles as seen on the SEM images). The carbon content was roughly half of the concentration observed at the two compost samples, indicating significantly higher organic matter content. Nevertheless, the treatment affected the concentration of some elements, leading to a decrease especially in the Na, Cl, S and K content. Because of the heterogeneous structure and composition of the compost, the chemical elemental analysis was expected to show the chemical constitutes which could influence the heavy metal adsorptive capacity of the adsorbent.

3.1.2 Energy dispersive X-ray spectroscopy (EDX)

EDX analysis was used to determine qualitatively the elemental composition of the raw compost and after treatment before and after adsorption for Cu^{2+} and Cd^{2+} using Felgyő and Garé respectively. The samples were coated with gold prior to analysis to avoid electron charging. The elemental composition percentages of these samples are given in tables 3.1 and 3.2, the major findings in EDX show that the main peaks are silicate, carbon and oxygen in the compost after loaded with heavy metals. The appearance of Cu^{2+} and Cd^{2+} features can be observed on EDX spectrum at different energy values indicates that the biosorbents studied were able to bind metal ions. This indicates that the catalyst is not uniformly distributed on the compost substrate; this fact can also be seen in all SEM micrographs. The disappearance of some metal after metal ion adsorption may be due to the ion-exchange mechanism; this is also incurred with (Kamari et al. 2014). EDX analysis provided direct confirmation for the heavy metal adsorption onto the compost material.

Table 3.1. The EDX chemical composition of raw Felgyő compost before and after loaded with Cu^{2+} and Cd^{2+}

Sample	Raw compost		Raw compost		Cu^{2+} loaded		Cd^{2+} loaded	
Mag	x35		x50		x50		x50	
Element	At. Ratio	Wt %	At. Ratio	Wt %	At. Ratio	Wt %	At. Ratio	Wt %
C	41.22	32.164	44.708	35.233	29.235	21.398	29.235	21.398
N	12.9	11.738	10.048	9.235	13.81	11.79	13.81	11.787
O	38.163	39.667	38.043	39.936	44.618	43.502	44.618	43.502
Na	0.267	0.399	0.197	0.297	-	-	-	-
Mg	0.395	0.623	0.357	0.57	0.535	0.792	0.535	0.792
Al	0.771	1.351	0.806	1.428	2.26	3.72	2.261	3.718
Si	2.759	5.035	2.552	4.703	7.158	12.25	7.158	12.252
P	0.444	0.893	0.442	0.899	0.18	0.339	0.18	0.339
S	0.288	0.599	0.352	0.74	0.096	0.188	0.096	0.188
Cl	0.124	0.286	0.097	0.225	-	-	-	-
K	0.69	1.753	0.639	1.64	0.329	0.783	0.329	0.783
Ca	1.652	4.301	1.302	3.423	0.98	2.38	0.976	2.384
Fe	0.328	1.19	0.456	1.672	0.53	1.81	0.532	1.809
Cu	-	-	-	-	0.27	1.046	-	-
Cd	-	-	-	-	-	-	0.27	1.046

Table 3.2. The EDX chemical composition of raw Garé compost and after loaded with Cu^{2+} and Cd^{2+}

Sample	Raw compost		Raw compost		Cu^{2+}		Cd^{2+}	
Mag	x35		x50		x50		x50	
Element	At. Ratio	wt%	At. ratio	wt%	At. ratio	wt%	At. ratio	wt%
C	42.478	33.232	44.960	36.711	41.372	33.629	43.788	35.276
N	10.427	9.513	10.054	9.574	11.433	10.838	12.409	11.658
O	39.605	41.275	40.439	43.985	42.915	46.467	38.569	41.39
Na	0.243	0.364	0.287	0.449	-	-	-	-
Mg	0.484	0.767	0.349	0.577	0.154	0.253	0.252	0.411
Al	0.739	1.298	0.528	0.968	0.753	1.376	0.656	1.187
Si	2.338	4.277	1.565	2.988	2.15	4.087	2.289	4.311
P	0.598	1.207	0.310	0.653	0.269	0.563	0.375	0.779
S	0.274	0.573	0.240	0.522	0.125	0.272	0.163	0.35
Cl	0.135	0.311	0.084	0.202	-	-	-	-
K	0.613	1.562	0.298	0.793	0.098	0.259	0.104	0.274
Ca	1.841	4.807	0.733	1.996	0.495	1.344	1.099	2.954
Fe	0.224	0.816	0.153	0.583	0.18	0.678	0.219	0.822
Cu	-	-	-	-	0.055	0.235	-	-
Cd	-	-	-	-	-	-	0.078	0.589

3.1.3 Fourier transform infrared spectroscopy (FTIR)

FTIR conducted in this research to know the functional groups that the compost material contains. The FTIR supported the metal binding is mainly due to the ionic interaction of the metal cations with the carboxyl groups in the humic substances, a shift in the ratio of the peaks related to the protonated and dissociated carboxyl groups could indicate the metal binding. FTIR spectra for compost material before and after loaded with Cu and Cd are depicted in figures 3.1 and 3.2.

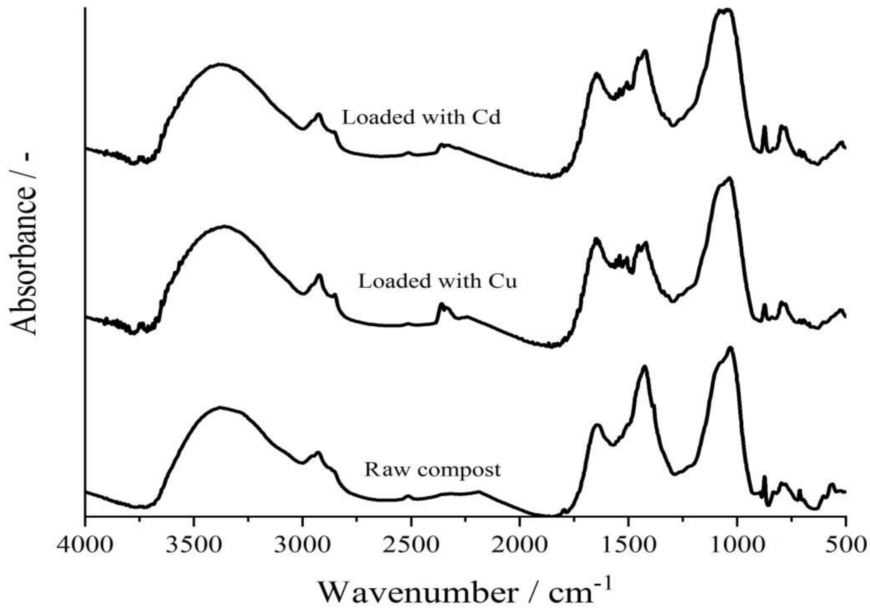

Fig. 3.1 FTIR spectra of raw Garé compost loaded with Cu^{2+} and Cd^{2+}.

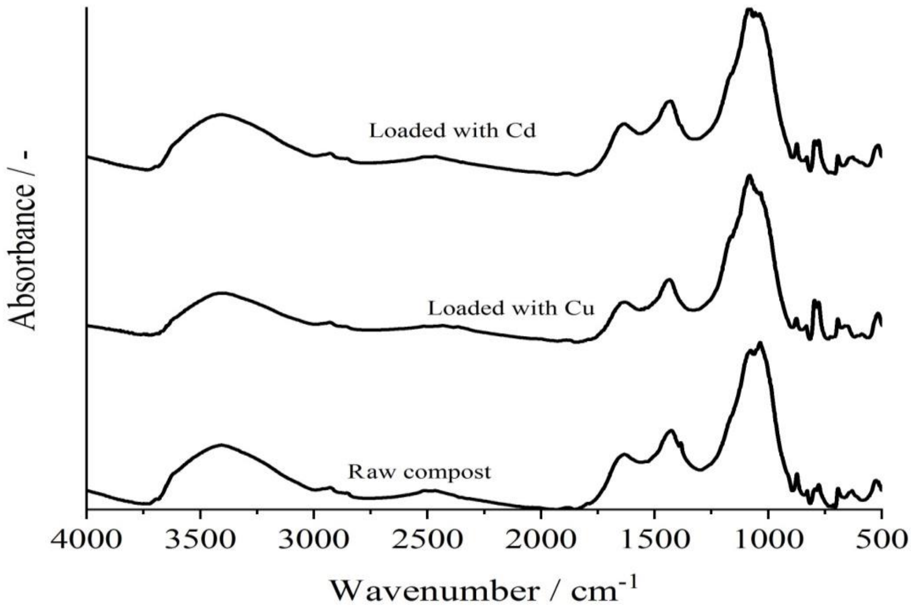

Fig. 3.2 FTIR spectra of raw Felgyő compost loaded with Cu^{2+} and Cd^{2+}.

3.2 Batch experiment

3.2.1 Langmuir isotherm

The Langmuir isotherm deals with the unimolecular thick layer of adsorbate upon the surface of adsorbents without having any interactions between adsorbed molecules. Its mathematical form is given by (Langmuir, 1918).

$$q_e = \frac{q_{max}\, KC_e}{1+KC_e} \qquad (3.1)$$

Where C_e is the equilibrium concentration (mg L^{-1}), q_e and q_{max} are respectively the amount and maximum amount of metal ion sorbed at equilibrium per unit weight of sorbent (mg L^{-1}) and K_L is the equilibrium adsorption constant. The compost has a significant impact on the uptake of heavy metals in this research. The results obtained are shown in Figures 3.3 and 3.4 and in terms of compost effect on the sorption of Cd^{2+} and Cu^{2+} from the aqueous solution onto the different sorbents in relation of the metal ions removed percentage. It is clear that Cd^{2+} and Cu^{2+} ions were effectively adsorbed in the composts and the maximum adsorption of Cd^{2+} and Cu^{2+} ions using compost occurred at 0 to 10000 µg g^{-1} by 100% as illustrated in table 3.3.

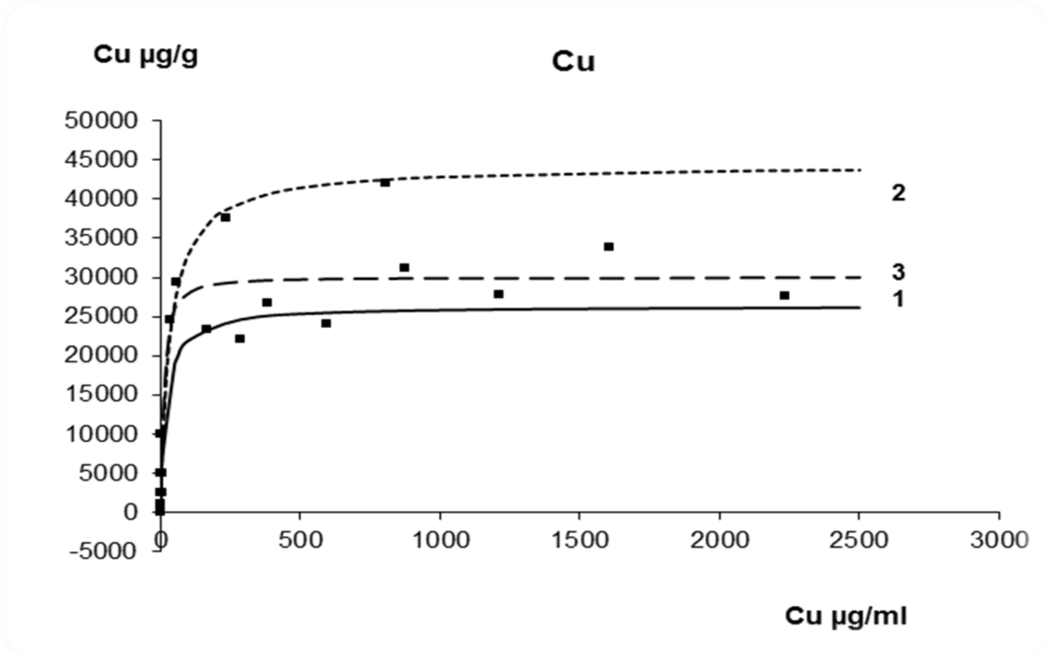

Fig. 3.3 Experimental data of Cu^{2+}adsorbed by compost (Sioagárd, Garé and Felgyő) fitted to Langmuir model

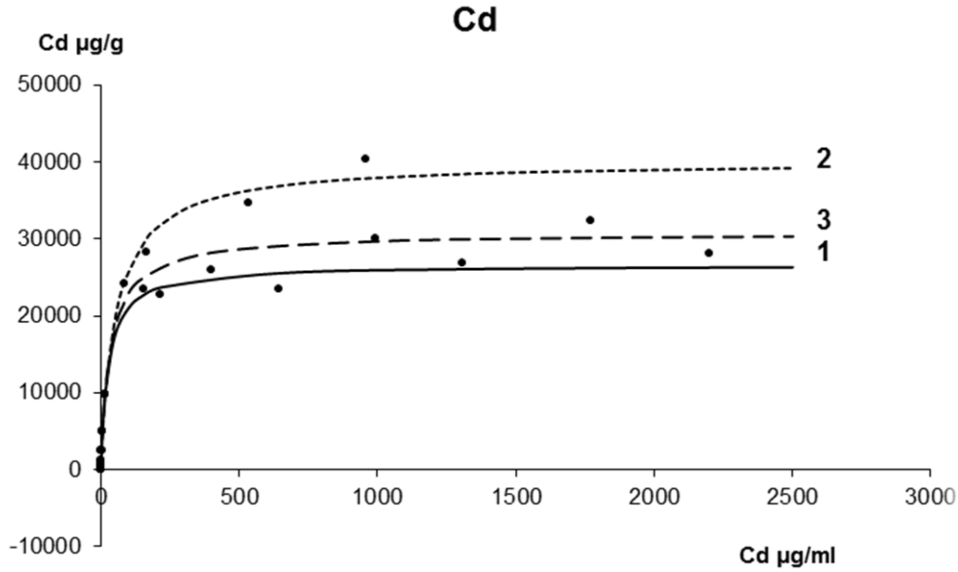

Fig. 3.4 Experimental data of Cd^{2+} adsorbed by compost (Sioagárd Garé Felgyő) fitted to Langmuir model

Table 3.3. Removal percentages of Cu^{2+} and Cd^{2+}, compost (Sioagárd, Garé and Felgyő)

	Removal percentage of Cadmium			Removal percentage of copper		
C_0	Felgyő Compost	Garé Compost	Sioagárd Compost	Felgyő Compost	Garé Compost	Sioagárd Compost
50	97	96	97	90	86	86
100	98	97	97	93	92	92
250	98	97	98	95	93	96
500	98	98	98	97	96	97
1000	98	98	99	97	97	98
2500	99	98	99	98	98	99
5000	99	98	99	99	98	99
10000	98	98	98	99	99	99
25000	91	96	94	88	98	93
30000	78	94	86	80	98	87
40000	67	86	75	69	94	78
50000	56	80	63	55	83	67

3.3 Bed column and breakthrough curve

3.3.1 Mathematical description

The performance of the bed column system can be estimated using the shape of the breakthrough curve attained from the plot of C_{eff}/C_0 contrary to time t, where C_{eff} and C_0 are the effluent and influent concentrations. The adsorbed metal ion concentrations in the column are observed by a plot of the adsorbed metal concentration, C_{ad} = (1) or normalized concentration defined as the ratio of effluent metal concentration to influent concentration (C_{eff}/C_0) as a function of time or volume of effluent V_{eff} .The essential dynamics for column demonstration at various operating a breakthrough curve study are the bed height, flow rate, and initial inlet concentration. The effects of these factors on the profile of the breakthrough curve and column performance were studied and illustrated in tables 3.4, 3.5, 3.6 and 3.7.

$$C_{ad} = \text{Inlet concentration } (C_0) - \text{Outlet concentration } (C_{eff}) \quad (3.2)$$

$$V_{eff} \text{ (mL)} = Q_{total} \quad (3.3)$$

where Q = Volumetric flow rate (mL min^{-1})

t_{total}= Total flow time (min)

$$q_{total}(\text{mg}) = \frac{Q}{1000} = \frac{Q}{1000}\int_{t=0}^{t=t_{total}} C_{ad}dt \quad (3.4)$$

$$q_{eq}\left(\frac{mg}{g}\right) = \frac{q_{total}}{X} \quad (3.5)$$

The metal removal percentage was determined from the relationship (3.6):

$$\%R = [(C_0 - C_{eff})\ Q.t / mt] \times 100 \quad (3.6)$$

3.3.2 Effect of initial inlet concentration on breakthrough curves.

The effect of the initial inlet concentration on breakthrough curves was evaluated using 20 and 100 mg L^{-1} of Cu^{2+}inlet concentration solutions, while setting up the bed height at 2.4, 3.1 and 6.5 cm of Garé absorbent respectively, the flow rate was manipulated at 4 mL min^{-1} and 8 mL min^{-1}.

3.3.3 Effect of inlet flow rate on breakthrough curves adsorption.

The flow rate is a very crucial parameter for column operation because it determines the duration the sorbate is in contact with sorbent packed in the column. Generally, the column attains a breakthrough point early at a high flow rate (Kumar et al. 2016). The effect of the initial inlet concentration on breakthrough curves was evaluated using 20 and 100 mg L^{-1} of Cu^{2+} and Cd^{2+} inlet concentration solutions, by applying different compost material. The flow rate was manipulated at 4 ml min^{-1} and 8 ml min^{-1}.

3.3.4 Effect of bed depth on breakthrough curves.

This is to analysis the breakthrough curves at different bed heights for the compost material used in this study, using a constant influent concentration of 20 mg L^{-1} with a flow rate of 4 and 8 mL min^{-1} Furthermore, using 100 mg L^{-1} concentration while changing the rate flow from 4 to 8 mL min^{-1}, it is clear that the shape and slope of curves are changing with the discrepancy of the bed depth. The breakthrough time increases at higher bed depth of adsorbent. The slope of the breakthrough curve decreases with the increase in bed height, which result in a higher mass transfer zone (Ahmad and Hameed, 2010). As stated in the tables below, when the bed height increases, the removal percentage increases from and the maximum adsorption capacity of the column is also increased. A correlation is found between the reduction of bed height and the lower retention of metallic ions in consequence of this is because the adsorbent has insufficient contact time to attract Cu^{2+} and Cd^{2+}.

Table 3.4. Mathematical description of column parameters (Garé compost, Cu^{2+} treated)

Q / mL min^{-1}	Bed Height / cm	C_0 / mg L^{-1}	Amount / g	q_{total} / mg	q_{exp} / mg g^{-1}	Total Removal / (%)
4	2.4	20	5 g	19.17	3.84	96
4	3.1	20	10 g	19.55	1.95	98
4	6.5	20	15 g	19.78	1.31	99
8	2.4	20	5 g	17.68	3.53	88
8	3.1	20	10 g	18.76	1.87	94
8	6.5	20	15 g	19.3	1.28	97
4	2.4	100	5 g	78.24	15.6	78
4	3.1	100	10 g	85.86	8.58	86
4	6.5	100	15 g	95.1	6.34	95
8	2.4	100	5 g	75.61	15.1	76
8	3.1	100	10 g	83.19	8.31	83
8	6.5	100	15 g	89.89	5.99	90

Table 3.5. Mathematical description of column parameters (Felgyő compost, Cu^{2+} treated)

Q / mL min^{-1}	Bed Height / cm	C_0 / mg L^{-1}	Amount / g	q_{total} / mg	q_{exp} / mg g^{-1}	Total Removal / %
4	1.1	20	5 g	19.4	3.88	97
4	2	20	10 g	19.56	1.95	86
4	3.1	20	15 g	19.77	1.31	84
8	1.1	20	5 g	17.26	3.45	80
8	2	20	10 g	19.08	1.98	97
8	3.1	20	15 g	19.37	1.29	95
4	1.1	100	5 g	85.25	17.55	91
4	2	100	10 g	91.22	9.12	90
4	3.1	100	15 g	95.12	6.34	98
8	1.1	100	5 g	80.57	16.14	96
8	2	100	10 g	90.06	9.66	95
8	3.1	100	15 g	93.13	6.29	93

Table 3.6. Mathematical description of column parameters (Felgyő compost, Cd^{2+} treated)

Q / mL min^{-1}	Bed Height / cm	C_0 / mg L^{-1}	Wight / g	q_{total} / mg	q_{eq} / mg g^{-1}	Total Removal / %
4	1.1	20	5 g	19.65	3.93	98
4	2	20	10 g	19.73	1.97	98
4	3.1	20	15 g	19.83	1.32	99
8	1.1	20	5 g	19.48	3.89	97
8	2	20	10 g	19.85	1.98	99
8	3.1	20	15 g	19.9	1.32	99
4	1.1	100	5 g	81.07	16.2	81
4	2	100	10 g	93.49	9.34	93
4	3.1	100	15 g	98.82	6.58	98
8	1.1	100	5 g	86.04	17.2	86
8	2	100	10 g	94.71	9.47	94
8	3.1	100	15 g	97.33	6.48	97

Table 3.7. Mathematical description of column parameters (Garé compost, Cd^{2+} treated)

Q / mL min^{-1}	Bed Height / cm	C_0 / mg L^{-1}	Weight / g	q_{total} / mg	q_{eq} / mg g^{-1}	Total Removal / %
4	2.4	20	5g	19.81	3.96	99
4	3.1	20	10g	19.84	1.98	99
4	6.5	20	15g	19.86	1.32	99
8	2.4	20	5g	19.84	3.96	99
8	3.1	20	10g	19.88	1.98	99
8	6.5	20	15g	19.9	1.32	99
4	2.4	100	5g	93.91	18.7	93
4	3.1	100	10g	98.12	9.81	98
4	6.5	100	15g	99.57	6.63	99
8	2.4	100	5g	95.55	19.1	95
8	3.1	100	10g	97.14	9.71	97
8	6.5	100	15g	99.62	6.64	99

3.4 Kinetic models of fixed bed column adsorption

The experimental data attained from the continuous adsorption system were fitted to the most commonly used kinetic models for adsorption in a fixed bed. Models were used to predict the dynamic behavior of the adsorbent-adsorbate system in this study, in addition, is to calculate the column kinetic constants and evaluate the fixed-bed columns' adsorption capacity. Authors have used different models for Cu^{2+} and Cd^{2+} adsorption onto different adsorbents. In order to describe the fixed bed column performance and to scale it up for industrial applications, three models were implied. (Bohart and Adams, 1920), (Yoon and Nelson, 1984) and (Thomas 1940) models were used to analyse the behaviour of adsorbent–adsorbate adsorption in this research.

3.4.1 Adams –Bohart model.

The Adams–Bohart adsorption model was applied to experimental data for the description of the initial part zone of the breakthrough curve. Plotting $ln\, C_0/C_{eff}$ against t, using linear regression analysis on all breakthrough curves have been plotted, the respective values of k_{AB} and N_0 were calculated and presented in table 3.8, 3.9 and 3.10. This model assumed that the biosorption rate is proportional to the residual capacity of the solids and the concentration of the sorbent substances (Calero et al. 2009). The Adam's–Bohart model is used for the description of the initial part of the breakthrough curve. The Adams-Bohart is given in equation 3.7 as:

$$ln\left[\frac{C_0}{C_{eff}}\right] = k_{AB}C_0t - \frac{K_{AB}N_0Z}{U_0} \qquad (3.7)$$

Where C_0= influent concentration (mg L^{-1}); C_{eff} = effluent concentration (mg/L); k_{AB}= adsorption rate coefficient (L mg min^{-1}); N_0 = adsorption capacity coefficient (mg L^{-1}); Z = bed depth (cm); U_0= linear velocity (cm min^{-1}); and t = time (min). The amount of metal concentration adsorbed mg/g is calculated through the factor N_0 (adsorption capacity coefficient in mg L^{-1}). The kinetic constant value of k_{AB} and N_0 are determined from the slope and intercept of ln (C_0/C_{eff}) versus *t*.

Table 3.8. Parameters predicted by Adam-Bohart model (Garé compost, Cu^{2+} treated)

Column Parameters				Bohart Parameters		
C_0 / mg L^{-1}	Weight / g	Bed heights / cm	Q / mL min^{-1}	K_{AB} / L min^{-1} mg^{-1}	N^0 / mg L^{-1}	R^2
20	5	2.4	4	0.000235	45.5	0.93
20	10	3.1	4	0.00019	48.5	0.96
20	15	6.5	4	0.00019	23.1	0.96
20	5	2.4	8	0.000325	17.8	0.91
20	10	3.1	8	0.000365	18.1	0.9
20	15	6.5	8	0.000485	7.53	0.92
100	5	2.4	4	0.000032	351	0.88
100	10	3.1	4	0.00004	275	0.97
100	15	6.5	4	0.000024	244	0.9
100	5	2.4	8	0.000078	134	0.91
100	10	3.1	8	0.000095	116	0.9
100	15	6.5	8	0.000054	98.9	0.89

Table 3.9. Bohart-Adams parameters for Felgyő compost, Cu2 treated

Column Parameters				Bohart Parameters		
C_0 / mg L^{-1}	Weight / g	Bed heights / cm	Q / mL min^{-1}	K_{AB} / L min^{-1} mg^{-1}	N^0 / mg L^{-1}	R^2
20	5	1.1	4	0.000185	103.64	0.91
20	10	2	4	0.00026	49.92	0.92
20	15	3.1	4	0.000135	66.88	0.92
20	5	1.1	8	0.00051	29.48	0.93
20	10	2	8	0.000425	22.74	0.98
20	15	3.1	8	0.00038	18.84	0.9
100	5	1.1	4	0.000073	377.04	0.92
100	10	2	4	0.000044	335.66	0.92
100	15	3.1	4	0.000033	384.51	0.96
100	5	1.1	8	0.000086	244.82	0.97
100	10	2	8	0.000116	130.14	0.96
100	15	3.1	8	0.000165	79.31	0.91

Table 3.10. Parameters predicted by the Adam-Bohart model (Felgyő compost, Cd^{2+} treated)

C_0 / mg L^{-1}	Compost weight / g	Bed height / cm	Q / mL min^{-1}	N_0 / mg g^{-1}	K_{AB}/ L min^{-1} mg	R^2
20	5g	1.1	4	43.77	0.000765	0.97
20	10g	2	4	33.23	0.00019	0.92
20	15g	3.1	4	25.05	0.000255	0.95
20	5g	1.1	8	63.19	0.00049	0.91
20	10g	2	8	12.2	0.000715	0.96
20	15g	3.1	8	9.435	0.00082	0.85
100	5g	1.1	4	390.6	0.000222	0.94
100	10g	2	4	120.7	0.000051	0.92
100	15g	3.1	4	98.98	0.000098	0.94
100	5g	1.1	8	368.8	0.000143	0.97
100	10g	2	8	206.7	0.000164	0.94
100	15g	3.1	8	120.1	0.000222	0.92

3.4.2 Thomas model kinetics

Thomas model assumes plug flow behavior in the bed. This is most general and widely used to describe the performance theory of the sorption process in fixed-bed column (Sharma and Singh, 2013). This model was expressed through the second-order law of kinetic reaction without the presence of axial dispersion even when the bed depth was at the minimum and the breakthrough occurred immediately after the flow started (Apiratikul and Pavasant, 2008). Tables 3.11, 3.12 and 3.13 are illustrated results obtained for Thomas model. The linearized form of this model can be described by the following expression:

$$ln\left[\frac{C_0}{C_{eff}}-1\right] = 1+\frac{k_{thqo}m}{Q} - k_{th}q_0\mathrm{t} \qquad (3.8)$$

Where C_0 is the initial metal concentration (mg L^{-1}), C_{eff} is effluent Cd^{2+}concentration (mg L^{-1}), at time t, k_{th} is Thomas model constant, L min^{-1}.mg. q_0 is maximum Cu^{2+}adsorption capacity (mg g^{-1}), m is mass of the adsorbent (g) and Q is flow rate (ml/min). The kinetic coefficient k_{th} and the adsorption capacity of the column q_0 can be determined from a plot of $ln\left[\frac{C_0}{C_{eff}}-1\right]$ against t at a given flow rate using linear regression. A linear regression was then performed on each set to transform the data to determine the coefficient from the slope and the intercept. Inspection of the regressed lines indicated that they were all acceptable fits with linear regression coefficients ranging from 0.90 to 0.99. Thomas model aims at calculating the adsorption rate constant of the solid phase concentration of the metals on the adsorbent from the continuous mode studies.

Table 3.11. Parameters predicted by Thomas model (Garé compost, Cu^{2+} treated)

Column Parameters				Thomas Parameters		
C_0 / mg L^{-1}	Compost weight / g	Bed height / cm	Q / mL min^{-1}	q_0 / mg g^{-1})	K_{th} / mL min^{-1}.mg	R^2
20	5	2.4	4	10.3	0.0002	0.92
20	10	3.1	4	7.59	0.0002	0.9
20	15	6.5	4	4.46	0.00025	0.93
20	5	2.4	8	10.3	0.00037	0.92
20	10	3.1	8	7.49	0.000385	0.9
20	15	6.5	8	4.46	0.0005	0.93
100	5	2.4	4	49.5	0.000037	0.93
100	10	3.1	4	27.1	0.000044	0.97
100	15	6.5	4	35.5	0.000025	0.95
100	5	2.4	8	35.3	0.000096	0.91
100	10	3.1	8	22.8	0.000105	0.9
100	15	6.5	8	27.8	0.000058	0.9

Table 3.12. Parameters predicted by Thomas model (Felgyő compost loaded with Cu^{2+})

Column Parameters				Thomas Parameters		
C_0 / mg L^{-1}	Weight / g	Bed heights / cm	Q / mL min^{-1}	q_0 / mg g^{-1}	K_{th} / L mg^{-1} min^{-1}	R^2
20	5	2.4	4	15.6	0.00019	0.91
20	10	3.1	4	6.91	0.000265	0.92
20	15	6.5	4	9.47	0.00014	0.92
20	5	2.4	8	8.08	0.00057	0.94
20	10	3.1	8	6.02	0.00045	0.99
20	15	6.5	8	5.27	0.000395	0.91
100	5	2.4	4	23.89	0.000093	0.93
100	10	3.1	4	20.37	0.00005	0.93
100	15	6.5	4	26.25	0.000035	0.96
100	5	2.4	8	27.74	0.000112	0.98
100	10	3.1	8	15.24	0.000138	0.97
100	15	6.5	8	10.65	0.00018	0.92

Table 3.13. Parameters predicted by Thomas model (Felgyő compost, Cd^{2+} treated)

C_0 / mg L^{-1}	Compost weight / g	Bed height / cm	Q / mL min^{-1}	q_0 / mg g^{-1})	K_{th} / mL min^{-1}.mg	R^2
20	5g	1.1	4	20.8	0.000175	0.97
20	10g	2	4	9.78	0.0002	0.92
20	15g	3.1	4	9.29	0.00015	0.95
20	5g	1.1	8	11.8	0.00062	0.91
20	10g	2	8	10.3	0.00043	0.96
20	15g	3.1	8	5.27	0.000395	0.91
100	5g	1.1	4	36.3	0.000047	0.95
100	10g	2	4	25.7	0.000054	0.92
100	15g	3.1	4	16.2	0.000099	0.94
100	5g	1.1	8	29.8	0.000165	0.97
100	10g	2	8	19.7	0.000172	0.94
100	15g	3.1	8	12.8	0.000226	0.92

3.4.3 Yoon–Nelson kinetic model

The Yoon–Nelson model is based on the assumption that the rate of adsorption is decreasing in the probability of adsorption, of adsorbate molecules, and is proportional to the probability of the adsorbate adsorption and the adsorbate breakthrough on the adsorbent (Han et al. 2008). The values of (k_{YN}) and τ are determined from the slope and intercept of ln(C_0/(C_0-C_{eff})) versus t and the results are given in tables 3.14, 3.15 and 3.16 for Cu^{2+} treated by Felgyő, Cu^{2+} treated by Garé and Cd^{2+} treated by Felgyő respectively. The Yoon Nelson model is given in equation 3.9.

$$\ln\left[\frac{C_0}{C_0 - C_{eff}}\right] k_{YN} t - \tau k_{YN} \qquad (3.9$$

Table 3.14. Parameters predicted by Yoon–Nelson model (Garé compost, Cu^{2+} treated)

Column Parameters				Nelson Parameters		
C_0 / mg L^{-1}	Weight / g	Bed heights / cm	Q / mL min^{-1}	K_{YN} / min^{-1}	τ / min	R^2
20	5	2.4	4	0.0033	303	0.92
20	10	3.1	4	0.0048	208	0.93
20	15	6.5	4	0.0038	263	0.96
20	5	2.4	8	0.0074	135	0.92
20	10	3.1	8	0.0077	129	0.9
20	15	6.5	8	0.01	100	0.93
100	5	2.4	4	0.0037	270	0.89
100	10	3.1	4	0.0044	400	0.97
100	15	6.5	4	0.0025	104	0.9
100	5	2.4	8	0.0096	95	0.91
100	10	3.1	8	0.0105	227	0.9
100	15	6.5	8	0.0058	174	0.9

Table 3.15. Parameters predicted by Yoon-Nelson model (Felgyő compost, Cu^{2+} treated)

Column Parameters				Nelson Parameters		
C_0 / mg L^{-1}	Weight / g	Bed heights / cm	Q / mL min^{-1}	K_{YN} / min^{-1}	τ / min	R^2
20	5	2.4	4	263	0.0038	0.91
20	10	3.1	4	188	0.0053	0.92
20	15	6.5	4	357	0.0028	0.92
20	5	2.4	8	111	0.009	0.98
20	10	3.1	8	87	0.0114	0.94
20	15	6.5	8	126	0.0079	0.91
100	5	2.4	4	107	0.0093	0.93
100	10	3.1	4	200	0.005	0.93
100	15	6.5	4	285	0.0035	0.96
100	5	2.4	8	89	0.0112	0.91
100	10	3.1	8	72	0.0138	0.92
100	15	6.5	8	55	0.018	0.92

Table 3.16. Parameters predicted by Yoon-Nelson model (Felgyő compost, Cd^{2+} treated)

C_0 / mg L^{-1}	Weight / g	Bed heights / cm	Q / mL min^{-1}	τ / min	K_{YN} / min^{-1}	R^2
20	5g	1.1	4	285	0.0035	0.97
20	10g	2	4	250	0.004	0.92
20	15g	3.1	4	333	0.003	0.95
20	5g	1.1	8	116	0.0086	0.96
20	10g	2	8	80	0.0124	0.91
20	15g	3.1	8	64	0.0154	0.85
100	5g	1.1	4	212	0.0047	0.95
100	10g	2	4	185	0.0054	0.92
100	15g	3.1	4	101	0.0099	0.94
100	5g	1.1	8	60	0.0165	0.97
100	10g	2	8	58	0.0172	0.94
100	15g	3.1	8	44	0.0226	0.92

4. NEW SCIENTIFIC RESULTS

I. This study proved that the compost material used for removing the heavy metal from contamination water has the capability of removing Cu^{2+} and Cd^{2+} in high percentages rate.

II. Compost material used in this study is contained carboxyl functional groups which is supposed to interact with Cu^{2+} and Cd^{2+} ions for an ion exchange that leads to reduce heavy metal from contaminated water

III. The bed column is significantly affected by the change of flow rate, metal concentration and bed heights.

IV. Langmuir model can be used for compost material which is ununiformed and heterogeneous distributed, this model is to be used for uniform surface which is proved that is not valid.

V. Thomas model used in the column experiment was performed well than Adamas and Yoon models.

5. CONCLUSIONS AND SCOPE FOR FUTURE RESEARCH

5.1 CONCLUSIONS

I. The results provide a good indication that all compost used in the batch experiment could remove Cd^{2+} and Cu^{2+} with favour for Garé compost and also favour for Cu^{2+}. All the 3 compost materials used for cleaning the water polluted in batch study could sorb practically the total amount of 100% of heavy metals up to 10000 μg g^{-1} concentrations.

II. Batch experiment could treat heavy metal in small volume, however in large volume, fixed bed is preferable.

III. The results obtained from bed column showed that the adsorption of metals is affected by initial concentration, flow rate and bed height. The heavy metal removal yield decreased with increasing flow rate, bed depth and rise of metal concentration.

IV. The total removal percentage acquired from fixed bed column is ranging from 88 to 99% at lower concentration; with higher concentration it could remove the heavy metal from 78 to 98%. The system required longer time for better performance.

V. Among those models, the Thomas model was found to be most suitable to represent the kinetics of biosorption of the heavy metals.

VI. Compost is proved to reduce heavy metal in very low level, therefore can be applied to remove other heavy metals from wastewaters.

5.2 Scope for future research

The following recommendations are the scope for future research:

I. To explore the possibilities, modifications / pre-treatment of adsorbent to improve its adsorption capacity.

II. Studies with actual industrial wastewater to evaluate parameters for field applications.

III. Investigation of compost material adsorption capacity of removing other heavy metal from wastewaters.

IV. Applying new and modifying mathematical models to evaluate their fitting with experimental data.

V. Conducting experimental investigation in industrial scales to evaluate the applicability and capacity of compost material on removing heavy metals.

VI. Designing continues fixed bed column system with computer stimulation programs.

6. Summary

Water pollution due to heavy metals is an issue of great environmental concern. Heavy metal ions are discharged into the water system from numerous manufacturing activities such as electroplating industries, electronic equipment manufacturing, and chemical processing plants. Due to the rapid development of industrial activities, the levels of heavy metals in water systems have significantly increased. The water-soluble forms of heavy metals can easily enter the food chain. Therefore various researchers conducted several experiments in order to remove a different type of heavy metal by applying different adsorbent materials. Most of the adsorption studies have been focused on low-cost adsorbents. Some of the advantages of using these materials for wastewater treatment include involvement of simple techniques requirement of very little processing, good adsorption capacity, selective adsorption of heavy metal ions, low cost, free availability. In this study conducted to remove tow heavy metals from contaminated water by using cost-effective techniques and effective adsorbent material. This study has gathered deep information about the usability of adsorption by different material and elimination of various heavy metals. The studies in the literature on adsorbents related to Cd^{2+} Cu^{2+} ions were examined and compared with the values achieved in the current study. This research is aiming to try two different experimental methods, batch and continues column bed. The batch experiments carried out to evaluate three types of compost material and to test their ability to remove cadmium and copper. The results obtained from this study were satisfactory and encouraging to test other heavy metal with the same approach. Specifically, removal percentages attained from the results have shown the high affinity of these adsorbent materials and their capacity to remove cadmium and copper. The known Langmuir model fitted for batch experiments provides good adjustments to strongly favorable isotherms. One should bear in his mind that the Langmuir isotherm is derived assuming a uniform surface, which in many cases is not valid. This relation works fairly well, even with adsorbents with high heterogeneity such as compost, clays or activated carbon. The column bed aimed to test the compost material in continues flow by different bed heights, and high, low concentration of Cd^{2+} and Cu^{2+}. The parameters applied in the present study showed the influence on the breakthrough for heavy metal ions adsorption. Metal removal efficiencies and adsorbent adsorption capacities for each of the columns was estimated to assess the suitability of these adsorption media and the preferred operating conditions for the treatment of cadmium and copper. The

increase in bed height increased the amount of adsorbent used thus increasing the total removal of heavy metal removed and prolonged the lifespan of the compost column. However, the increase in flow rate and influent concentration resulted in the shortened lifespan of the column. Kinetic models applied in this study were useful tools to evaluate the column performance and the adsorption capacity; however different parameters of the column could be improved such as length of operation time. The analytical methods used in this study were accommodating tools to understand more about the adsorption process as indicated by FTIR for the presence of functional groups. The humic substances contain functional groups that are responsible for the sorption of metal ions; these functional groups are generally negatively charged which allows for the strong attraction of metal ions to compost. This work provides a better understanding of the processes and mechanisms involved in the sorption of pollutants on the environment in order to prevent their adverse consequences.

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8. RELATED PUBLICATIONS

Journal articles with IF

1. **Published Article:**

- Kinetics Study of the Ability of Compost Material for Removing Cu^{2+} from Wastewater. Ramadan Benjreid, Mohammed Matouq, Mutaz Al-Alawi, Füleky György. Global nest Journal. DOI: https://doi.org/10.30955/gnj.002865

2. **Articles in provisional submission:**

- Fixed Bed Adsorption Column Studies for the Removal of Cd (II) Using compost Material. Ramadan. Benjreid, Mutaz Al-Alawi, György. Füleky, Prokainé. Ágnes. Desalination and Water Treatment.

- Evaluation of the performance of encapsulated lifting system composting technology with a GORE(R) cover membrane: physico-chemical properties and spectroscopic analysis" Environmental Engineering Research.

Conference proceedings:

- Title: "Cleaning Heavy Metal Pollution of Wastewater with Compost Application" Ramadan Benjared, György Füleky. International Youth Science Forum "LITTERIS ET ARTIBUS" 24–26 November 2016, LVIV, UKRAINE 498 – 501.

- Title: "Examination of Zinc Adsorption Capacity of Soils Treated with Different Pyrolysis Products". Acta CTA Universitatis Sapientiae Agriculture and Environment. Cluj Napoca, Romania, 6(2014) 33– 38.

International conferences:

- Title: "Cadmium Copper and Zink Sorption on Compost Materials. ORBIT 2016, 10th International Conference on Circular Economy and Organic Waste, Heraklion, Crete, Greece. 25-28 of May 2016.

- Title: "Soil Quality Improvement Using Natural Materials". The 2016 ESSC International Conference. Babeş-Bolyai University, Cluj Napoca, Romania. 15-18 June 2016.

Title: "KOMPOSZTANYAGOK KADMIUM, RÉZ ÉS CINK MEGKÖTŐ KÉPESSÉGE" Talajtani Vándorgyűlést. Debrecen, Hungary. 1-3 September 2016.

- Title: "Removal of Cu and Cd from wastewater by compost application" WORKSHOP SOIL WASTE WATER 2018. Reusing wastewater and solid residues in agriculture, Landau in der Pfalz , Germany. 26th – 28th of March 2018.

- Title: "Cleaning heavy metal pollution of wastewater with compost application" XIV. Kárpát-medencei Környezettudományi Konferencia, Gödöllő, Hungary. 5-7 April 2018.

- Title: "Ólom és cink megkötés komposztokon" LVIII Georgikon Napok, International Scientific Conference. University of Pannonia, Keszthely, Hungary 29-30. Sept 2016.