Removal of Heavy Metals from Wastewater Using Sustainable Low-Cost Absorbents

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Abstract

This work examines the adsorption performance of several inexpensive adsorbent materials, namely peanut husk charcoal, fly ash, and natural zeolite, for the removal of Cu^{2+} and Zn^{2+} ions, with the aim of applying these materials to the treatment of metal-finishing wastewater. Batch adsorption experiments were conducted to evaluate the effects of pH, contact time, and initial metal ion concentration. The impact of solution pH on metal uptake by the different adsorbents was investigated over a pH range of 4–11. Optimal removal of copper and zinc occurred at pH 6 for peanut husk charcoal and natural zeolite, while a pH of 8 was optimal for fly ash. Equilibrium adsorption was achieved within 2 hours for Cu(II) and Zn(II) on peanut husk charcoal and fly ash, whereas 3 hours were required for natural zeolite. Adsorption characteristics were analyzed using both Langmuir and Freundlich isotherm models; however, the experimental results showed a better fit with the Langmuir model. Overall, the findings indicate that peanut husk charcoal, fly ash, and natural zeolite are effective for the removal of cationic heavy metals from industrial wastewater, with adsorption efficiency increasing in the order: fly ash < peanut husk charcoal < natural zeolite.

KEYWORDS: Adsorption; Low-cost adsorbents; Industrial wastewater

Introduction

Water contamination caused by the discharge of heavy metals remains a major environmental issue worldwide. As a result, the treatment of industrial wastewater has become a global priority, since effluents generated from municipal, industrial, and community sources must eventually be discharged into natural water bodies or onto land [1].

Heavy metal contamination is commonly found in industrial effluents originating from activities such as metal plating, mining, battery production, paint and pigment manufacturing, as well as ceramic and glass industries. These wastewaters typically contain metals including Cd, Pb, Cu, Zn, Ni, and Cr [2]. When toxic heavy metals are released into the environment, they can accumulate in living organisms through direct exposure or through the food chain, posing serious risks to human health. Therefore, preventing the discharge of heavy metals into natural ecosystems is essential [3].

Various conventional treatment techniques have been applied to remove toxic heavy metals from water systems, including chemical precipitation, coagulation, ion exchange, solvent extraction, filtration, evaporation, and membrane-based processes [4]. Among these methods, adsorption using traditional adsorbents such as activated carbon has been widely adopted due to its high effectiveness. Activated carbon, typically produced by the carbonization of organic materials, is one of the most commonly used adsorbents. However, its widespread application in wastewater treatment is limited by the high cost associated with its activation process [5].

Agricultural waste represents a promising and inexpensive source of adsorbent materials, alongside industrial by-products and natural substances. Due to their wide availability, agricultural residues such as peanut husks, rice husks, wheat bran, and sawdust have low economic value and often create disposal challenges [6]. Activated carbons produced from peanut husk and rice husk have been successfully utilized for the removal of heavy metals from aqueous solutions [7]. The application of peanut husk–based carbon for metal removal has therefore attracted considerable attention.

The removal of Cu(II) ions from wastewater using peanut husk charcoal was investigated by Periasamy and Namasivayam [8]. Their comparison with commercial granular activated carbon (GAC) demonstrated that peanut husk charcoal exhibited an adsorption capacity approximately 18 times greater than that of GAC.

Fly ash is a solid by-product generated from coal combustion in thermoelectric power stations [9–11]. Numerous studies have explored its reuse for controlling water and air pollution, particularly focusing on its effectiveness in removing heavy metal ions from aqueous solutions [12,13]. Shim et al. [14] examined the adsorption behavior of heavy metals using bottom ash with different particle size fractions. Natural materials locally available in certain regions can be employed as low-cost adsorbents due to their metal binding capacity. Zeolites are naturally occurring hydrated aluminosil- icate minerals. Most common natural zeolites are formed by the alteration of glass-rich volcanic rocks (tuff) by fresh water in playa lakes or by sea water [16]. The structures of zeolites consist of three-dimensional frameworks of SiO^{4+} and AlO^{4+} tetrahedra. The fact that zeolite exchangeable ions are relatively innocuous (sodium, calcium and potassium ions) makes them particularly suitable for removing undesirable heavy metal ions from industrial effluent waters. The adsorp- tion behavior of natural zeolite (Clinoptilolite) with respect to Co^{2+}, Cu^{2+}, Zn^{2+} and Mn^{2+} was studied by Erdem et al. [17]; the results show that natural zeolite can be used effectively for the removal of metal cations from wastewater. Besides, the adsorption behavior of formulated zeolite- portland cement mixture for heavy metals removal efficiency was studied as a substitute for activated carbon for wastewater treatment [4,18].

Other researchers have studied arsenic adsorption and phosphate ions adsorption from aqueous solutions on syn- thetic zeolites [19,20].

The objective of this work is to study the adsorption behav- ior of some low-cost adsorbents such as peanut husk charcoal, fly ash, and natural zeolite, with respect to Cu^{2+} and Zn^{2+} ions. The batch method was employed: parameters such as pH, contact time, and initial metal concentration, were studied.

Material and methods

Preparation of adsorbents

Peanut husks were collected from the local market, washed thoroughly to remove dust using distilled water, dried in an oven at 100 °C for 18 h, ground using a laboratory mill, sieved to 0.5–0.8 mm, and rinsed using 0.1 N HCl. Then the pH was adjusted with 0.1 N HCl at values (6–7). Finally, PHC was dried and stored in an oven at 80 °C till it reached constant density and humidity [7].

Fly ash was taken from the Geos Company, Egypt. The fly ash samples were dried at 110 °C for 2 h before tests, and sieved to the desired particle size of 250 lm before use.

Samples of zeolite were taken from Dar el Emara Com- pany, Egypt. The crushed original zeolite was ground and passed through 300 · 600 lm sieves and was dried in an oven at 100 ± 5 °C for 24 h.

Characterization of adsorbents

The specific surface area of peanut husk charcoal (PHC) was determined to be 485 $m^2\ g^{-1}$, which is considerably higher than that of many conventional carbons, whose surface areas typically range from 10 to 100 $m^2\ g^{-1}$. The adsorption performance of carbon materials is largely governed by the chemical nature of their surfaces, particularly the presence of carbon–oxygen functional groups. Commonly reported surface functionalities include carboxylic groups, phenolic hydroxyl groups, carbonyl groups (such as quinone-type structures), and lactone groups [7]. The chemical composition of PHC is presented in Table 1, with values expressed on a weight-by-weight basis.

The overall chemical composition of fly ash was determined using X-ray diffraction (XRD), and the results are summarized in Table 2. Silicon dioxide (SiO_2), aluminum oxide (Al_2O_3), and iron oxide (Fe_2O_3) were identified as the predominant constituents, while other components were present in minor amounts.

Zeolites possess a three-dimensional framework structure composed of SiO_4^{4-} and AlO_4^{5-} tetrahedra. These materials were characterized using X-ray diffraction (XRD) and chemical analysis techniques [19]. The contents of Al_2O_3, Fe_2O_3, CaO, and MgO were determined by titrimetric methods, whereas SiO_2 was analyzed gravimetrically. Sodium oxide (Na_2O) and potassium oxide (K_2O) were measured using flame photometry. The results of the chemical analyses are also reported in Table 2.

Chemical and reagents

Stock solutions of copper chloride and zinc chloride of 400 mg/l were used as adsorbate, and solutions of various con- centrations were obtained by diluting the stock solution with distilled water. Copper and zinc concentrations were deter- mined by spectrophotometer. All the chemicals used were of analytical grade reagent and all experiments were carried out in 500 ml glass bottles at the laboratory ambient temperature of 27 ± 2 °C.

Table 1 Chemical composition of peanut husk charcoal.

Elements	C	H	O	N	Ca	Na	K	Al	Fe	Si
(% w/w)	55	1	15.9	0.5	1.2	2.8	2.6	1	1	19

Methodology

Batch adsorption experiments were carried out by shaking a series of bottles containing various amounts of the different adsorbents used and heavy metal ions separately at optimum pH. The adsorbents used were mixed with 500 ml of distilled water with an adsorbent dose 5 g/l; the pH of the mixture was adjusted to the desired value using 0.1 N HCl and 0.1 N NaOH until the pH was stabilized, and was agitated in a jar test at 27 ± 2 °C for one hour; then the copper and zinc ions in the form of chloride salts were added to the bottles to make an initial concentration of (10–100) mg/l, and the bottles were agitated for further one hour until equilibrium was attained; at the end of mixing the adsorbent particles were separated from the suspensions by filtration through 0.43 lm filter paper. The residual concentration of heavy metals was determined by the spectrophotometer Model CE3021 made by CECIL Instru- ments, USA. In addition to adsorption tests, a set of blank tests was conducted to evaluate the removal by metal hydrox- ide precipitation at various pH values.

MgO	0.13	4.49
L.O.I.	0.8	14.49
Others	0.52	5.15

Results and discussions

Effect of pH

The pH of the solution has a significant impact on the uptake of heavy metals since it determines the surface charge of the adsor- bent and the degree of ionization and speciation of the adsor- bate [11]. The results obtained are shown in Fig. 1(a) and (b) and show the effect of pH on the adsorption of Cu^{2+}, and Zn^{2+} ions from the aqueous solution onto the different adsor- bents in terms of the metal ions removed percent. It is clear that Cu^{2+}, and Zn^{2+} ions were effectively adsorbed in the pH range (4–7), and the maximum adsorption of Cu^{2+}, and Zn^{2+} ions using peanut husk charcoal occurred at pH 6 and 7, respec- tively, while the maximum adsorption of Cu^{2+} and Zn^{2+} ions using fly ash occurred at pH 8, and the maximum adsorption of Cu^{2+} and Zn^{2+} ions using natural zeolite occurred at pH 6; thus, these pH values was chosen for all experiments. These re- sults are similar to results obtained by Rodda et al. [21] for hea- vy metal ions sorption onto agricultural waste sorbents.

The results in Fig. 1(a) and (b) show that the equilibrium capacity of copper and zinc removal by the different adsor- bents increased significantly as the pH of the solution in- creased. If the initial pH was too high, copper and zinc ions precipitated out and this deflected the purpose of employing the sorption process as the sorption process is kinetically faster than the precipitation [5]. The adsorptive capacities of Cu^{2+}, and Zn^{2+} ions increased rapidly as the pH value increased; at pH values above 6 the adsorptive capacities of Cu^{2+} and Zn^{2+} ions increased, but at a slower rate because of the com- petitive adsorption between hydrogen ion and the heavy metal cation [22]. This is in agreement with the results obtained by Periasamy and Namasivayam [23] for adsorption of Ni (II) from aqueous solutions onto peanut hulls.

Effect of contact time

The effect of contact time on the removal efficiency of different adsorbents for copper and zinc ions was studied: the results are shown in Fig. 2(a) and (b). The rate of uptake of metal ions was quite rapid; the metal removal in the first 30 min, using natural zeolite, was 60% for copper and 62% for zinc. At equi- librium, 97.5% of copper ions and 90% of zinc ions were re- moved from the solution using natural zeolite. Equilibrium was reached for copper and zinc removal within 2 h using pea- nut husk carbon and fly ash and within three hours using nat- ural zeolite. This is in agreement with the results obtained by Sharma et al. [24] for remediation of chromium rich waters and wastewaters by fly ash.

Effect of initial metal concentration

The effect of initial metal concentration on copper and zinc re- moval was studied by batch adsorption experiments, which were carried out at 27 ± 2 °C using different initial metal ion concentrations (10, 20, 40, 60, 80 and 100 mg/l) at optimum pH and rpm 150. To choose the metal ion concentration range, we collected wastewater samples from different units in selected electroplating industries, and we measured the average copper and zinc concentration in the effluents. The results are shown in Fig. 3(a) and (b), which indicate that the percentage removal decreases with the increase in initial metal ion concentration. This is because there were no more adsorption sites on the adsorption surface of the adsorbent material. The maximum re- moval of Cu using natural zeolite was 91% at copper ion con- centration 10 mg/l, and the maximum removal of zinc using natural zeolite was 96% at a metal concentration 10 mg/l. This is in agreement with the results obtained by Ragheb et al. [25] for heavy metals removal by low-cost adsorbents.

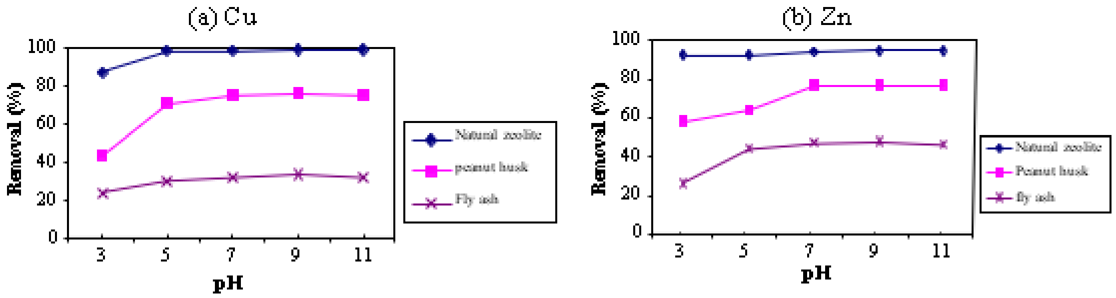

Fig. 1 Effect of pH on copper and zinc removal for different adsorbent at 27 ± 2 °C.

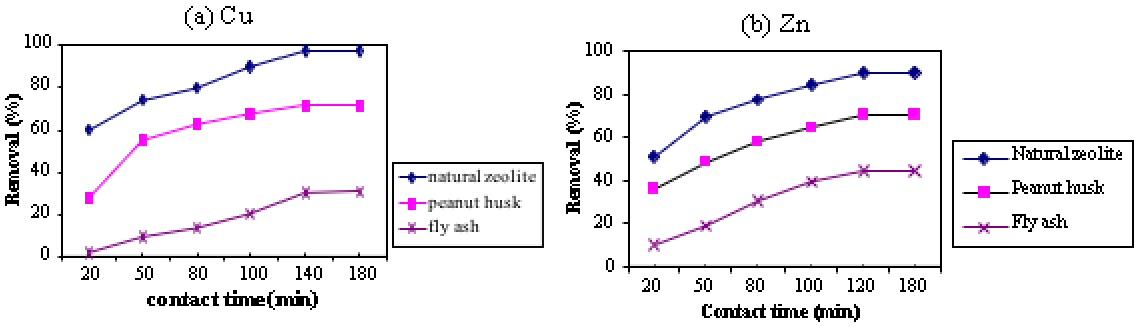

Fig. 2 Effect of contact time on copper and zinc removal for different adsorbents at 27 ± 2 °C.

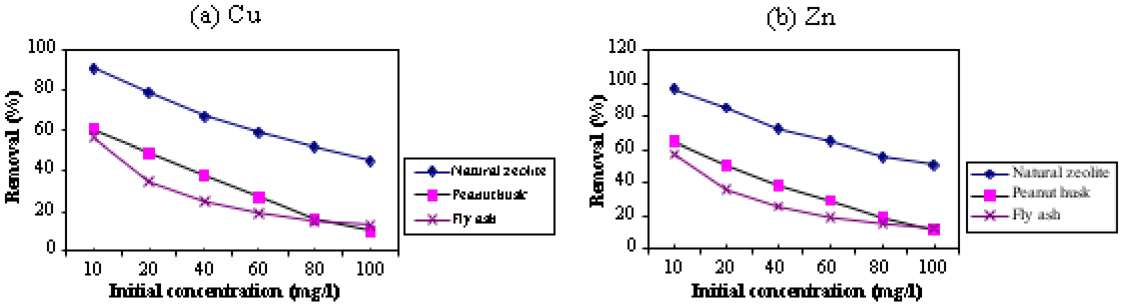

Fig. 3 Effect of initial metal concentration on copper and zinc removal for different adsorbents at 27 ± 2 °C.

Initial concentration (mg/l)

The maximum re- moval of Cu using natural zeolite was 91% at copper ion con- centration 10 mg/l, and the maximum removal of zinc using natural zeolite was 96% at a metal concentration 10 mg/l. This is in agreement with the results obtained by Ragheb et al. [25] for heavy metals removal by low-cost adsorbents.

Adsorption isotherm

An adsorption isotherm equation is an expression of the rela- tion between the amount of solute adsorbed and the concentration of the solute in the fluid phase, since the adsorption isotherms are important to describe how adsorbates will inter- act with the adsorbents and so are critical for design purposes; therefore, the correlation of equilibrium data using an equa- tion is essential for practical adsorption operation [22]. Two isotherm equations were adopted in this study, as follows tration of the solute in the fluid phase, since the adsorption isotherms are important to describe how adsorbates will inter- act with the adsorbents and so are critical for design purposes; therefore, the correlation of equilibrium data using an equa- tion is essential for practical adsorption operation [22]. Two isotherm equations were adopted in this study, as follows.

Freundlich isotherm equation

The Freundlich sorption isotherm, one of the most widely used mathematical descriptions, gives an expression encompassing the surface heterogeneity and the exponential distribution of active sites and their energies.

The Freundlich isotherm is defined as:

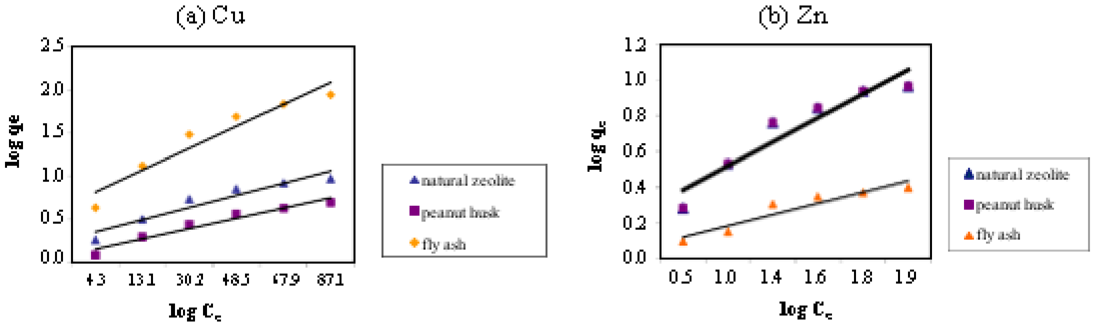

Fig. 4 Freundlich plot of different adsorbents for copper and zinc removal at 27 ± 2 °C.

where C_e is the equilibrium concentration in mg/l, q_e = amount of adsorbate adsorbed per unit weight of adsorbent (mg/g). ''k'' is a parameter related to the temperature and ''n'' is a characteristic constant for the adsorption system un- der study, The plots of log Q_e against log C_e are shown in Fig. 4(a) and (b); the adsorption of copper and zinc ions onto the different adsorbents gave a straight line; values of ''n'' be- tween 2 and 10 show good adsorption [26]. The Freundlich iso- therm constants and their correlation coefficients R^2 are listed in Table 3.

Langmuir isotherm equation

The Langmuir equation is based on the assumptions that max- imum adsorption corresponds to a saturated mono-layer of adsorbate molecules on the adsorbent surface, that the energy of adsorption is constant, and that there is no transmigration of adsorbate in the plane of the surface [27].

The Langmuir isotherm is defined as:

$Q_e = (bQ_mC_e)/(1 + bC_e)$ (3)

and in linearized form is:

$C_e/Q_e = (C_e/Q_m) + 1/(bQ_m)$ (4)

where Q_m and b are Langmuir constants related to the sorption capacity, and sorption energy, respectively, C_e is the equilib- rium concentration in mg/l, and Q_e is the amount of adsorbate adsorbed per unit weight of adsorbent (mg/g). The plots of C_e/Q_e against C_e are shown in Fig. 5(a) and (b); the adsorption of copper and zinc ions on different adsorbents give a straight line. It is clear that the linear fit is fairly good and enables the appli- cability of the Langmuir model. The Langmuir isotherm con- stants and their correlation coefficients R^2 are listed in Table 4. As can be observed, experimental data were better fitted to the Langmuir equation than to the Freundlich equation, and therefore it is more suitable for the analysis of kinetics. Conse-

Table 3 Freundlich constants for the sorption of Cu(II) and Zn(II) ions onto different adsorbents.

Heavy metal	Adsorbent	Freundlich constants		R^2
		k	*n*	
Cu	Peanut husk charcoal	2.814	3.67	0.955
	Fly ash	3.629	3.94	0.9243
	Peanut husk charcoal	2.604	3.604	0.95
Zn	Natural zeolite	1.632	7.102	0.9166
	Fly ash	1.139	15.848	0.8982
	Natural zeolite	1.773	7.413	0.9038

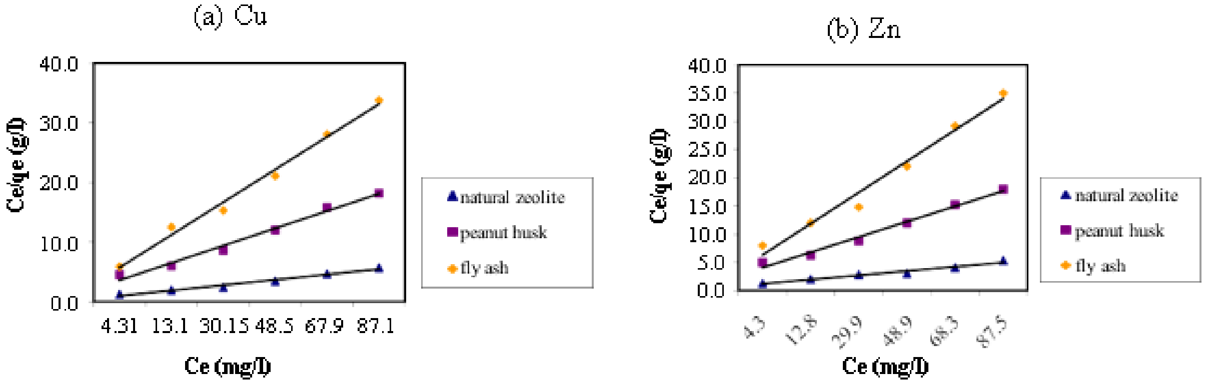

Fig. 5 Langmuir plot of different adsorbents for copper and zinc removal at 27 ± 2 °C.

quently, the sorption process of metal ions on natural zeolite follows the Langmuir isotherm model, where the metal ions are taken up independently on a single type of binding site in such a way that the uptake of the first metal ion does not affect the sorption of the next ion. Budinova et al. and Lopez et al. [28,16] reported a similar relationship when activated car- bon obtained from different raw materials was used as an adsorbent.

Cost of adsorbents

Commercial activated carbon of the cheapest variety (generally used for effluent treatment) costs about L.E. 10,000/ton. The adsorbent material used in the present study is generally avail- able at a relatively cheap rate, L.E. 5000/ton for peanut husk,

L.E. 1500/ton for fly ash, and L.E. 4000/ton for natural zeolite. The finished products would cost approximately L.E. 7000/ton for peanut husk, L.E. 3500/ton for fly ash, and L.E. 6000/ton for natural zeolite including all expenses (transportation, han- dling, chemicals, electrical, energy, drying, etc.).

Conclusion

Low-cost adsorbents like peanut husk charcoal, fly ash and nat- ural zeolite are effective for the removal of Cu^{2+} and Zn^{2+} ions from aqueous solutions. The batch method was employed; parameters such as pH, contact time, adsorbent dose and metal concentration were studied at an ambient temperature 27 ± 2 °C. The optimum pH corresponding to the maximum adsorption of copper and zinc removal was 6–8. Copper and zinc ions were adsorbed onto the adsorbents very rapidly within the first 30 min, while equilibrium was attained within 2–3 h for copper and zinc ions using different adsorbents. The Langmuir isotherm better fitted the experimental data since the correlation coefficient for the Langmuir isotherm was higher than that of the Freundlich isotherm for both metals.

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