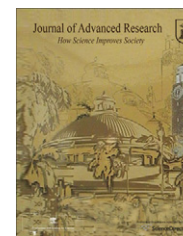




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**ORIGINAL ARTICLE**

A study of the removal characteristics of heavy metals from wastewater by low-cost adsorbents

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Abstract In this study, the adsorption behavior of some low-cost adsorbents such as peanut husk charcoal, fly ash, and natural zeolite, with respect to Cu^{2+} , and Zn^{2+} ions, has been studied in order to consider its application to the purification of metal finishing wastewater. The batch method was employed: parameters such as pH, contact time, and initial metal concentration were studied. The influence of the pH of the metal ion solutions on the uptake levels of the metal ions by the different adsorbents used were carried out between pH 4 and pH 11. The optimum pH for copper and zinc removal was 6 in the case of peanut husk charcoal and natural zeolite, and it was 8 in case of fly ash. An equilibrium time of 2 h was required for the adsorption of Cu(II) and Zn(II) ions onto peanut husk charcoal and fly ash and an equilibrium time 3 h was required for the adsorption of Cu(II) and Zn(II) ions onto natural zeolite. Adsorption parameters were determined using both Langmuir and Freundlich isotherms, but the experimental data were better fitted to the Langmuir equation than to Freundlich equation. The results showed that peanut husk charcoal, fly ash and natural zeolite all hold potential to remove cationic heavy metal species from industrial wastewater in the order fly ash < peanut husk charcoal < natural zeolite.

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Introduction

Water pollution due to the disposal of heavy metals continues to be a great concern worldwide. Consequently, the treatment of polluted industrial wastewater remains a topic of global concern since wastewater collected from municipalities, communities and industries must ultimately be returned to receiving waters or to the land [1].

Heavy metals pollution occurs in much industrial wastewater such as that produced by metal plating facilities, mining operations, battery manufacturing processes, the production of paints and pigments, and the ceramic and glass industries. This wastewater commonly includes Cd, Pb, Cu, Zn, Ni and

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Nomenclature

b	Langmuir constant related to sorption energy	PHC	peanut husk charcoal
C_e	equilibrium concentration of the adsorbate (mg/l)	q	the amount of adsorbate adsorbed per unit weight of adsorbent (mg/g)
C_o	initial concentration of adsorbate (mg/l)	q_e	the amount of adsorbate adsorbed per unit weight of adsorbent at equilibrium (mg/g)
GAC	granular activated carbon	q_m	Langmuir constant related to sorption capacity
k	Freundlich constant related to adsorption intensity, $n > 1$ shows good adsorption		

Cr [2]. Whenever toxic heavy metals are exposed to the natural eco-system, accumulation of metal ions in human bodies will occur through either direct intake or food chains. Therefore, heavy metals should be prevented from reaching the natural environment [3]. In order to remove toxic heavy metals from water systems, conventional methods have been used such as chemical precipitation, coagulation, ion exchange, solvent extraction and filtration, evaporation and membrane methods [4]. Adsorption of heavy metals on conventional adsorbents such as activated carbon have been used widely in many applications as an effective adsorbent, and the activated carbon produced by carbonizing organic materials is the most widely used adsorbent. However, the high cost of the activation process limits its use in wastewater treatment applications [5].

Agricultural waste is one of the rich sources of low-cost adsorbents besides industrial by-product and natural material. Due to its abundant availability agricultural waste such as peanut husk, rice husk, wheat bran and sawdust offer little economic value and, moreover, create serious disposal problems [6]. Activated carbons derived from peanut husk and rice husk have been successfully employed for the removal of heavy metals from aqueous solutions [7]. The use of peanut hull carbon for the adsorption of Cu(II) from wastewater was studied by Periasamy and Namasivayam [8]; their comparative study of commercial granular activated carbon (GAC) showed that the adsorption capacity of PHC was 18 times larger than that of GAC.

Fly ash is a waste material that is produced from the combustion of coal in thermoelectric power plants [9–11]; many researchers have reused fly ash for wastewater or air pollutants control and studied the removal characteristics of heavy metal ions from aqueous solutions [12,13]. The adsorption characteristics of heavy metals using various particle sizes of bottom ash were reported by Shim et al. [14]. In another study, fly ash from a coal-fired power plant was used for the removal of Zn(II) and Ni(II) from aqueous solutions; it is proved to be effective as activated carbon at high dosages [15].

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 aluminosilicate 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^{4-} and AlO_4^{5-} 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 adsorption 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 synthetic zeolites [19,20].

The objective of this work is to study the adsorption behavior 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 μm before use.

Samples of zeolite were taken from Dar el Emara Company, Egypt. The crushed original zeolite was ground and passed through 300 \times 600 μm sieves and was dried in an oven at 100 \pm 5 °C for 24 h.

Characterization of adsorbents

The surface area of PHC has been found to equal to 485 $\text{m}^2 \text{g}^{-1}$; this value is very high in comparison with other carbons, which have a surface area about of 10–100 $\text{m}^2 \text{g}^{-1}$. The adsorption capacity of carbon is strongly influenced by the chemical structure of its surface, which are of carbon-oxygen. Functional groups suggested most often are carboxyl groups, phenolic hydroxyl groups, carbonyl groups (e.g. quinone type), and lactone groups [7]. The chemical composition of PHC is shown in Table 1, and the values are expressed in w/w.

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

The bulk chemical composition of fly ash was measured using XRD; the results are given in Table 2. The main components were SiO₂, Al₂O₃, and Fe₂O₃ with others found in low concentrations.

The structures of zeolites consist of three-dimensional frameworks of SiO⁴⁺ and AlO⁴⁺ tetrahedra. They were characterized by X-ray diffraction (XRD) and chemical analysis [19]. Al₂O₃, Fe₂O₃, CaO, and MgO were analyzed using titrimetric methods and SiO₂ was analyzed with a gravimetric method. Na₂O and K₂O were found by flame photometry. The results of chemical analysis are presented 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 concentrations were obtained by diluting the stock solution with distilled water. Copper and zinc concentrations were determined 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.

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 µm filter paper. The residual concentration of heavy metals was determined by the spectrophotometer Model CE3021 made by CECIL Instruments, USA. In addition to adsorption tests, a set of blank tests was conducted to evaluate the removal by metal hydroxide precipitation at various pH values.

Table 2 Chemical composition of fly ash and natural zeolite.

Species	Chemical composition (% w/w)	
	Fly ash	Natural zeolite
SiO ₂	89.56	45.09
Al ₂ O ₃	4.74	14.43
Fe ₂ O ₃	4.24	10.59
CaO	0.01	5.76
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 adsorbent and the degree of ionization and speciation of the adsorbate [11]. The results obtained are shown in Fig. 1(a) and (b) and show the effect of pH on the adsorption of Cu²⁺, and Zn²⁺ ions from the aqueous solution onto the different adsorbents in terms of the metal ions removed percent. It is clear that Cu²⁺, and Zn²⁺ ions were effectively adsorbed in the pH range (4–7), and the maximum adsorption of Cu²⁺, and Zn²⁺ ions using peanut husk charcoal occurred at pH 6 and 7, respectively, while the maximum adsorption of Cu²⁺ and Zn²⁺ ions using fly ash occurred at pH 8, and the maximum adsorption of Cu²⁺ and Zn²⁺ ions using natural zeolite occurred at pH 6; thus, these pH values was chosen for all experiments. These results are similar to results obtained by Rodda et al. [21] for heavy 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 adsorbents increased significantly as the pH of the solution increased. 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 Cu²⁺, and Zn²⁺ ions increased rapidly as the pH value increased; at pH values above 6 the adsorptive capacities of Cu²⁺ and Zn²⁺ ions increased, but at a slower rate because of the competitive 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 equilibrium, 97.5% of copper ions and 90% of zinc ions were removed from the solution using natural zeolite. Equilibrium was reached for copper and zinc removal within 2 h using peanut husk carbon and fly ash and within three hours using natural 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 removal was studied by batch adsorption experiments, which were carried out at 27 ± 2 °C using different initial metal ion

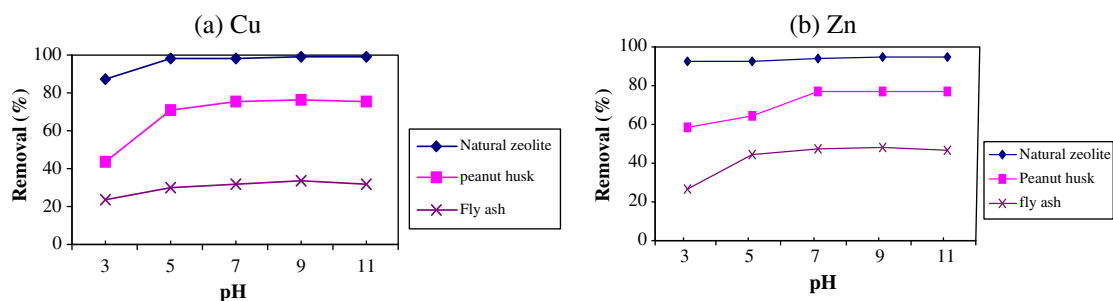


Fig. 1 Effect of pH on copper and zinc removal for different adsorbent at 27 ± 2 °C.

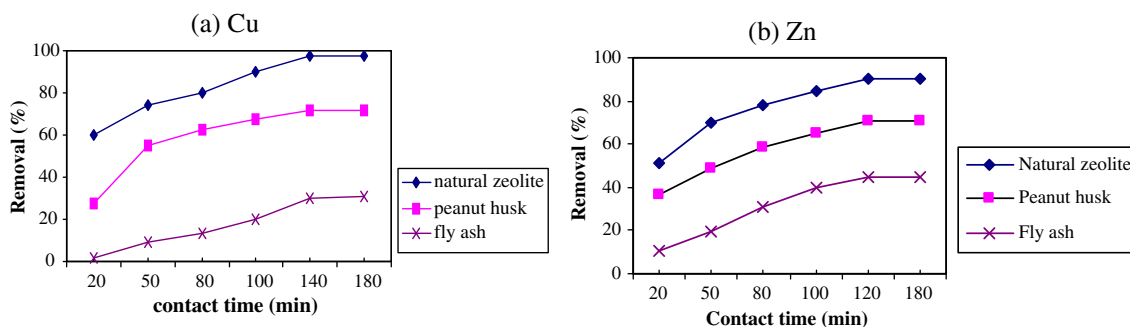


Fig. 2 Effect of contact time on copper and zinc removal for different adsorbents at 27 ± 2 °C.

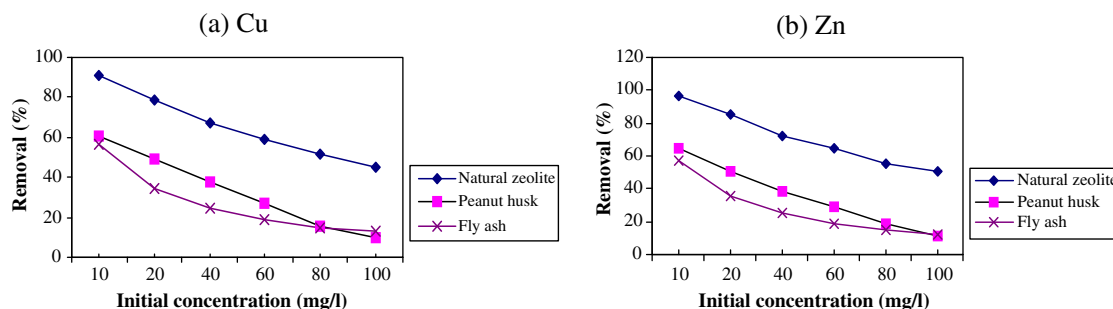


Fig. 3 Effect of initial metal concentration on copper and zinc removal for different adsorbents at 27 ± 2 °C.

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 removal of Cu using natural zeolite was 91% at copper ion concentration 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 relation between the amount of solute adsorbed and the concen-

tration of the solute in the fluid phase, since the adsorption isotherms are important to describe how adsorbates will interact with the adsorbents and so are critical for design purposes; therefore, the correlation of equilibrium data using an equation 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:

$$q_e = k C_e^{1/n} \quad (1)$$

and in linearized form is:

$$\log q_e = \log k + (1/n) \log C_e \quad (2)$$

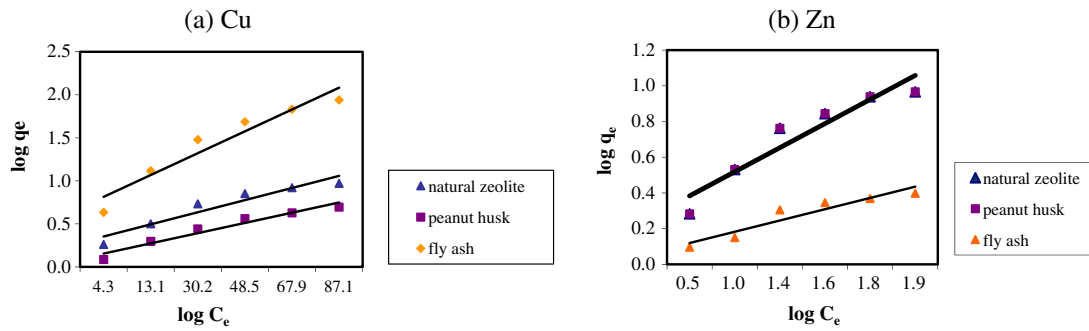


Fig. 4 Freundlich plot of different adsorbents for copper and zinc removal at $27 \pm 2^\circ\text{C}$.

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 under 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 ” between 2 and 10 show good adsorption [26]. The Freundlich isotherm constants and their correlation coefficients R^2 are listed in Table 3.

Langmuir isotherm equation

The Langmuir equation is based on the assumptions that maximum 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:

$$Q_e = (bQ_m C_e)/(1 + bC_e) \tag{3}$$

and in linearized form is:

$$C_e/Q_e = (C_e/Q_m) + 1/(bQ_m) \tag{4}$$

where Q_m and b are Langmuir constants related to the sorption capacity, and sorption energy, respectively, C_e is the equilibrium 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 applicability of the Langmuir model. The Langmuir isotherm constants 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

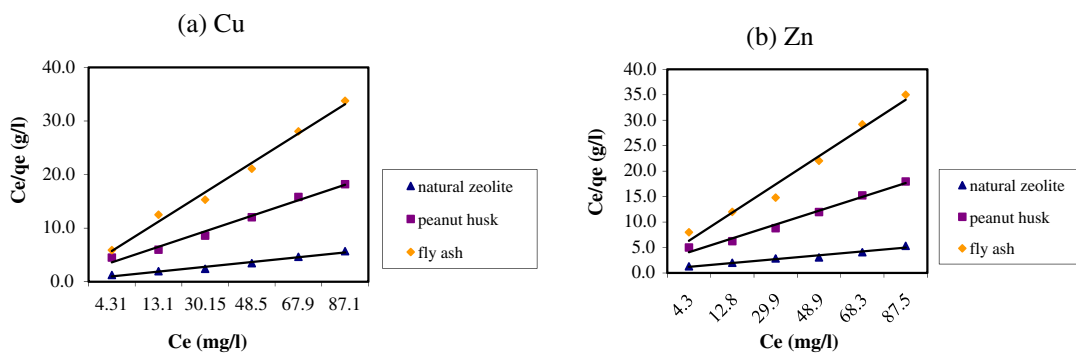


Fig. 5 Langmuir plot of different adsorbents for copper and zinc removal at $27 \pm 2^\circ\text{C}$.

Table 4 Langmuir constants for the sorption of Cu(II) and Zn(II) ions onto different adsorbents.

Heavy metal	Adsorbent	Langmuir constants		R^2
		b	q_m	
Cu	Peanut husk charcoal	4.071	0.3451	0.9854
	Fly ash	21.124	0.1825	0.9899
	Natural zeolite	8.66	1.118	0.9778
Zn	Peanut husk charcoal	1.986	0.3681	0.9850
	Fly ash	7.0	0.1806	0.9783
	Natural zeolite	1.7	1.3189	0.9668

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 carbon 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 available 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, handling, chemicals, electrical, energy, drying, etc.).

Conclusion

Low-cost adsorbents like peanut husk charcoal, fly ash and natural 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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