

Removal of Heavy Metals from Groundwater by Hydrous Ferric Oxide-Modified Peanut Shell

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Citation: Desouky AM, Saber RA (2022) Removal of Heavy Metals from Groundwater by Hydrous Ferric Oxide-Modified Peanut Shell. J Environ Pollut Control 5(2):202

Abstract

This study reports the adsorption capacity of copper Cu (II) and nickel Ni (II) of biochar obtained from peanut shell. The kinetics and equilibrium of biosorption were examined in detail. Two kinetic models (pseudo-first order and pseudo-second order) were used to correlate the experimental data and to determine the kinetic parameters. Two well-known adsorption isotherms were chosen to describe the biosorption equilibrium (Langmuir and Freundlich). The equilibrium isotherms showed that modified peanut shells possess high affinity, sorption capacity for Cu (II) and Ni (II) ions, sorption capacities of 37.443 mg/g Cu (II) and 28.626 mg/g Ni (II) biomass, respectively. All results showed that peanut shells biomass is an attractive, alternative low-cost bio sorbent for removal of heavy metal ions from aqueous media, therefore biomass materials find good application prospects.

Keywords: Pollution, Removal, Water Treatment, Heavy Metal, Peanut Shell

Introduction

With the rapid pace of urbanization and industrialization, heavy metal pollution has spread broadly over the world [1]. Water contamination caused by heavy-metal ions generated from alloys, pigments, electroplating, mining, metallurgical activities [2]. Various technologies have been developed for the removal of heavy metals from aqueous solutions including chemical precipitation [3], coagulation and flocculation, electrochemical methods, reverse osmoses, membrane separation and ion exchange [4]. Metallic oxides such as Fe (III), Mn (IV), Zr (IV), and Ti (IV) Oxides are always recognized as the promising adsorbents for heavy metal sequestration regardless of the sorption capacity or selectivity owing to their great reactive activity and strong and specific affinity to metal ions. Compared to other metallic oxides, hydrous ferric oxides possess the advantages of low cost and excellent environmental friendliness, and thus it is widely studied in the field of heavy metal cleanup from water [5]. Peanut shell are a processing waste product with potential as a low-cost source of polyphenols for nutraceutical or functional food ingredient use [6]. Aqueous extractions of peanut shell and subsequent concentration of these extracts can result in normally innocuous levels of heavy metals present to be increased to concentrations of human health concern. Adsorption utilizing waste biomasses is a promising method of removing these contaminants from extracts [7]. Heavy metals in water promote toxicity, and they are not biodegradable [8]. Recently, efforts have been made to use cheap and readily available agricultural wastes such as coconut shells, orange peel, and rice husk peanut shell and saw dust as adsorbents to remove heavy metals from waste water. We use peanut shell as the adsorbent [9]. The biomass material, as an adsorbent applied for controlling heavy metals contamination, is becoming a hot research topic. Biomass materials have the advantage of widespread-sources, convenience, low-cost, directly-treated and thus greatly reduce the cost of the treatment of heavy metals. Therefore, biomass materials find good application prospects [10]. Biosorption is a process that utilizes low-cost bio sorbent to sequester toxic heavy metals. Biosorption has distinct advantages over the conventional methods, which include reusability of biomaterial, low operating cost, selectivity for specific metal, short operation time and no chemical sludge [11]. Due to its abundant pore structure and adsorption capacities, biochar has been widely applied to study heavy-metal wastewater treatment [12]. Peanut husk has been observed to be cellulosic material which possesses some unique properties which can be made use of in wastewater remediation processes [13]. However, some adverse effects (such as low adsorption capacities and difficulty with removal after the adsorption process) have been noted with their use in pristine form [14-15]. Therefore, several modification agents have been employed in order to minimize these effects as well as to improve upon its effectiveness [16-20]. Recently, simultaneous electroreduction of heavy metals during the electro sorption process is also attempted to reduce heavy metals toxicity using magnetite (Fe_3O_4) particles [21-22]. This Fe_3O_4 based composite would possess the synergistic effects of high redox electrocatalytic behavior ascribed to Fe_3O_4 portion and high surface area/pore size distribution attributed to the peanut shell portion [23]. The main objective of the current study is to prepare a hydrous ferric oxide-modified biochar and investigate its performance for effective removal of heavy metals from water. A widely used inorganic adsorbent was employed as the active component for improving the sorption ability of biochar to heavy metal. Finally hydrous Ferric oxide-modified peanut shell possess the advantages of low cost and excellent environmental friendliness, and thus it is widely studied in the field of heavy metal cleanup from polluted water.

Materials and Methods

Materials

The stock solution of Cu^{2+} and Ni^{2+} were prepared by dissolving their respective salts, $\text{CuSO}_4 \cdot 6\text{H}_2\text{O}$, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, in deionized water. All of the reagents were of analytical grade and purchased from Sigma Aldrich (AR). The sodium hydroxide (NaOH) and nitric acid (HNO_3) purchased from Meryer chemical technology Co. Ltd.

Preparation of Modified Peanut Shell

First, the peanut shell (5g) was put into the quartz cell and then placed into a muffle furnace. Then, the temperature of the muffle furnace was elevated from room temperature to 600 °C with a rate of 10 °C/min and subsequently held for 1 h, followed by a natural cooling process. Finally, the black solids were rinsed with pure water until neutral pH and dried at 60 °C for 24 hrs. hydrous Ferric

oxide - peanut shell was synthesized by employing peanut shell as the host according to the following procedures. First, 5.0 g peanut shell was added into 1 mol/L FeCl_3 solution and then constantly agitated for 24 h at 298 K. Second, the Fe (III)-laden peanut shell was separated from the solution and then dispersed into 2% NaOH solution. After that, the solution was stirred for another 24 hrs. to generate ferric oxide precipitate in situ. Finally, the obtained solids were washed with deionized water until neutral pH and then desiccated at 60 °C until reaching the constant weight. The peanut shell with a size of 0.1 - 0.15 mm was chosen and sealed for later.

Batch Adsorption Tests

Applicability of modified peanut shell for Cu (II) and Ni (II) removal was studied using batch experiments in a reaction mixture of 0.25 g of adsorbent and 0.02 L of metal solution containing Cu (II) and/or Ni (II) at concentrations ranging from 200 to 1000 mgL^{-1} . The effect of pH was studied at metal concentration of 20 mgL^{-1} in the pH range of 1–5. Alkaline solutions were not used to avoid the hydroxide formation (Orion 2-star pH Bench top "Thermo"). The effect of contact time was studied at metal concentration of 20 mgL^{-1} . Agitation was undertaken using a rotary shaker type SK 300 (Lab companion). At designated contact time, the adsorbent was separated from the solution. The metal concentrations in the filtrates were analyzed by Atomic Absorption Spectrophotometer, (Unicam model Solaar 929. The adsorption capacities (mg g^{-1}) of modified peanut shell were calculated as follows:

$$q_e = (C_i - C_e) V(L)/W$$

where C_i and C_e are the initial and the equilibrium concentrations, respectively (mg L^{-1}), while $W(\text{g})$ and $V(\text{L})$ represent the weight of the adsorbent and the volume of the solution, respectively.

Characterization of Modified Peanut Shell

The formation of additional functional groups on peanut shell surface after modification with Ferric oxide was studied using X-ray and FTIR-spectroscope type Nicolet Nexus 8700 (USA). Infrared spectra (FTIR) were obtained with a Perkin-Elmer spectrum. The peanut shell and modified peanut shell were dried overnight at 60 °C under reduced pressure and pressurized with a glass slide on top of the quartz window of the ATR instrument. High angle X-ray diffraction (XRD) patterns were recorded on X-ray diffractometer (D/Max2500VB2+/Pc, Rigaku, Japan) with Cu $K\alpha$ characteristic radiation ($\lambda = 1.54178 \text{ \AA}$) at a voltage of 40 kV and a current of 50 mA. The scanning rate was 5°/min and the scanning scope of 2θ was from 5° to 70° at room temperature

Results and Discussion

Characterization of Modified Peanut Shell

FTIR spectra of the peanut shell before and after modified are shown in Figure 1A and B. As can be seen in Figure 1A, the absorption band observed in the region 1125 cm^{-1} occur with the broadest, the strongest overlapping bands involving the stretching vibrations of the C=O bond. It has been also noted by several authors using different carbon materials [24]. The 1410 cm^{-1} band may be attributed to the CH and carboxyl-carbonate structures. The 2420 cm^{-1} band characteristic of the carboxylic acid group. The 3490 cm^{-1} band may be attributed to the OH group. But the FTIR spectra after modified (Figure 2B), another band placed in 642 cm^{-1} representing the Fe–O group is also observed except the aforementioned peaks in Figure 1A further indicating the successful loading of peanut shell.

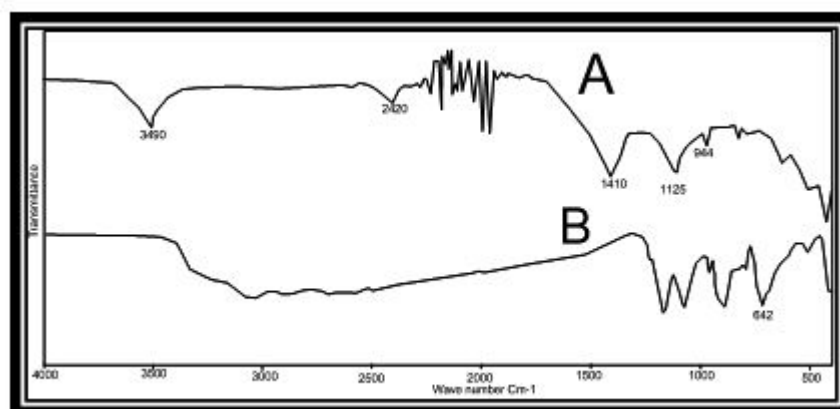


Figure 1: IR shows of the samples (A) peanut shell, (B) modified peanut shell

The X-ray diffraction pattern, recorded at room temperature in the range of 2θ values from 5° to 70° , was employed for the investigation on the crystalline carbon contents presented in the product biochar, as the results were subsequently analyzed by comparing with that of the Figure 2A shows three broad peaks located at 15.8 , 25.7 and 42.8 respectively, matching well with peaks in the database entry obtained from the PDF card (#46.0943), which suggests the typical formation of crystalline carbonaceous structures. Also Figure 2B shows three broad peaks with some changes with comparison with Figure 2A it's due to successful overlapping of Ferric oxide into peanut shell.

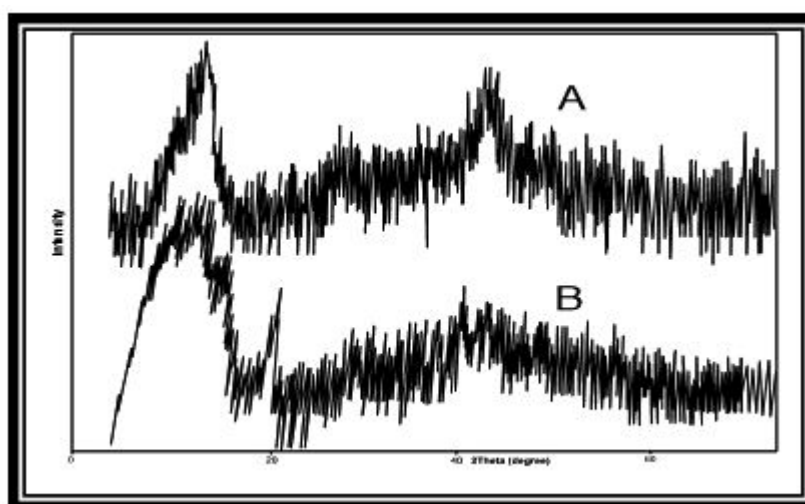


Figure 2: X-Ray diffraction patterns (XRD) of (A) peanut shell, (B) modified peanut shell

Effects of pH

The pH of a solution strongly affects the adsorption capacity of the modified peanut shell. So, the effect of solution pH on metal ions removal after soaking of 24 hr. The effect of pH on the adsorption amount of Cu (II) and Ni (II), on modified peanut shell was investigated within pH ranges between 1 and 5, by adjusting the solution pH using 0.1N HCl or 0.1N NaOH. Figure (3), shows that at low pH values, the modified peanut shell acquire very low adsorption. By increasing pH of the medium ($pH > 2$), the metal uptake increased with the increasing pH in the range of 2 to 5. At pH values of about 5, sorption capacities achieved maximum values. When the pH decreased, concentrations of protons increased and competition in binding the active sites on the surface of the bio sorbent, by the H^+ and metal ions, started. Protonated active sites were incapable of binding the bind metal ions, leading to free ions remaining in the solution. When the initial pH of the solution was adjusted to a value higher than 5, Cu (II) and Ni (II), ions precipitated

because of the higher concentration of hydroxyl anions in the solution. For this reason, the experiments were not conducted at pH values higher than 5.

The low absorption at low pH values ($\text{pH} < 2$) could be referred to the electrostatic repulsion between the metal ions in the medium (M^+) and the positive charges of highly acidic solution $[\text{H}^+]$ accumulated on the surface of the modified peanut shell.

Such repulsion prevents the approach of the metal ions to the modified peanut shell surface at higher pH, such positive charge density decreases allowing the metal ions to approach the sorbent modified peanut shell surface which result in higher adsorption values.

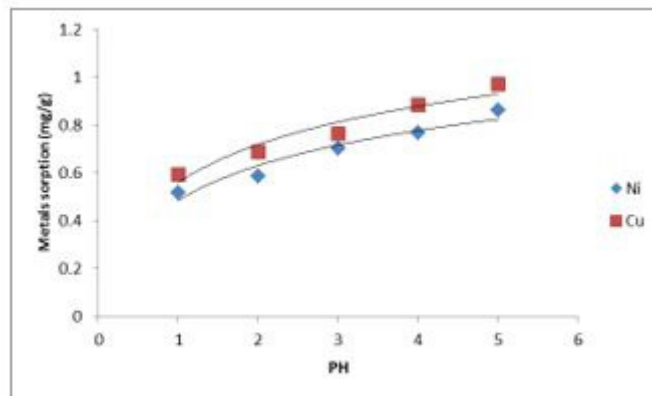


Figure 3: pH-dependent metal uptake of different metal ions

Effects of Contact Time

The effects of contact time on the removal of Cu (II) and Ni (II), on modified peanut shell are depicted in Figure 4. Initially the metal uptake was fast due to the many vacant adsorption sites, all the active sites were occupied by target Cu (II) or Ni (II) within 140 min after which the adsorption rate gradually decreased and became constant at equilibrium to attain equilibrium conditions where the concentration of adsorbate in the bulk solution was in dynamic balance with that at the interface. It is possible that some of the adsorption sites of modified peanut shell were easily obtained due to increases of the functional groups on its surface. This was also seen from the higher kinetics of copper adsorption by modified peanut shell compared to nickel ions.

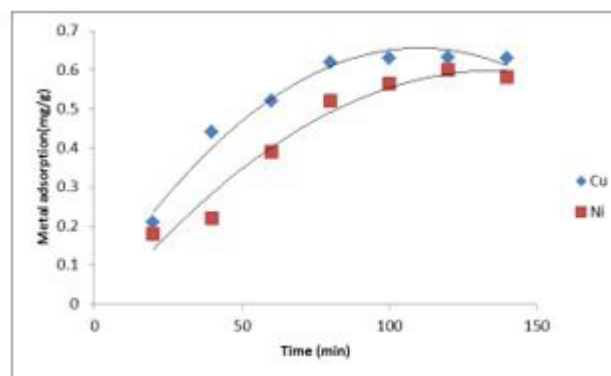


Figure 4: Contact time-dependent metal uptake of different metal ions

Metals Adsorption by Modified Peanut Shell

Total adsorption capacity of the prepared modified peanut shell presents evaluating property in determining the amount needed for the removal of certain amount of polluting metal ions. Figure (5) shows the maximum adsorption capacity of modified peanut shell towards two different individual metal ions at their respective optimum pH value (pH = 5). The data show that the affinity of the chelating and exchange of modified peanut shell towards the studied metal ions proceeds in the following order $\text{Cu}^{2+} > \text{Ni}^{2+}$, (18.6, 14.2 mg/g, respectively) at constant concentration of different heavy metal ions (1000 mg/l). On the other hand, the maximum adsorption of modified peanut shell for Cu^{2+} and Ni^{2+} since the surface has cation exchange sites for removal metal cations (H^+ of carboxyl and hydroxyl groups). In addition, in an aqueous solution of above a pH of 3.5, the functional groups of modified peanut shell acquire a negative charge and are able to absorb cationic species through electrostatic attraction [25-26].

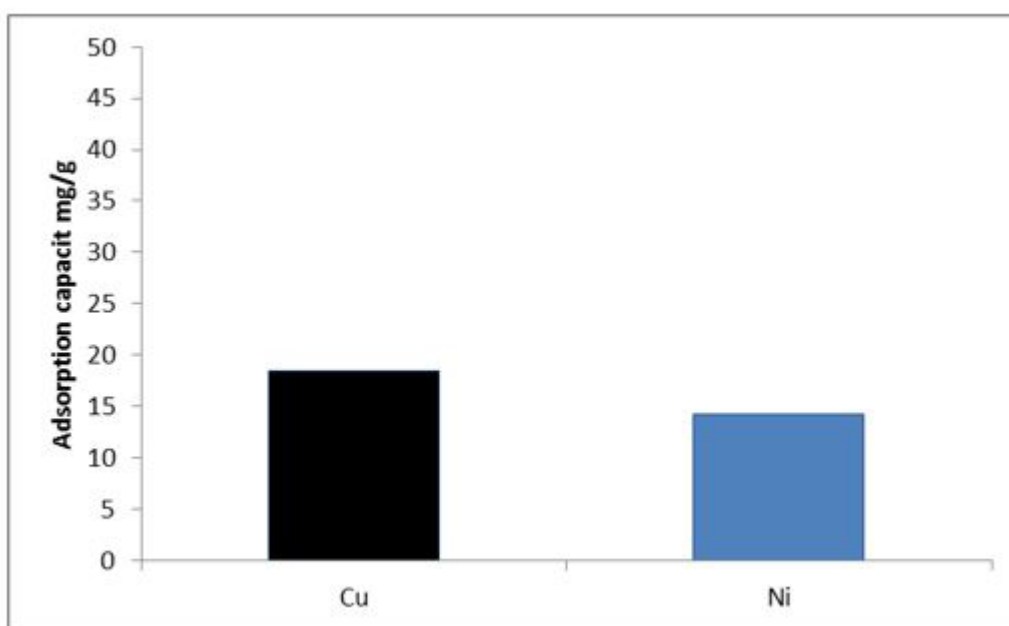


Figure 5: Maximum sorption capacity of modified peanut shell towards two different individual metal ion solutions at PH 5

Regeneration Studies

To evaluate their reusability, regeneration of the spent adsorbents were performed in acidic conditions. At first, adsorbent were loaded by metal ions by mixing around 0.25 g of the adsorbent with 25 ml of 1000 mgL^{-1} Cu^{+2} or Ni^{+2} solution. Regeneration studies were performed using higher metal ions concentrations to make separation procedure easier. After attaining equilibrium, the spent adsorbent was separated from the solution by centrifuge. Metal ions were eluted using 1M HNO_3 . The regeneration efficiency (%RE) of the adsorbent was calculated using Eq. $\%RE = (q_r/q_0) \times 100$

where q_0 and q_r are the adsorption capacities of the adsorbents (mg g^{-1}) before and after regeneration, respectively.

Regeneration of the spent adsorbent is necessary to restore its original adsorption capacity and it enables valuable metals to be recovered from wastewater streams for reuse. In this study, Cu^{+2} and Ni^{+2} were desorbed from of modified peanut shell using 1M HNO_3 . From Table 1 we can suggests that the regeneration efficiency of both adsorbents was almost complete for both metals. These results indicate the suitability of HNO_3 as the regenerant for the adsorbent. It seems that the of modified peanut shell stabilized to resist acidic regenerate.

Type of adsorbent	No. of cycles	RE%	RE%
		Cu (II)	Ni (II)
Modified peanut shell	1	97.00	95.40
	2	98.30	97.56
	3	96.50	97.00
	4	97.80	96.89
	5	98.50	97.90
	6	98.70	97.50

Table 1: Regeneration of modified peanut shell for Cu⁺² and Ni⁺² by 1M HNO₃

Modeling of Adsorption Kinetics

There are several parameters which determine sorption rate, like structural properties of the sorbent (size, surface area, porosity), metal ion properties (e.g., hydrated ionic radius), initial concentration of metal ions, pH, temperature, chelate formation rate or presence of the competing ions [27].

There are essentially three stages in the adsorption process by porous adsorbents: (1) solute transfer from the bulk solution to the external surface of the sorbent through a liquid boundary layer (film resistance); (2) solute transfer from the sorbent surface to the intraparticle active sites (intraparticle resistance); and (3) interactions of the solute with the available sites on both the external and internal surfaces of the sorbent (reaction resistance) Therefore, It is known that adsorption process could be dependent on and controlled with different kinds of mechanisms, like mass transfer, diffusion control, chemical reactions and particle diffusion [28]. In order to clarify the adsorption process, several adsorption models were applied to evaluate the experimental data.

Pseudo-First-Order Kinetic Model

Pseudo-first-order equation for the sorption of liquid/solid system based on solid capacity [29]. It assumes that the rate of change of sorbate uptake with time is directly proportional to the difference in the saturation concentration and the amount of solid uptake with time Table 2. The Lagergren equation is the most widely used rate equation in liquid phase sorption. The general equation is expressed as:

$$\log (q_e - q_t) = \log (q_e) - k_1 t / 2.303 \quad (1)$$

where q_e and q_t are the amounts of metal ions adsorbed onto the adsorbents (mmol/g) at equilibrium and at time t , respectively. k_1 is the rate constant of the first order (min^{-1}). By plotting $\log (q_e - q_t)$ versus t , the first-order constant k_1 and equilibrium capacity q_e can be obtained from the slope and intercept, respectively.

Pseudo-Second-Order Kinetic Model

Ho and Mackay developed a psuedo-second-order equation based on the amount of sorbed sorbate on the sorbent [30]. If the rate of sorption is a second-order mechanism, the pseudo-second-order chemisorption kinetics rate equation is expressed as:

$$dq_t / dt = k_2 (q_e - q_t)^2 \quad (2)$$

For the boundary conditions $t = 0$ to $t = t$ and $q_t = 0$ to $q_t = q_t$, the integrated form of equation (2) becomes:

$$1/(q_e - q_t) = 1/q_e + k_2 t \quad (3)$$

which is the integrated rate law for a pseudo-second-order reaction. Eq.(3) can be rearranged to obtain a linear form:

$$t/q_t = 1/k_2 q_e^2 + t/q_e \quad (4)$$

The constants can be determined by plotting t/q_t versus t . The second-order sorption rate constant k_2 (g /mmol min) and q_e (mmol/g) can be determined from the intercept and the slope of the plot. This model is based on the assumption that the rate limiting step may be a chemical sorption involving valence forces through sharing or exchange of electrons between the adsorbent and the adsorbate [31].

Applying the different kinetic models on the adsorption of Cu (II) and Ni (II) ions on modified peanut shell was investigated. The lines resulting from plotting $\log(q_e - q_t)$ versus t , and t/q_t versus t show the degree of fitting of the metal sorption to the pseudo-first and or pseudo-second order rate kinetic model, respectively. Figure (6) show the kinetics of metal ions adsorption onto modified peanut shell.

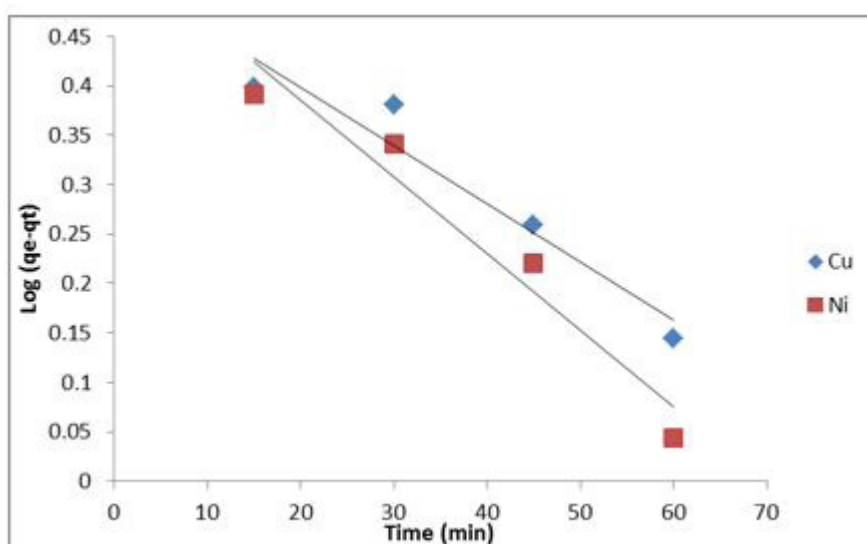


Figure 6: Plots of $\log(q_e - q_t)$ against time for the exchange of Cu (II) and Ni (II) ions on modified peanut shell

It was observed that the pseudo-first-order model not fitted well for Cu (II) and Ni (II) ions where the correlation coefficient (R^2) less than 0.98. The values of k_1 and theoretical and experimental q_e for Cu (II) and Ni (II) are listed in Table (2). On the other hand, by applying the pseudo-second-order model on the sorption of Cu (II) and Ni (II) ions on the modified peanut shell at different concentrations, it was found that the kinetic data can be more fitted as shown in Figure (7) for all Cu (II) and Ni (II) ions in the studied sorption system. This indicates the chemisorption occur involving valence forces through sharing or the exchange of electrons between the exchanger and adsorbed metal ions as covalent forces. The pseudo-second-order equation has the following advantages: it does not have the problem of assigning an effective adsorption capacity, i.e., the adsorption capacity, the rate constant of pseudo-second-order, and the initial adsorption rate all can be determined from the equation without knowing any parameter beforehand. The corresponding parameters of the different kinetic models were determined by linear regression.

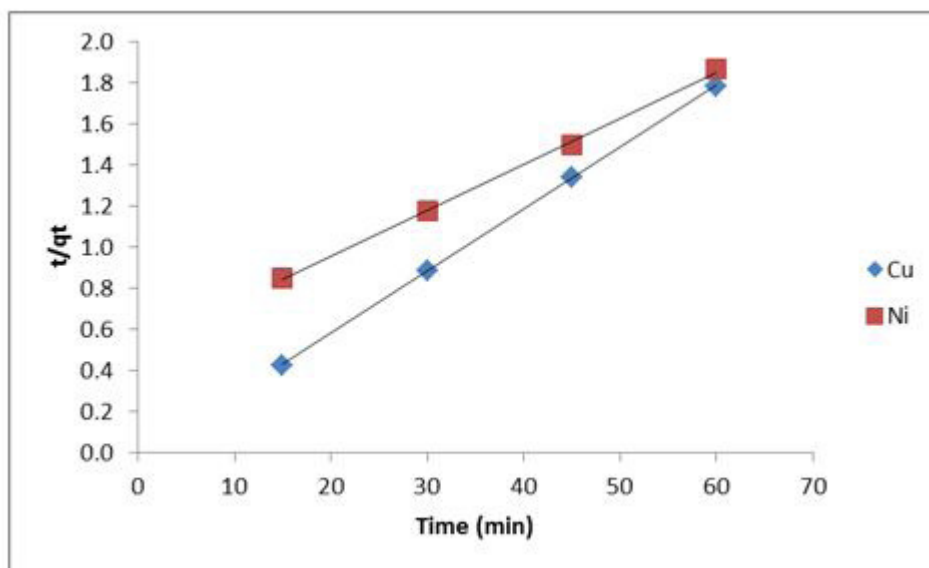


Figure 7: Pseudo second order model for the exchange of Cu (II) and Ni (II) on modified peanut shell

Table (2) list the results obtained from experimental data, which indicate that the pseudo-second-order kinetic equation provided the best model for describing the adsorption of Cu (II) and Ni (II) ions on modified peanut shell.

In addition, analysis of the data presented in Table (2) clears that, the apparent pseudo-rate constants K_1 , K_2 and the corresponding squares of the regression coefficients, R^2 , which indicate the soundness of the correlations to the kinetic models and indicate that the correlation coefficients of the second order kinetic model were greater than 0.98 for all cases, and the theoretical q_e values were also agreed well with the Experimental data. On the other hand, the correlation coefficients for the pseudo-first order kinetics were lower than those for the second order. These imply the sorption of Cu (II) and Ni (II) ions on modified peanut shell follows the pseudo-second order kinetics rather than the pseudo-first order one. These imply the sorption of Cu (II) and Ni (II) ions on modified peanut shell follows the pseudo-second order kinetics.

Metal Ions	$q_{e,cal}$ (mg/g)	$q_{e,exp}$ (mg/g)	$K_1 \times 10^{-3}$ (min ⁻¹)	R^2	$q_{e,cal}$ (mg/g)	$q_{e,exp}$ (mg/g)	$K_2 \times 10^3$ (gmg ⁻¹ min ⁻¹)	R^2
Cu(II)	43.53	15.83	7.35	0.94	24.53	15.83	5.18	0.983
Ni(II)	31.25	13.72	5.56	0.95	1879	13.72	3.23	0.985

Table 2: Pseudo - First and second order parameters for the adsorption of Cu (II) and Ni (II) on modified peanut shell

Modeling Adsorption Isotherms

Equilibrium sorption isotherms (capacity studies) are of fundamental importance in the design of adsorption systems since they indicate how metal ions are partitioned between the adsorbent and liquid phases at equilibrium as a function of metal concentration. When an adsorbent comes into contact with a metal ion solution, the concentration of metal ions on the surface of the adsorbent will increase until a dynamic equilibrium is reached; at this point, there is a clearly defined distribution of metal ions between the solid and liquid phases. As metal concentration increased, the removal efficiencies decreased. Thus, increasing the initial metal concentrations in the solutions decreased the removal efficiency. It is likely that a given mass of adsorbent material has a finite number of adsorption sites, and that as metal concentrations increase, these sites become saturated. That is, there is some metal concentration that produces the maximum adsorption for a given adsorbent mass, and thereafter, adding more metal cannot increase adsorption because no more sites are available: all are occupied. Another cause may have been a progressive decrease in the proportion of

covalent interaction and an increase in the proportion of electrostatic interactions at sites with a lower affinity for metals as the initial metal concentrations increased. The Langmuir, Freundlich isotherms are commonly used for wastewater treatment applications [32]. The Langmuir equation was developed by Langmuir in 1916 to describe the adsorption of gas molecules on a planar surface [33]. The Langmuir model suggests, as a hypothesis, that uptake occurs on a homogenous surface by monolayer sorption without interaction between sorbed molecules. The Langmuir equation has the form [34]:

$$q_e = q_m b C_e / (1 + b C_e) \tag{5}$$

where q_e is the amount adsorbed at equilibrium (mg/g), C_e the equilibrium concentration (mg/L), b is a constant related to the rate of adsorption (L/mg), and q_m is the maximum adsorption capacity (mg/g). The Langmuir equation can be described by the linearized form as follows:

$$C_e / q_e = 1 / (q_m b) + C_e / q_m \tag{6}$$

By plotting (C_e / q_e) versus C_e , q_m and b can be determined if a straight line obtained. The Freundlich model assumes a heterogeneous adsorption surface with sites that have different energies of adsorption and are not equally available. The Freundlich isotherm is more widely used but provides no information on the monolayer adsorption capacity in contrast to the Langmuir model can be written as [35]:

$$q_e = K_F C_e^{1/n} \tag{7}$$

where q_e is the amount adsorbed at equilibrium (mg/g) and C_e is the equilibrium concentration (mg/L). K_F and n are equilibrium constants indicative of adsorption capacity and adsorption intensity, respectively. In general, as the K_F value increases, the adsorption capacity of the adsorbent, for the given adsorbate, increase, n values between 1 and 10 show beneficial adsorption. If n is close to 1, the surface heterogeneity could be assumed to be less significant and as n approaches 10 the impact of surface heterogeneity becomes more significant [36]. The linearized form of Freundlich sorption isotherm is:

$$\log q_e = \log K_F + 1/n \log C_e \tag{8}$$

By applying the different isotherm models (Langmuir and Freundlich) on the sorption of Cu (II) and Ni (II) on modified peanut shell shown in Figures (8-9).

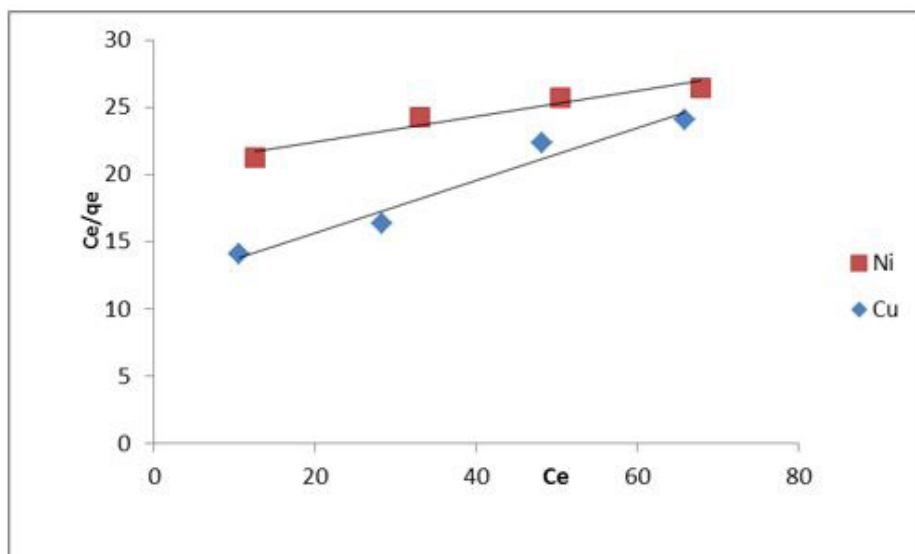


Figure 8: Langmuir Adsorption equilibrium isotherms of Cu (II) and Ni (II) ions on modified peanut shell

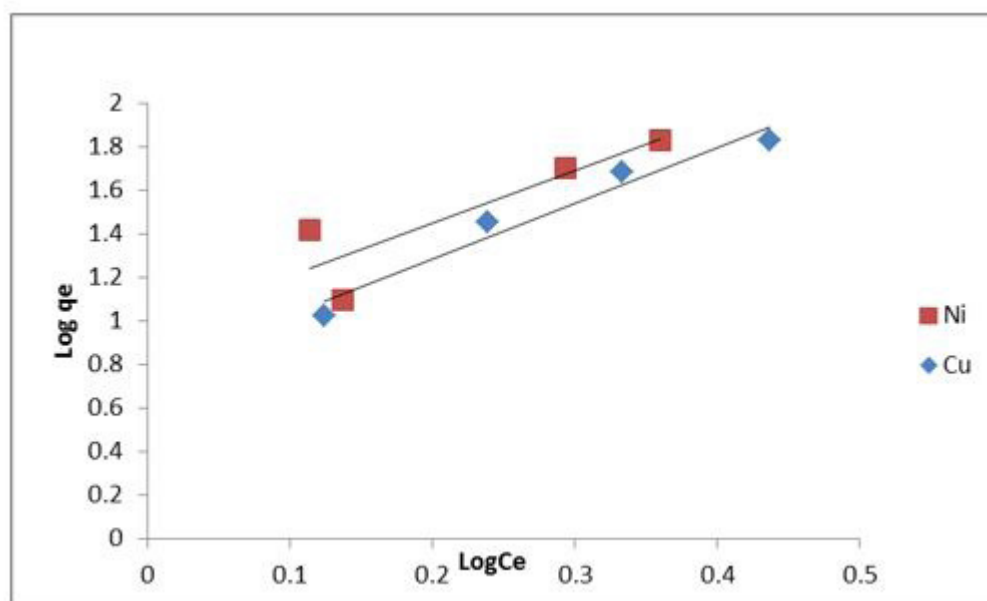


Figure 9: Freundlich Adsorption equilibrium isotherms of Cu (II) and Ni (II) ions on modified peanut shell

Parameters related to each isotherm were determined by using linear regression analysis and the square of the correlation coefficients (R^2) have been calculated. A list of the parameters obtained together with R^2 values is provided in Table (3). It has been found that the best fitted isotherm equation was Langmuir with R^2 more than (0.94). The parameter of the Langmuir equation describes adsorption on strongly homogeneous surfaces but Freundlich equation reveals that the adsorption sites have narrow energy distribution [37]. The correlation coefficient of Langmuir isotherm equation is more than that obtained for the Freundlich equation. Although the Langmuir equation describes adsorption on strongly homogeneous surfaces, which is not the case for natural adsorbents because they exhibit a chemical heterogeneity as represented by different functional groups, however, the n parameter of the Freundlich adsorption equation reveals adsorption sites with low energetically heterogeneity of this natural adsorbent [36]. Based on this reason it can be seen from the obtained data the Langmuir equation can be fitted with a desirable $R^2 = 0.96$ with a monolayer capacity are suitable than other reported natural adsorbents. This could indicate the superiority of modified peanut shell in removing Cu (II) and Ni (II) as compared to other adsorbents. The maximum adsorption capacity of modified peanut shell adsorbent for the removal heavy metals is compared with other adsorbents reported in previous works, Table 4.

Metals	Langmuir constants (modified peanut shell)			Freundlich constants (modified peanut shell)		
	Q_{max} (mg/g)	K_L	R^2	K_F	$1/n$	R^2
Cu (II)	37.443	0.037	0.968	5.98	0.39	0.92
Ni (II)	28.626	0.033	0.949	9.3	0.42	0.87

Table 3: Regression parameters for the Langmuir and Freundlich isotherms for solutions of Cu (II) and Ni (II) on modified peanut shell

Adsorbent	qm (mg/g)	Ref.
NH2-MS for Cu (II)	163.16	2
NH2-MS for Pb (II)	147.79	2
peanut shell for Cu (II)	13.678	6
Potassium Chloride Modified Peanut Shell for Cr (VI)	14.30	12
iminodiacetic acid modified peanut husk for Pb (II)	23.6	13
iminodiacetic acid modified peanut husk for Cu (II)	23.4	13
modified peanut shell for Cu (II)	37.443	This study
modified peanut shell for Ni (II)	28.626	This study

Table 4: Comparison of the maximum adsorption capacity of heavy metals onto different adsorbents

Application

In El-Salihya groundwater contains heavy metals. From the chemical analysis of the groundwater samples, it is clear that, the soluble heavy metals of groundwater samples such as Fe^{3+} and Mn^{2+} are more than the permissible limit (0.3 and 0.1 mg/l), respectively. To overcome this problem, two of groundwater samples were chosen for the treatment process. The efficiency of the treatment was measured by chemical analysis samples before and after this process using modified peanut shell. It was found that the soluble Fe^{3+} and Mn^{2+} in the first sample was 0.62 ppm and 0.18 ppm and pH 7.7 before treatment and 0.14 ppm and 0.032 ppm and after treatment, 0.43 ppm and 0.24 ppm and pH 7.9 before treatment and 0.09 ppm and 0.06 ppm after treatment for the second sample, respectively for overnight. It can be concluded that the surfaces of modified peanut shell had adsorption sites that were able to bind Fe^{3+} and Mn^{2+} ions.

Conclusions

In this study, to promote the adsorption capacity and selectivity of peanut shell to heavy metals, a new composite adsorbent named modified peanut shell was prepared through immobilizing Ferric oxide within the pore region of peanut shell. The as-obtained hybrid material showed excellent sorption performance to Cu (II) and Ni (II). The removal of Cu (II) and Ni (II) onto modified peanut shell can be facilitated by the increased solution p^{H} . Modified peanut shell is an effective adsorbent for the removal of Cu (II) and Ni (II) from aqueous solutions. It would be useful for the economic treatment of wastewater containing these heavy metals. The 2nd kinetic model according to the reaction rate equation was found to be the most in agreement with this system and the Langmuir isotherm model suggested that the adsorption was of monolayer coverage, and that chemical adsorption dominated in the adsorption process.

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