

## Potassium Hydroxide Activated Peanut Shell as an Effective Adsorbent for the Removal of Zinc, Lead and Cadmium from Wastewater

Rusol Maki<sup>1</sup>, Bashar Qasim<sup>1\*</sup>

<sup>1</sup> Applied Chemistry Branch, Department of Applied Sciences, University of Technology, Baghdad, Iraq

\* Corresponding author's e-mail: as.20.42@grad.uotechnology.edu.iq

### ABSTRACT

The toxic heavy metals, as non-biodegradable pollutants, have become a serious threat to aquatic environment. This study aimed to assess the efficiency of the low cost, available and environment-friendly peanut shell as an effective adsorbent for the removal of Zn, Pb and Cd from wastewater. The peanut shell was prepared by carbonization by pyrolysis process at 550 °C, activated with 7M potassium hydroxide(KOH) at 750 °C, and then characterized by using Scanning Electron Microscopy (SEM), and Fourier Transform Infrared spectroscopy (FTIR), X-ray diffraction (XRD) and Brunauer-Emmett-Teller (BET) surface area analysis. The optimum conditions for metal ions adsorption were investigated as a function of various parameters. The optimum conditions included: pH of 6, initial metal concentrations of 20 mg/l for Pb and Zn as well as 40 mg/l for Cd, adsorbent mass of 2 g, optimum temperature of 45 °C and the preferable contact time of 60 min. The removal percent for the studied metal ions exceeded 98%. The adsorption isotherm showed that the Langmuir model was the best fitted model for the metal ions adsorption onto activated peanut shell surface, and the kinetic of adsorption followed the pseudo-first order model. The obtained results showed that the KOH-activated peanut shell possess higher adsorption efficiency for the removal of the studied metal ions from wastewater.

**Keywords:** adsorption, activated peanut shell, heavy metals, wastewater.

### INTRODUCTION

Potentially toxic heavy metals occur naturally in low concentrations, but with the development of the human industrial activities such as mining and smelting operations, batteries production, metal plating, and fertilizer applications, the concentrations of these metals were significantly increased above the allowable ranges, which consequently threatened the environment due to their adverse toxic effect on humans and animals (Esmaeili & Aghababai Beni, 2015; Jauberty et al., 2017; Qasim et al., 2021).

The heavy metals from the industrial wastes discharged result in water pollution which transforms the clean water to unwanted wastewater which therefore affect the quality of natural resources of water and the water

ecosystem due to their immunogenic, carcinogenic and mutagenic action (Witek-Krowiak, 2013) Therefore, the wastewater treatment became one of an important things that attracted the researcher's interest.

In the recent years, various conventional methods have been applied for heavy metals removal from wastewater. These methods were mainly categorized as chemical, physical and biological methods (Crini & Lichtfouse, 2019; Peng et al., 2021; Shakor et al., 2021). These conventional methods included ion exchange, membrane filtration, precipitation, coagulation and flocculation (Dong et al., 2019; Karim et al., 2019). In fact, the above mentioned conventional methods suffered from some limitations in terms of operating cost, chemical consumption, producing of toxic sludge and environmental

impact. Among them, the adsorption of heavy metals using agricultural by-products such as saw dust, maize corn cob, wheat straw, rice husk as activated carbon is considered as a proficient technique due to its high adsorption capacity, cost-effectiveness, ease of use and also simple regeneration of adsorbent (Thompson et al., 2016; Hina Khatoun and Jai Prakash Narayan Rai, 2016; Wang et al., 2019). Therefore, the choice of appropriate adsorbents with low cost and highly adsorption capacity is necessary for removal of heavy metals. The peanut shell that is produced in huge quantities constitutes a substance rich in cellulose and polymer materials that contain reactive functional groups which make it good raw material source for activated carbon preparation. The activated carbon is characterized as a porous carbonaceous material with highly surface area, it considered as an effective adsorbent and a good chelating agent that forms stable complexes with heavy metals in aqueous solutions which are used to purify the wastewater (AL-Othman et al., 2012; Wang et al., 2020; Al-Jadir & Siperstein, 2018). The physical and chemical activation are the traditional methods for preparing the activated carbon. Various chemical activators such as  $H_3PO_4$ ,  $H_2SO_4$ ,  $Ca(OH)_2$  have been already used for the preparation of activated carbon (Liu et al., 2020). The alkaline agent such as KOH is one of the most effective activators that enhance the peanut shell adsorption properties by: *i*) improving its swelling as well as its capacity for cationic pollutants adsorption, *ii*) improving its ability to disintegrate the lignocellulose internal structure which enhances its pore structure and subsequently increases its adsorption capacity, *iii*) removing the impurities from peanut shell surface thereby exposing chemically the reactive functional groups like hydroxyl (OH), and *iv*) increase the concentration of the oxygenated complexes on peanut shell surface (L. Huang et al., 2014; Ashrafi et al., 2016; H. Huang et al., 2017; Nam et al., 2018).

In the literature, the information concerning the efficiency of the KOH-activated carbon for heavy metals removal is still limited. For this reason, the aim of the current study was to: *i*) prepare KOH-activated peanut shells; *ii*) study its efficiency for Zn, Pb and Cd removal from wastewater; and *iii*) study the isotherm and the kinetic process to understand the adsorption process.

## MATERIALS AND METHODS

### Activated peanut shell preparation

The peanut shells used in current study were collected locally from farming markets. The collected material was firstly washed with tap water for two hours to remove the dirt and coloration, and then washed several times with distilled water. To reduce the water content, the washed peanut shells were dried using a laboratory oven set at 110 °C for 24 h. The dried material was powdered using a laboratory grinder, and sieved using a mesh sieve to obtain 100 µm particles size. The sieved peanut shells were dried at 110 °C for 24 h using a laboratory oven. A suitable weight of the prepared peanut shells was carbonized at 550 °C in a closed furnace equipped with argon tank to supply 2 ml/min of argon gas to obtain a carbonized peanut shell (biochar). The collected biochar were chemically activated using 7M KOH solution, immersed in 500 ml of KOH at 60 °C for 4 h, filtered by using 45 µm filter paper, and then dried at 110 °C for 24 h. The obtained KOH activated biochar then activated at the same above mentioned furnace for 2 h at 750 °C (Wang et al., 2020). After cooling the samples to room temperature, the resulting material was washed with deionized water and dried in oven at 110 °C for 24 h.

### Metal ions solution preparation

The stock solutions for the studied metal ions were prepared by dissolving an appropriate amount of  $Zn(NO_3)_2$ ,  $Pb(NO_3)_2$  and  $Cd(NO_3)_2$  in distilled water to achieve 1000 mg/l of  $Zn^{+2}$ ,  $Pb^{+2}$  and  $Cd^{+2}$  respectively. The prepared stock solutions were used to prepare different initial metal ion concentrations. To adjust the pH of the prepared solutions, 0.1M of both HCl and NaOH was prepared and used to achieve the desired pH values.

### Physico-chemical characterization study

The activated peanut shell was characterized by SEM (scanning electron microscope INPECT S50, Germany) to investigate its external surface morphology. The BET (Brunauer–Emmett–Teller; Micro active for Tri-Star II Plus 2.03, U.S.A) method that is based on adsorption–desorption isotherm of nitrogen was performed to observe the specific surface area of the activated peanut shell. The XRD (X-ray diffraction analysis; Shimadzu

6000, Japan) was performed to observe the mineral composition of the activated peanut shell. The FTIR (Fourier Transform Infrared spectrophotometry, Shimadzu, Japan) was used before and after adsorption to identify the reactive functional groups on the activated peanut shell surface. The metal ion concentrations were determined using ICP-MS spectrophotometry (Finnigan Element XR, Thermo Electron, Germany).

### Batch adsorption analysis

The batch adsorption experiments were performed to evaluate the effect of variable parameters on the adsorption efficiency of the activated peanut shell as a metal ions adsorbent. These parameters included: value of the solution pH, peanut shell dose, initial metal ion concentrations, contact adsorption time and temperature. The batch experiments were performed by shaking a known weight of activated peanut shell with 100 ml of individual metal ions in 250 ml conical flasks at 200 rpm using a rotary shaker. The adsorbed solutions were filtered using 45 µm filter paper, and the metal ion concentrations in the filtrates were determined by ICP-MS spectrophotometry.

The effect of solution pH was conducted by adding 0.5 g of adsorbent to 10 mg/l of individual metal ion at time of 120 min with different pH values (3 – 8) at 25 °C. The effect of contact time was performed by adding 0.5 g of adsorbent to individual metal ions (10 mg/l) at 25 °C and optimum pH with different time intervals (5 – 240 min). The effect of initial metal ions was performed by adding 0.5 g of adsorbent to different individual metal ion concentrations (5 – 100 mg/l) by adding 0.5 g from adsorbent at optimum pH and contact time. The effect of activated peanut shell dose was conducted by adding different amounts of adsorbent (0.5 – 4 g) to 100 ml at optimum metal ion concentration, optimum pH and optimum contact time. The effect of temperature was conducted at 25 – 60 °C.

### Isotherm study

To clarify the adsorption equilibrium as well as the relationship between the content of adsorbed metal ions per unit mass of activated peanut shell, an adsorption isotherm experiment was performed by adding a desired amount of adsorbent to 100 ml of metal ion aqueous solutions at varying concentrations (5 – 700 mg/l) at optimum pH value and

25 °C. After equilibrium, the adsorbed solutions were filtered, and the concentrations of the studied metal ions were determined by ICP-MS.

The removal percentage of the metal ions by activated peanut shell as well as the adsorption capacities were calculated from the following equations:

$$\text{Removal \%} = \frac{C_o - C_e}{C_o} \times 100 \quad (1)$$

$$q_e = \frac{(C_o - C_e) V}{m} \quad (2)$$

where:  $C_o$  and  $C_e$  – the initial and final (at equilibrium) metal ion concentrations (mg/l);  
 $q_e$  – the adsorption capacity (mg/g);  
 $V$  – the volume of the solution (L);  
 $m$  – the mass (g) of the adsorbent.

Two models of isotherms named Langmuir and Freundlich were applied in this study to investigate the affinity of the adsorbent to remove the metal ions from aqueous solution and also to correlate the obtained results.

The Langmuir model which is expressed as the following equation describes the monolayer adsorption of the metal ions onto the homogeneous adsorbent surface at constant temperature (Abdelfattah et al., 2016):

$$q_e = \frac{q_{\max} K_l C_e}{1 + K_l C_e} \quad (3)$$

where:  $q_e$  – the uptake capacity of the adsorbent metal (mg/g);  
 $q_{\max}$  – the maximum metal ion uptake capacity;  
 $K_l$  – the Langmuir constant (L/mg) that represents the affinity of metal ions to adsorbent;  
 $C_e$  – the metal ion concentrations (mg/L) when reached equilibrium.

The Freundlich isotherm expresses the multilayer adsorption of metal ions onto the reactive sites of the heterogeneous adsorbent surface. The Freundlich isotherm model can express as follows (Barquilha et al., 2017):

$$q_e = K_f \cdot C_e^{1/n} \quad (4)$$

where:  $K_f$  – the Freundlich constant at equilibrium (mg/g). (L/mg)<sup>1/n</sup>;  
 $n$  – the Freundlich constant of the bio-adsorption intensity.

## Kinetic study

The following equation that represents the pseudo-first-order model proposed by Lagergren, is describes that the rate of adsorption onto the occupied sites is proportional to a number of unoccupied sites (Tounsadi et al., 2015), in addition, this kinetic model works only when the adsorption occurs rapidly:

$$q_t = q_e(1 - \exp(-k_1 t)) \quad (5)$$

where:  $q_t$  (mg/g) – the adsorption capacity at time  $t$ ;  
 $q_e$  (mg/g) – the adsorption capacity at equilibrium;  
 $k_1$  – the constant of the 1<sup>st</sup> order kinetic (min<sup>-1</sup>).

The pseudo-second order kinetic which occurred in the solid phase and referred to that the adsorption capacity is based on the available adsorbent active surface site and can be expressed as follows (Vijayaraghavan et al., 2017):

$$q_t = \frac{q_e^2 k_2 t}{1 + q_e k_2 t} \quad (6)$$

where:  $k_2$  – the constant of the 2<sup>nd</sup> order kinetic (g.mg<sup>-1</sup>.min<sup>-1</sup>).

## RESULT AND DISCUSSION

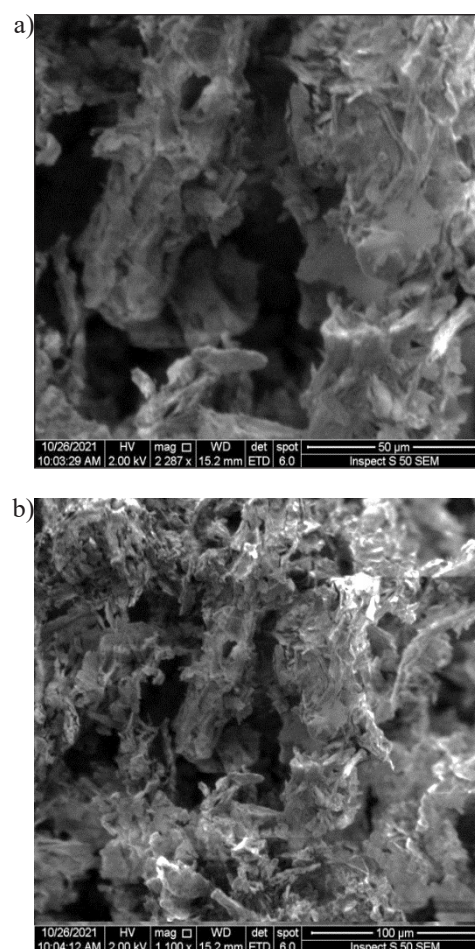
### Characterization of activated peanut shell

The images of the SEM for KOH-activated peanut shell are shown in Figure 1. It can be seen that a rougher, irregular and rigid surface with porous structure was observed in comparison to the inactivated peanut shell. The activation of peanut shell by KOH enhanced the formation of peanut shell porous structure surface which made it capable of adsorbing the metal ions from their solutions onto its accessible surface active sites and also promoting the metal ions diffusion onto adsorbent surface (Dotto et al., 2014). In addition, increasing the temperature of carbonization also played an important role in the formation of cleaner and smoother pore size via completely removing the residues that were generated from the carbonization process (Nazir et al., 2021).

The FTIR spectrum for the activated peanut shell is presented in Figure 2. The broad peak at 3385 cm<sup>-1</sup> was assigned to stretching vibrations

of the O–H groups with intra-molecular hydrogen bonds of the cellulose stretching (Huo et al., 2013). The band at 2970 cm<sup>-1</sup> was assigned to C–H stretching vibration of alkyl groups (Iqbal et al., 2009). The band at 1637 cm<sup>-1</sup> represents the C=O stretching of carboxylic acid in hemicelluloses, lignin or and pectin (Adiana & Mazura, 2011). The peak of 1404 cm<sup>-1</sup> corresponds to the C–C stretching vibration (Georgin et al., 2016). The peak at 1001 cm<sup>-1</sup> was assigned to stretching C–O bond in alcohols or ethers. The peaks at 701 cm<sup>-1</sup> and 833 cm<sup>-1</sup> were attributed to C–H stretching vibration.

The X-ray diffraction (XRD) test showed that the activated peanut shell contains an amorphous phase for hemicelluloses, lignin and also pectin (Fig. 3). The cellulose is the only substance that represents a crystalline phase which is represented by its peaks at: 22.4°, 24.4°, 30.6° and 31.8°  $2\theta$ , meaning that the peanut shell is mainly composed from cellulose.



**Figure 1.** SEM images for KOH-activated peanut shell

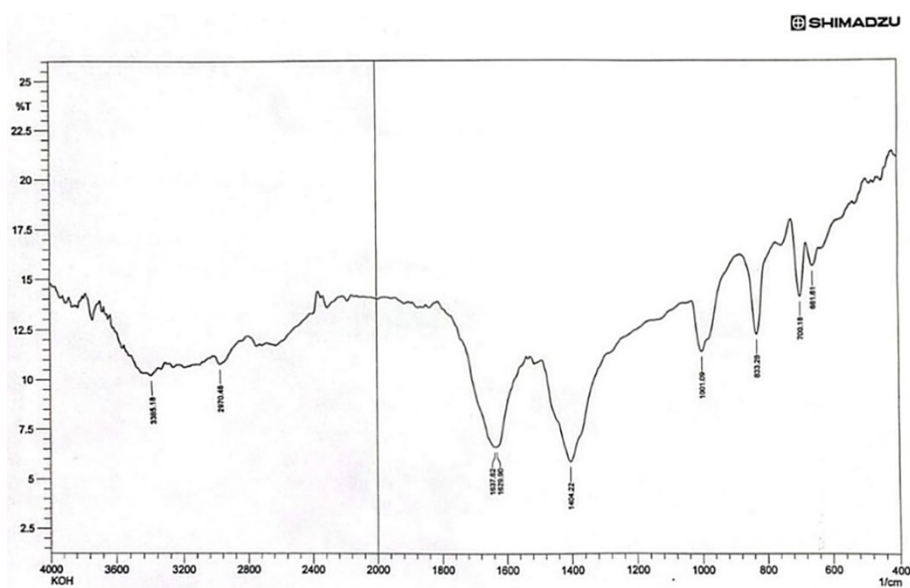


Figure 2. FTIR spectra of activated peanut shells

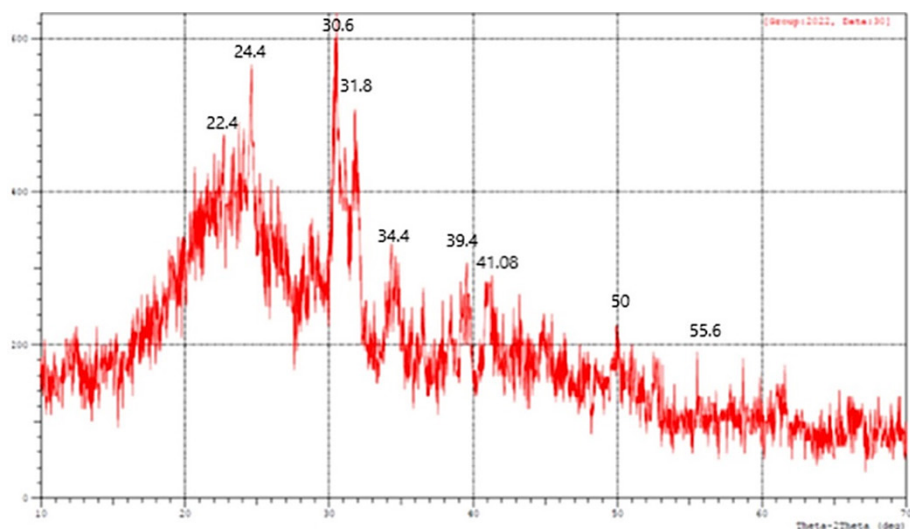


Figure 3. XRD analysis for the activated peanut shells

Table 1. Textural properties of the activated peanut shells

Type of peanut shells	Surface area (m <sup>2</sup> /g)	V <sub>total</sub> (cm <sup>3</sup> /g)	V <sub>micro</sub> (cm <sup>3</sup> /g)	Pore size (nm)
Normal peanut shells	2.884	0.004948	0.000593	34.47
KOH-activated peanut shells	349.2	0.222801	0.180	3.85

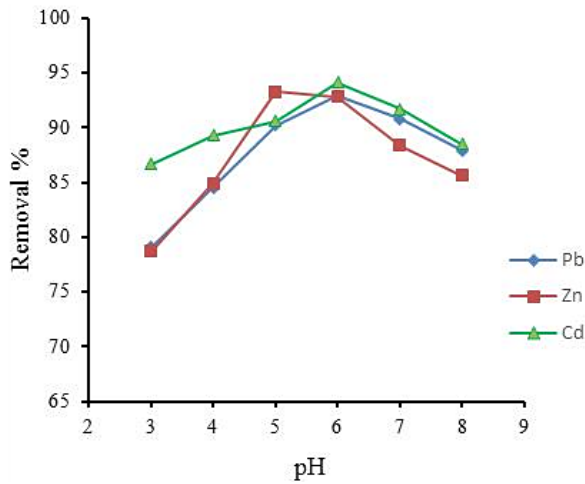
The textural properties of the activated peanut shell are shown in Table 1. It can be seen that the KOH activated peanut shell had a highly BET value and a highest micro pores volume and total pore volume, compared to unactivated peanut shell. This result actually confirmed mesoporous nature and the high peanut shell surface density as a result of its highly surface area. The porosity of the peanut shell surface promotes the binding of the metal ions onto the active sites and therefore makes it as an efficient adsorbent.

### Factors affecting the efficiency of metal ions adsorption

The adsorption of the studied metal ions onto the surface of KOH-activated peanut shell was affected by various factors such as:

#### pH value

The effect of pH values (3 – 8) on the efficiency of the adsorption process are presented

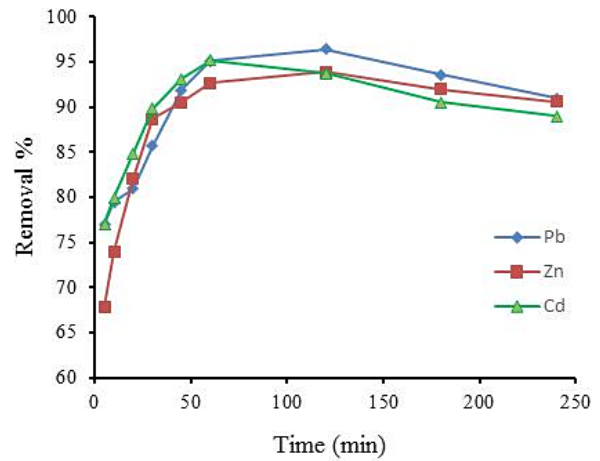


**Figure 4.** Effect of pH on metal ion adsorption

in Figure 4. It can be seen that the percentage of metal ions removal was increased by increasing the value of solution pH from 4 to 6. The maximum values for the adsorption capacities were achieved at pH 6. Afterwards, the adsorption efficiency for metal ions removal was decreased with the increasing pH value. These results can be explained based on the fact of that the protonation of the active functional groups such as carboxyl as well as amino groups is altered by the solution pH. It is well known that at lower pH, the concentration of protons increased and take place on the peanut shell surface which subsequently increased the competition between metal ions and protons onto the available active sites of peanut shell surface causing an increase in the remaining free metal ions in the solution (Witek-Krowiak et al., 2011). On the other hand, when pH increased, the metal ions will precipitate as a result of hydroxyl anion, increasing in the solution which reduces the removal percentage of the studied ions (Aryee et al., 2021). Therefore, the pH value was adjusted at 5 to 6 not higher. These results were consistent with many researchers (Zanin et al., 2017), reported that when pH solution increased up to 5, the reduction of Cu concentration was also increased. In the same trend (Nageeb Rashed et al., 2016), found that the adsorption of the methylene blue by activated carbon increased along with the pH.

### Contact time

The data that obtained from the removal of the studied metal ions by activated peanut shell at



**Figure 5.** Effect of contact time on metal ion adsorption

various contact times (5 – 240 min) at optimum pH is presented in Figure 5.

It can be seen that the removal percent increased along with contact time from 5 to 60 min, and then it remained constant or decreased gradually with the increasing of contact time. At the initial stages of contact time, the removal of the studied metal ions happened rapidly, which might be attributed to the availability of a large amount of active sites that enhance the removal percentage of the metal ions onto the adsorbent surface (Abo-El-Enein et al., 2017). In contrast, when the contact time increased, the remaining active sites as well as the uncovered surface area decreased. Therefore, according to obtained data, 60min of contact time was the best time to reach the maximum adsorption of metal ions onto the activated peanut shell surface where the removal percent was up to 95%.

### Initial metal ion concentrations

The data of the effects of the different metal concentrations (5–100 mg/l) on the adsorption efficiency of the activated peanut shell is shown in Figure 6. The obtained results showed that the removal percentage for the studied metal ions increased along the initial metal concentrations from 5 to 40 mg/l. These results can be explained depending on the fact of that the increasing of the metal concentration caused an increase in the adsorption efficiency. This can be explained by the fact that at higher concentration, the metal ion molecules occupied more active binding sites (Georgin et al., 2016). The removal rate for Zn, Pb and Cd ranged from 95–97%, which

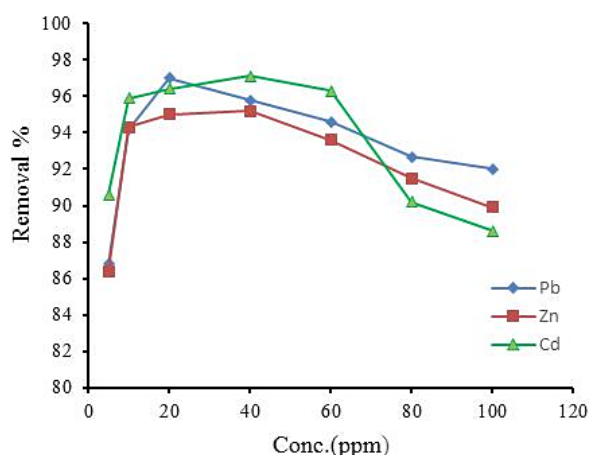


Figure 6. Effect of initial concentrations on metal ion adsorption

reached the maximum capacity when the initial metal ion concentrations was 20 mg/l for Zn and Pb and 40 mg/l for Cd. Afterwards, the removal percent of the metal ions decreases considerably. Therefore, the optimum initial concentration of 20 and 40 mg/l was chosen to be the optimum concentrations.

### Adsorbent dose

The amount of adsorbent is responsible for the number of the available active sites on adsorbent surface. For this reason, the effect of the activated peanut shell dose was studied at optimum pH, contact time and initial concentration of metal ions value by varying the dosage of activated peanut shell from 0.5 to 4 g. The removal efficiency of the different adsorbent doses was presented in Figure 7. The results showed that the best removal percentage was observed with using 2 g of activated peanut shell. This result is attributed to

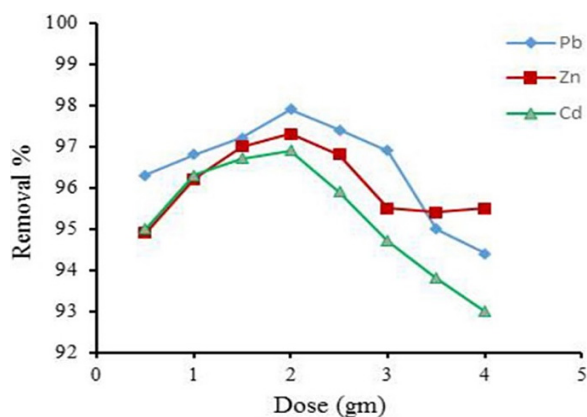


Figure 7. Effect of Adsorbent dose on metal ion adsorption

the increasing of the potential active binding sites with the increase of the adsorbent dose (Garg et al., 2019). The decrease of the removal efficiency with adsorbent dose higher than 2.5 g can be attributed to the increasing of the covered active sites by metal ions which subsequently cause a loading in adsorbent capacity. Therefore, the optimum adsorbent was chosen to be 2 g for the next adsorption experiment.

### Temperature

The effect of temperature on removal percentage of the metal ions by activated peanut shell at different temperatures (25–60 °C) with optimum experimental conditions is presented in Figure 8. The results showed that the varying of temperature was affected the adsorption efficiency. With the increase of temperature from 25–45 °C, the removal percent was also increased, and then it decreased gradually. The decrease of the metal ions removal percent with increasing of temperature can be attributed to the weakness of the adsorptive forces between metal ions and the active sites onto peanut shell surface. On the other hand (Isawi, 2020; Mohammed & Kareem, 2019), reported that the increasing of temperature will increase the viscosity of the solution resulting in low metal ions movements which finally reduce the adsorption efficiency. From the obtained results, 45 °C was chosen as a best temperature for the adsorption of metal ions.

### Adsorption isotherm and kinetic studies

The study of the adsorption isotherm provides important information about the relationship between the mass of the studied metal ions per unit

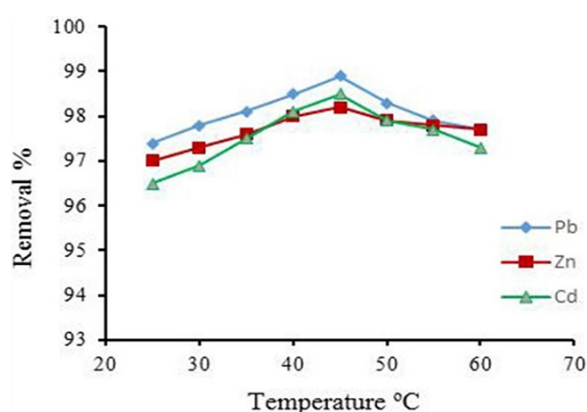


Figure 8. Effect of temperature on metal ion adsorption

mass of the adsorbent as well as the metal ion concentrations in the solution when reached equilibrium.

In this work, two well-known adsorption isotherm models named Langmuir and Freundlich were chosen to fit the obtained experimental data that related to the sorption of the metal ions onto peanut shell using Origin Pro 8 software. The higher correlation coefficient ( $R^2$ ) as well as the lower error values can be used to determine the best fitted isotherm model.

The values of the isotherm data for the Langmuir and Freundlich models were calculated by nonlinear regression as shown in Figure 9, whereas the other related constants were presented in Table 2.

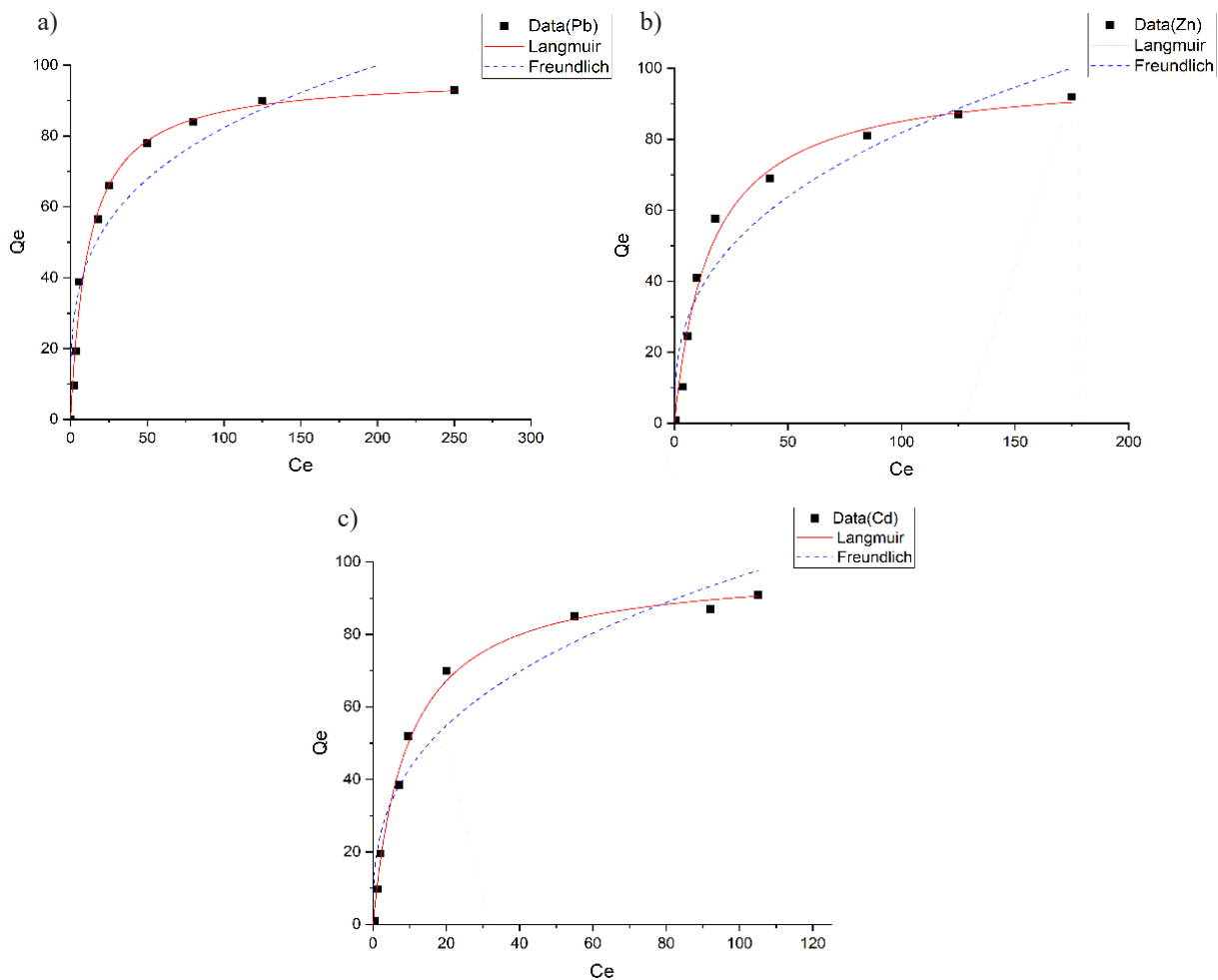
The data that were obtained from the Langmuir model showed a higher correlation coefficient with a value of  $R^2$  which ranged from 0.989 to 0.994 for the studied metal ions as compared to that obtained from the Freundlich model which ranged from 0.873 to 0.917.

The separation factor  $R_L$  that represents the adsorption modes can be expressed as: when  $R_L =$

0, the adsorption is irreversible, when  $R_L = 1$ , the adsorption is linear, the adsorption is favorable when  $0 < R_L < 1$ , whereas adsorption is unfavorable when  $R_L > 1$ . The obtained  $R_L$  values for the studied metal ions were ranged from 0.016 to 0.76 which indicates that the adsorption of Zn, Pb and Cd onto the surface of the activated peanut shell were favorable.

The  $n$  value that represents the intensity of the metals adsorption in Freundlich equation can be expressed as follows: when  $n > 1$ , the adsorption process is physical,  $n = 1$  is linear, and when  $n < 1$  the adsorption is chemical. The presented results in Table 2, showed that the  $n$  value was  $> 1$ , indicating that the adsorption process of the metal ions onto peanut shell surface was physical adsorption.

The value of  $q_{\max}$  obtained from Langmuir was close to experimental data  $q_{\text{exp}}$ . In addition, the value of SSE (sum of the squared errors) that obtained from Langmuir model was lower than that obtained by the Freundlich model.



**Figure 9.** Adsorption isotherm models of Langmuir and Freundlich for (a) Pb, (b) Zn, (c) Cd

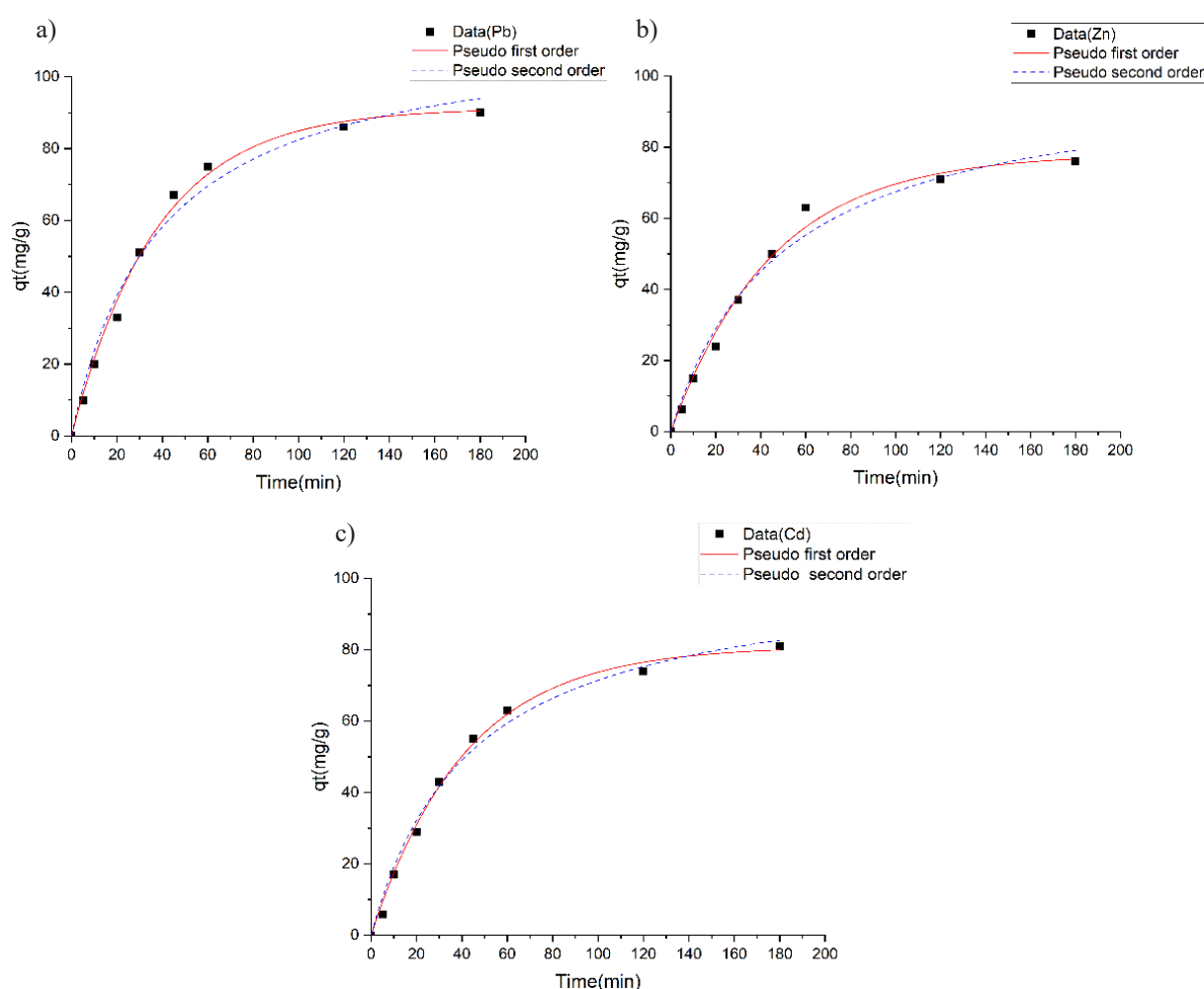


**Table 2.** Adsorption isotherm values for metal ions

KOH-activated peanut shells Metals	Langmuir				Freundlich		
	R <sup>2</sup>	K <sub>L</sub>	q <sub>exp.</sub>	q <sub>max.</sub>	R <sup>2</sup>	K <sub>F</sub>	n
Pb	0.990	0.085	91.16	87.11	0.873	22.739	2.793
Zn	0.989	0.062	90.55	88.73	0.917	15.655	3.591
Cd	0.994	0.106	90.00	88.64	0.917	19.306	3.482

According to the above results, the higher R<sup>2</sup> value, the small difference between q<sub>exp</sub> and q<sub>m</sub>, and the lower SSE values, makes the Langmuir model as the best fitted isotherm model for metal ions adsorption onto the activated peanut shell surface in comparison to Freundlich model.

To assess the rate of adsorption, the adsorption constants as well as the mechanism of the metal ions sorption onto peanut shell, the obtained data was fitted to two different kinetic models: pseudo-first order and pseudo-second order (Fig. 10). The correlation coefficient (R<sup>2</sup>) and the kinetic



**Figure 10.** Adsorption kinetic for (a) Pb, (b) Zn, (c) Cd

**Table 3.** Adsorption kinetic values for metal ion

KOH-activated peanut shells Metals	Pseudo first order			Pseudo second order		
	R <sup>2</sup>	K <sub>1</sub>	q <sub>e</sub>	R <sup>2</sup>	K <sub>2</sub>	q <sub>e</sub>
Pb	0.995	0.026	91.244	0.985	2.282	87.0389
Zn	0.991	0.022	78.056	0.982	1.999	75.91323
Cd	0.996	0.024	80.933	0.989	2.215	79.80685

**Table 4.** Effect of various concentration of ion strength on removal of metal ions

KOH-activated Peanut shells	PO <sub>4</sub>				SO <sub>4</sub>			NO <sub>3</sub>		
	Optimum condition	5mg/l	10 mg/l	20mg/l	5mg/l	10mg/l	20mg/l	5mg/l	10mg/l	20mg/l
Pb	96	94.6	92.2	82.3	96	93.5	89.7	96.3	94.7	90.8
Zn	98.3	98	96.3	83.5	98.1	97.2	87.7	98.1	97.4	89.6
Cd	97.8	95.4	94	81.2	96.9	95.6	88.3	97.2	94.7	90.8

constants that determined by using nonlinear regression were presented in Table 3.

From the fitting results, a good agreement has been observed between the proposed model and the experimental data for the studied metal ions. It can be seen that the obtained data was fitted better with the pseudo-first order kinetic than the pseudo-second order kinetic with a correlation coefficient ( $R^2$ ) > 0.99 which revealed a good applicability of the first-order kinetic for the adsorption of the metal ions using activated peanut shells.

### Effect of ionic strength

The presence of co-ions in water or in soil solutions may influence the metal ions adsorption efficiency. The effect of the ionic strength of different competitive ions such as PO<sub>4</sub><sup>3-</sup>, SO<sub>4</sub><sup>2-</sup> and NO<sub>3</sub><sup>-</sup> on the sorption ability of the Zn<sup>2+</sup>, Pb<sup>2+</sup> and Cd<sup>2+</sup> onto activated peanut shell surface is presented in Table 4. The results showed that the removal percentage of the metal ions decreased with the increasing of ionic strength from 5 to 20 mg/l and following the order PO<sub>4</sub><sup>3-</sup> > SO<sub>4</sub><sup>2-</sup> > NO<sub>3</sub><sup>-</sup>. No significant differences were observed with ionic strength of 5 mg/l, whereas, a significant decrease was observed with 20mg/l. (Yang et al., 2021), also reported that the increasing of the ionic strength reduced the adsorption capacity of Cd<sup>2+</sup> on biochar. The ionic strength is an important factor that affects the affinity between the aqueous phase and solutes which subsequently affect the equilibrium of the aqueous phase (Ahmaruzzaman, 2011). The ionic strength can affect the interface potential, as well as the double layer thickness between the metal ions solution and peanut shell surface and therefore limit the binding of metal ions with adsorbents (Li et al., 2012). The presence of some inorganic ions such as phosphate, sulfate and chloride in the aqueous solution will compete with the adsorbent to form complexes with metal ions and therefore reduce the removal percentage of adsorption by the current adsorbent (Gan, 2000; Weng & Huang, 2004).

### CONCLUSIONS

This work examined the potential and the efficiency of the available, natural and low cost peanut shells for the removal of Zn, Pb and Cd from wastewater.

The carbonization of peanut shell at 550 °C as well as the KOH-activation increased the S<sub>BET</sub> (349.2 m<sup>2</sup>/g) and also enhanced the availability of the active functional groups that contribute to adsorption of metal ions onto the adsorbent surface. The metal ions bio sorption was significantly affected by different parameters such as pH, adsorbent dose, metal concentrations, contact time and temperature. The adsorption isotherm models that were used in this study to describe the adsorption equilibrium showed that the maximum adsorption capacities were observed with the Langmuir model compared to the Freundlich model. The kinetic experiment for the metal ions adsorption followed the pseudo-first order model. The comparison of the obtained results from this work with the other reported results in the literature indicated that the carbonization as well as KOH-activation of peanut shells exhibits a good adsorption for the studied metal ions.

### REFERENCES

1. Abdelfattah, I., Ismail, A.A., Sayed, F.A., Almedolab, A., Aboelghait, K.M. 2016. Biosorption of heavy metals ions in real industrial wastewater using peanut husk as efficient and cost effective adsorbent. *Environmental Nanotechnology, Monitoring and Management*, 6, 176–183. <https://doi.org/10.1016/j.enmm.2016.10.007>
2. Abo-El-Enein, S.A., Shebl, A., Abo El-Dahab, S.A. 2017. Drinking water treatment sludge as an efficient adsorbent for heavy metals removal. *Applied Clay Science*, 146(May), 343–349. <https://doi.org/10.1016/j.clay.2017.06.027>
3. Adiana, M.A., Mazura, M.P. 2011. Study on *Senna alata* and its different extracts by Fourier

- transform infrared spectroscopy and two-dimensional correlation infrared spectroscopy. *Journal of Molecular Structure*, 991(1–3), 84–91. <https://doi.org/10.1016/j.molstruc.2011.02.005>
4. Ahmaruzzaman, M. 2011. Industrial wastes as low-cost potential adsorbents for the treatment of wastewater laden with heavy metals. *Advances in Colloid and Interface Science*, 166(1–2), 36–59. <https://doi.org/10.1016/j.cis.2011.04.005>
  5. Jadir, T.M., Siperstein, F.R. 2018. The influence of the pore size in Metal–Organic Frameworks in adsorption and separation of hydrogen sulphide: A molecular simulation study. *Microporous and Mesoporous Materials*, 271, 160–168. <https://doi.org/10.1016/j.micromeso.2018.06.002>
  6. AL-Othman, Z.A., Ali, R., Naushad, M. 2012. Hexavalent chromium removal from aqueous medium by activated carbon prepared from peanut shell: Adsorption kinetics, equilibrium and thermodynamic studies. *Chemical Engineering Journal*, 184, 238–247. <https://doi.org/10.1016/j.cej.2012.01.048>
  7. Aryee, A.A., Mpatani, F.M., Du, Y., Kani, A.N., Dovi, E., Han, R., Li, Z., Qu, L. 2021. Fe<sub>3</sub>O<sub>4</sub> and iminodiacetic acid modified peanut husk as a novel adsorbent for the uptake of Cu (II) and Pb (II) in aqueous solution: Characterization, equilibrium and kinetic study. *Environmental Pollution*, 268, 115729. <https://doi.org/10.1016/j.envpol.2020.115729>
  8. Ashrafi, S.D., Kamani, H., Soheil Arezomand, H., Yousefi, N., Mahvi, A.H. 2016. Optimization and modeling of process variables for adsorption of Basic Blue 41 on NaOH-modified rice husk using response surface methodology. *Desalination and Water Treatment*, 57(30), 14051–14059. <https://doi.org/10.1080/19443994.2015.1060903>
  9. Barquilha, C.E.R., Cossich, E.S., Tavares, C.R.G., Silva, E.A. 2017. Biosorption of nickel(II) and copper(II) ions in batch and fixed-bed columns by free and immobilized marine algae *Sargassum* sp. *Journal of Cleaner Production*, 150, 58–64. <https://doi.org/10.1016/j.jclepro.2017.02.199>
  10. Crini, G., Lichtfouse, E. 2019. Advantages and disadvantages of techniques used for wastewater treatment. *Environmental Chemistry Letters*, 17(1), 145–155. <https://doi.org/10.1007/s10311-018-0785-9>
  11. Dong, Q., Guo, X., Huang, X., Liu, L., Tallon, R., Taylor, B., Chen, J. 2019. Selective removal of lead ions through capacitive deionization: Role of ion-exchange membrane. *Chemical Engineering Journal*, 361, 1535–1542. <https://doi.org/10.1016/j.cej.2018.10.208>
  12. Dotto, G.L., Buriol, C., Pinto, L.A.A. 2014. Diffusional mass transfer model for the adsorption of food dyes on chitosan films. *Chemical Engineering Research and Design*, 92(11), 2324–2332. <https://doi.org/10.1016/j.cherd.2014.03.013>
  13. Esmacili, A., Aghababai Beni, A. 2015. Biosorption of nickel and cobalt from plant effluent by *Sargassum glaucescens* nanoparticles at new membrane reactor. *International Journal of Environmental Science and Technology*, 12(6), 2055–2064. <https://doi.org/10.1007/s13762-014-0744-3>
  14. Gan, Q. 2000. A case study of microwave processing of metal hydroxide sediment sludge from printed circuit board manufacturing wash water. *Waste Management*, 20(8), 695–701. [https://doi.org/10.1016/S0956-053X\(00\)00036-2](https://doi.org/10.1016/S0956-053X(00)00036-2)
  15. Garg, D., Kumar, S., Sharma, K., Majumder, C. B. 2019. Application of waste peanut shells to form activated carbon and its utilization for the removal of Acid Yellow 36 from wastewater. In *Groundwater for Sustainable Development*, Elsevier B.V., 8. <https://doi.org/10.1016/j.gsd.2019.01.010>
  16. Georgin, J., Dotto, G.L., Mazutti, M.A., Foletto, E.L. 2016. Preparation of activated carbon from peanut shell by conventional pyrolysis and microwave irradiation-pyrolysis to remove organic dyes from aqueous solutions. *Journal of Environmental Chemical Engineering*, 4(1), 266–275. <https://doi.org/10.1016/j.jece.2015.11.018>
  17. Khatoon H., Rai J.P.N. 2016. Agricultural Waste Materials As Biosorbents for the Removal. *Octa Journal of Environmental Research*, 4(3), 208–229. <http://www.sciencebeingjournal.com>
  18. Huang, H., Tang, J., Gao, K., He, R., Zhao, H., Werner, D. 2017. Characterization of KOH modified biochars from different pyrolysis temperatures and enhanced adsorption of antibiotics. *RSC Advances*, 7(24), 14640–14648. <https://doi.org/10.1039/c6ra27881g>
  19. Huang, L., Chen, B., Pistolozzi, M., Wu, Z., Wang, J. 2014. Inoculation and alkali coeffect in volatile fatty acids production and microbial community shift in the anaerobic fermentation of waste activated sludge. *Bioresource Technology*, 153, 87–94. <https://doi.org/10.1016/j.biortech.2013.11.049>
  20. Huo, S., Ulven, C. A., Wang, H., Wang, X. 2013. Chemical and mechanical properties studies of chinese linen flax and its composites. *Polymers and Polymer Composites*, 21(5), 275–286. <https://doi.org/10.1177/096739111302100502>
  21. Iqbal, M., Saeed, A., Zafar, S.I. 2009. FTIR spectrophotometry, kinetics and adsorption isotherms modeling, ion exchange, and EDX analysis for understanding the mechanism of Cd<sup>2+</sup> and Pb<sup>2+</sup> removal by mango peel waste. *Journal of Hazardous Materials*, 164(1), 161–171. <https://doi.org/10.1016/j.jhazmat.2008.07.141>
  22. Isawi, H. 2020. Using Zeolite/Polyvinyl alcohol/sodium alginate nanocomposite beads for removal of some heavy metals from wastewater. *Arabian Journal of Chemistry*, 13(6), 5691–5716. <https://doi.org/10.1016/j.arabjc.2020.04.009>

23. Jauberty, L., Villandier, N., Chaleix, V., Gloaguen, V. 2017. Removal of cesium ion from contaminated water: Improvement of Douglas fir bark biosorption by a combination of nickel hexacyanoferrate impregnation and TEMPO oxidation. *Ecological Engineering*, 100, 186–193. <https://doi.org/10.1016/j.ecoleng.2016.12.012>
24. Karim, M.R., Aijaz, M.O., Alharth, N.H., Alharbi, H.F., Al-Mubaddel, F.S., Awual, M.R. 2019. Composite nanofibers membranes of poly(vinyl alcohol)/chitosan for selective lead(II) and cadmium(II) ions removal from wastewater. *Ecotoxicology and Environmental Safety*, 169 July 2018, 479–486. <https://doi.org/10.1016/j.ecoenv.2018.11.049>
25. Li, J., Zhang, S., Chen, C., Zhao, G., Yang, X., Li, J., Wang, X. 2012. Removal of Cu(II) and fulvic acid by graphene oxide nanosheets decorated with Fe<sub>3</sub>O<sub>4</sub> nanoparticles. *ACS Applied Materials and Interfaces*, 4(9), 4991–5000. <https://doi.org/10.1021/am301358b>
26. Liu, C., Wang, W., Wu, R., Liu, Y., Lin, X., Kan, H., Zheng, Y. 2020. Preparation of Acid- And Alkali-Modified Biochar for Removal of Methylene Blue Pigment. *ACS Omega*, 5(48), 30906–30922. <https://doi.org/10.1021/acsomega.0c03688>
27. Mohammed, A.A., Kareem, S.L. 2019. Adsorption of tetracycline from wastewater by using Pistachio shell coated with ZnO nanoparticles: Equilibrium, kinetic and isotherm studies. *Alexandria Engineering Journal*, 58(3), 917–928. <https://doi.org/10.1016/j.aej.2019.08.006>
28. Nageeb Rashed, M., El-Daim El Taher, M.A., Fadlalla, S.M.M. 2016. Adsorption of methylene blue using modified adsorbents from drinking water treatment sludge. *Water Science and Technology*, 74(8), 1885–1898. <https://doi.org/10.2166/wst.2016.377>
29. Nam, H., Wang, S., Jeong, H.R. 2018. TMA and H<sub>2</sub>S gas removals using metal loaded on rice husk activated carbon for indoor air purification. *Fuel*, 213, 186–194. <https://doi.org/10.1016/j.fuel.2017.10.089>
30. Nazir, A., Um-E-laila, Firdaus-E-bareen, Hameed, E., Shafiq, M. 2021. Sustainable management of peanut shell through biochar and its application as soil ameliorant. *Sustainability (Switzerland)*, 13(24). <https://doi.org/10.3390/su132413796>
31. Peng, L., Shang, Y., Gao, B., Xu, X. 2021. Co<sub>3</sub>O<sub>4</sub> anchored in N, S heteroatom co-doped porous carbons for degradation of organic contaminant: role of pyridinic N-Co binding and high tolerance of chloride. *Applied Catalysis B: Environmental*, 282(August), 119484. <https://doi.org/10.1016/j.apcatb.2020.119484>
32. Qasim, B., Razzak, A.A., Rasheed, R. T. 2021. Effect of biochar amendment on mobility and plant uptake of Zn, Pb and Cd in contaminated soil. *IOP Conference Series: Earth and Environmental Science*, 779(1). <https://doi.org/10.1088/1755-1315/779/1/012082>
33. Shakor, Z.M., Mahdi, H.H., Al-Sheikh, F., Alwan, G.M., Al-Jadir, T. 2021. Ni, Cu, and Zn metal ions removal from synthetic wastewater using a watermelon rind (*Catullus landaus*). *Materials Today: Proceedings*, 42, 2502–2509. <https://doi.org/10.1016/j.matpr.2020.12.570>
34. Thompson, K.A., Shimabuku, K.K., Kearns, J.P., Knappe, D.R.U., Summers, R.S., Cook, S.M. 2016. Environmental Comparison of Biochar and Activated Carbon for Tertiary Wastewater Treatment. *Environmental Science and Technology*, 50(20), 11253–11262. <https://doi.org/10.1021/acs.est.6b03239>
35. Tounsadi, H., Khalidi, A., Abdennouri, M., Barka, N. 2015. Biosorption potential of *Diplotaxis harra* and *Glebionis coronaria* L. biomasses for the removal of Cd(II) and Co(II) from aqueous solutions. *Journal of Environmental Chemical Engineering*, 3(2), 822–830. <https://doi.org/10.1016/j.jece.2015.03.022>
36. Vijayaraghavan, K., Rangabhashiyam, S., Ashokkumar, T., Arockiaraj, J. 2017. Assessment of samarium biosorption from aqueous solution by brown macroalga *Turbinaria conoides*. *Journal of the Taiwan Institute of Chemical Engineers*, 74, 113–120. <https://doi.org/10.1016/j.jtice.2017.02.003>
37. Wang, S., Nam, H., Nam, H. 2019. Utilization of cocoa activated carbon for trimethylamine and hydrogen sulfide gas removals in a confined space and its techno-economic analysis and life-cycle analysis. *Environmental Progress and Sustainable Energy*, 38(6), 0–17. <https://doi.org/10.1002/ep.13241>
38. Wang, S., Nam, H., Nam, H. 2020. Preparation of activated carbon from peanut shell with KOH activation and its application for H<sub>2</sub>S adsorption in confined space. *Journal of Environmental Chemical Engineering*, 8(2), 103683. <https://doi.org/10.1016/j.jece.2020.103683>
39. Weng, C.H., Huang, C.P. 2004. Adsorption characteristics of Zn(II) from dilute aqueous solution by fly ash. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 247(1–3), 137–143. <https://doi.org/10.1016/j.colsurfa.2004.08.050>
40. Witek-Krowiak, A. 2013. Application of beech sawdust for removal of heavy metals from water: Biosorption and desorption studies. *European Journal of Wood and Wood Products*, 71(2), 227–236. <https://doi.org/10.1007/s00107-013-0673-8>
41. Witek-Krowiak, A., Szafran, R.G., Modelski, S. 2011. Biosorption of heavy metals from aqueous solutions onto peanut shell as a low-cost biosorbent.

- Desalination, 265(1–3), 126–134. <https://doi.org/10.1016/j.desal.2010.07.042>
42. Tingting, Y., Xu, Y., Huang, Q., Sun, Y., Liang, X., Wang, L., Qin, X., Zhao, L. 2021. Adsorption characteristics and the removal mechanism of two novel Fe-Zn composite modified biochar for Cd(II) in water. *Bioresource Technology*, 333(March), 125078. <https://doi.org/10.1016/j.biortech.2021.125078>
43. Zanin, E., Scapinello, J., de Oliveira, M., Rambo, C.L., Franscescon, F., Freitas, L., de Mello, J.M. M., Fiori, M.A., Oliveira, J.V., Dal Magro, J. 2017. Adsorption of heavy metals from wastewater graphic industry using clinoptilolite zeolite as adsorbent. *Process Safety and Environmental Protection*, 105, 194–200. <https://doi.org/10.1016/j.psep.2016.11.008>