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ADSORPTION OF HEAVY METALS FROM AQUEOUS SOLUTION USING PALM TREE POLLEN SHELLS AS LOW COST ADSORBENT

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Abstract

In the present study, factors influencing the adsorption of Pb (II), Ni (II) & Cd (II) from aqueous solution by pollen shells have been investigated at 30 ± 1 ◦C. Two techniques of adsorption were used; batch adsorption and continuing adsorption. The optimum results obtained from the first technique (600 µm for adsorbent and 7 pH) were used in the continuing adsorption tests. Highest adsorption occurred after passing the ionized water through the adsorption column filled with 20 cm of adsorbent materials for 30 min.

The study also showed that palm tree pollen shells can be used efficiently as an affordable adsorbent to remove heavy metal ions.

Keywords: Adsorption, heavy metals, pollen shells.

1. Introduction

Although the important inventions have changed industrial methods from manual production to machinery and led to increasing productivity, there are many negative impacts of that on the health of people and the environment. Increasing metals ions are considered one of the essential sources of water pollution. In fact, the common heavy metal contaminants such as cadmium, lead and nickel are becoming more prominent due to their routes of exposure and their toxic implications (Jaishankar et al., 2014). Many investigations have done to evaluate the concentrations of heavy metals in water sources, and a wide effort has spent to maintain their concentrations within acceptable standards to avoid the negative consequences such as the health problems for human and threat natural growth of flora and fauna (Nurchi and Villaescusa, 2008).

Among different methods that use in reducing the concentrations of heavy metals ions in aqueous effluents such as precipitation, flocculation, ion-exchange and filtration, adsorption techniques have become more important and popular due to their efficiency in the removal of pollutants and the possibility of using cheap materials as adsorbents. Some effective parameters such as adsorbent dosage, particle size, contact time and pH are very important in the adsorption process.

To explain that, Dowlatshahi *et al.* (2014) studied the effect of varying pH and the weight of adsorbent on the percentage of removal of heavy metal ions (cadmium and lead) from aqueous solution. The findings confirmed that the removal of metal ions increases with increasing pH up to 7 and decreases in the basicity medium. The optimum amount of adsorbent was 0.6 g, and the optimum contact times were 45 min for cadmium ions and 90 min for lead ion. In these optimum conditions, the removal efficiencies were 91.25% and 97.5%, respectively. On the other hand Dehghani et al. (2014) studied the ability of cotton stalks to remove Ni (II) from wastewater. The crude biomass was activated by sodium dodecyl sulfate. The findings showed removing more than 90% of nickel ions from the wastewater under these conditions (pH, 7.0; biomass dose, 0.5 g/100 mL; contact time, 120 min). Using adsorption column filled partially with activated carbon derived from palm date pits, Esmael et al. (2014a) studied the removal of three heavy metals: copper, hexavalent chromium, and iron from industrial wastewater samples collected from a tannery and an electroplating factory. The study showed that the heavy metals were adsorbed very rapidly within the first 30 min, while equilibrium was attained within 90 min, the optimum pH range for their adsorption was found to be (4.5-6.5), depth of adsorbent layer (70-90) cm, and particle size (0.5-0.75) mm.

This study is designed to provide information on the use of palm tree pollen shell as an adsorbent to remove Pb (II), Ni (II) and Cd (II) from aqueous solutions and evaluate the influence of contact time, depth of adsorbent layer, particle size and pH of aqueous solution on the batch and dynamic adsorption processes.

2. Material and Methods

2.1 Preparation of Adsorbent

Palm tree pollen shells were collected from Al Hartha district at the north-eastern of Basra, Iraq. The shells were cleaned using distilled water to eradicate possible strange materials (dirt and sands). Washed sample materials were sun-dried for 2-5 days and then crushed using a mill grinder to reduce the size, then washed several times with distilled water until a pH 7 was obtained. The adsorbents were then dried in an oven at 105 °C for 24 hr and then sieved to obtain the size of 212>, 400> and 600> µm (Al-Saeedi et al., 2019).

2.2 Preparation of Synthetic Solutions

The efficacy of the aqueous solutions of palm tree pollen shells as adsorbent was studied. The chemical materials were supplied by the University of Basrah. The metal solution used in this study were prepared as the stock solution containing 1000 ppm of each metal. It was then suitably diluted to the required initial concentrations of 10 ppm of Pb (II), Ni (II) and Cd (II), separately using deionized water (Tariq et al., 2018).

2.3 Batch Adsorption Experimental Studies

Metal investigations were conducted in the batch and continuous processes. The batch adsorption studies were conducted at various levels of process parameters of pH 2-8, metal ion concentration 10 ppm of each metal ions, particle size 213-600 µm. ZHICHENG analytical model thermal shaker was used for the batch experiments. The pH measurements were performed with LABQUEST2 analyser. The experiments were carried out by contacting precisely weighted samples of palm tree pollen shells powder (0.2, 0.5 & 1g) with 100 mL of Cd (II) or Pb (II) or Ni (II) solutions in the 250 ml leak proof corning reagent bottle. The initial pH of solutions was adjusted to the desired pH by adding 1 mol/L HCl or NaOH solutions. The suspensions were conducted on the shaker at a shaking speed of 150 rpm at 20 °C in triplicate. After the specified time (30 min), suspensions were passed through 0.45 µm pore size filters. The residual metal was determined by an atomic absorption spectrophotometer (Varian Model 202FS) (Al-Saeedi et al., 2019).

2.4 Column Adsorption System Set-up: Column Adsorption

Following the method that applied by Esmael et al. (2014b) to determine the dynamic adsorption capacity of an adsorbent under various conditions, a series of column adsorption experiments were performed in up-flow mode (expended bed) using palm tree pollen shells. A schematic diagram of the experimental model and process flow used in the study is shown in Figure 1. The model that modified to be more suitable to current work, it is composed of a column made of a PVC tube 0.65 m height and 0.5 inch inner diameter. At the bottom of the column, a fabric filter was placed. A known quantity powder of the pollen shells was packed in the column to yield the desired bed heights of the adsorbent, and then a fabric filter was placed on top of the bed. The samples of the effluent were collected at the outlet of the column at regular time intervals and the concentrations were measured. The samples were investigated after passing the ionized water through the adsorption column filled with 20 and 30 cm of adsorbent materials.

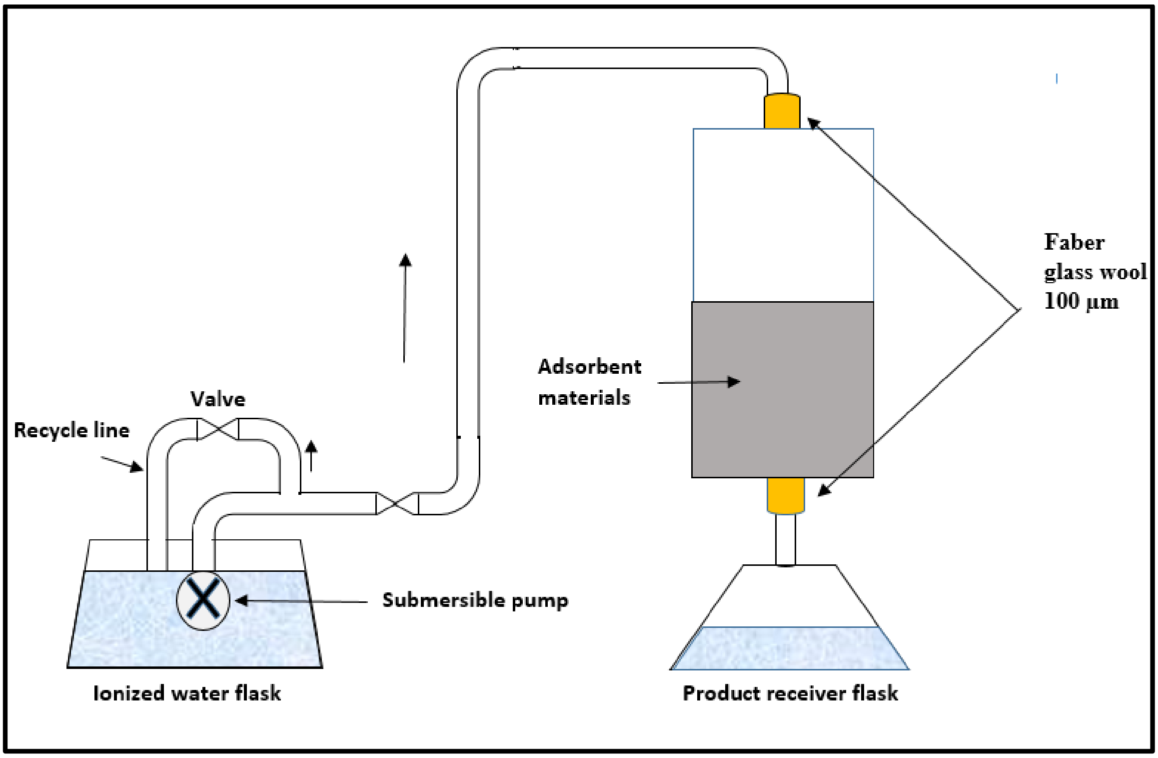

Figure 1: Experimental Setup.

2.4.1 Effect of Contact Time and Depth of Layer on the Dynamic Adsorption

To study the effect of contact time and depth of layer, pH and particle size values were fixed at the optimum values obtained from the first set of experiments (batch adsorption). The dynamic adsorption were conducted at two contact times 30 and 60 min with two depth of adsorbent layer 10 and 20 cm. The adsorbed quantities of the metal ions were calculated from the concentration of solutions before and after adsorption (batch and continuous) based on the equation (1) (Thilagavathy and Santhi, 2014).

$$Qe = (Co - Ce)\ V/W \qquad (1)$$

Where:

Qe: the equilibrium metal ions concentration on adsorbent (mg/g), Co: the initial concentration (mg/L), Ce: the equilibrium concentration (mg/L), V: the volume of aqueous solution (L), W: the weight of adsorbent (g).

3. Results and Discussion

3.1 Batch Adsorption

3.1.1 Effect of Size of the Adsorbent Particles on the Adsorption

The particle size of adsorbents is one of the key parameters for the selection of adsorbent in the adsorption process. The tests of removing Pb (II), Ni(II) & Cd (II) from aqueous solutions were performed using three particle sizes of adsorbents (212, 400 & 600 µm) under the specific conditions (0.5 g of adsorbent, initial pH of 7, contact time of 60 min, 150 rpm shaking speed and at room temperature of 30 ^{o}C).

The results are shown in Table (1) indicate that the pollen shell sample of the smallest particle size (212 µm) exhibited the highest capacity to adsorb metal ions. The removal percentage were 73.3, 49.2 and 92.4% for Pb (II), Ni (II) & Cd respectively, while the ions removal percentage decreased to 70.9, 47.6 & 90.3% with increasing the size of adsorbent up to 400 µm. The main reason of that is due to the fact that the adsorbents which have low particle size exhibit high surface area (Kannan and Rengasamy, 2005, Bo-Lin et al., 2012, Alshmery, 2013).

As a consequence, the saturation adsorption per unit mass of the adsorbent decreases. Moreover, Mondal (2008) confirmed that and referred that the diffusional resistance to mass transport is higher for larger particles, and most of the internal surface of the particle may not be utilized for adsorption. However, just one sample (600> µm) exhibited unexpectable result, the removal of Ni (II) ions increased up to 53.2% after using this size of adsorbent. The particle size 212> µm selected as the optimum adsorbent size to remove Pb, Ni & Cd metal ions in the work. Interestingly, the equilibrium concentration of all heavy metals ions (Q_e) in aqueous solution was less than 1.5 mg/L which represents the low potential of palm tree pollen shells in the adsorption of these ions.

Table 1: Effect of particle size on the percentage removal of heavy metal ions.

Ion	Particle size (mµ)	Ce (mg/L)	Qe (mg/L)	Removal % of the Ions
Pb(II)	212	2.67	1.47	73.3
	400	2.91	1.42	70.9
	600	3.13	1.37	68.7
Ni(II)	212	5.08	0.98	49.2
	400	5.24	0.95	47.6
	600	4.68	1.06	53.2
Cd(II)	212	0.76	0.19	92.4
	400	0.97	0.18	90.3
	600	1.62	0.17	83.8

3.1.2 Effect of pH on the Adsorption

The effect of pH of the aqueous solution on the efficiency of adsorbent was studied in this work from a range of 5 to 8 under the precise conditions (contact time of 60 min, 150 rpm shaking speed, with 0.2 g of the adsorbent, adsorbent particle size 212 µm, and at a room temperature of 30 ^{o}C). From Table (2), the percentage removal of Pb (II), Ni (II) & Cd (II) ions increased up to 73.3, 49.2 & 92.4% with increasing pH to 7. Actually, the most removal of metal ions was achieved even at pH is 5. This suggests that the competition between the H^+ ions and the metal ions to the adsorption sites (negative charges on the surface) did not affect significantly on the percentage of removing metal ions. These results are consistent with results obtained by Venkateswarlu *et al.* (2015) that explained the removal efficiency of metal ions increases gradually with increasing pH of the aqueous solution up to 7. However, this image has changed after increase the basicity of an aqueous solution. The removal of metal ions decreased to 64.7, 45.8 & 89.2 % for lead, nickel and cadmium, respectively with raising pH to 8 due to the inverse relationship between adsorption and ionic strength of the solution.

This study gives evidence that the removal of heavy metal ions is unfavourable with increasing basicity. It is noteworthy that Q_e value was less than 1.8 mg/L which represents non-high potential of palm tree pollen shells in the adsorption of these ions.

Table 2: Effect of pH on the percentage removal of heavy metal ions

Ion	pH	Ce (mg/L)	Qe (mg/L)	Removal % of the Ions
Pb(II)	5	3.48	1.30	65.2
	7	2.67	1.47	73.3
	8	3.53	1.29	64.7
Ni(II)	5	5.58	0.88	44.2
	7	5.08	0.98	49.2
	8	5.42	0.92	45.8
Cd(II)	5	1.22	1.76	87.8
	7	0.76	1.85	92.4
	8	1.08	1.78	89.2

3.2 Continuing Adsorption

Using 10 cm of the layer, the rate of uptake of metals was rapid; and during the first 30 minutes was 76.9%, 36.8% &83.7% for Pb, Ni& Cd respectively as shown in Table 3. The results were further illustrated in Fig. 2 for comparison.

Except the percentage removal of nickel ions using 20 cm of the layer of adsorbent and 60 min contact time, that increased about 13%, no big differences in the percentage removal of other ions were observed after increase the depth of the layer to 20 cm or/and the contact time to 60 min. As for the results of varying the depth of layer to 20 cm, the metal removal in 30 min was 81.0%, 45.3% & 88.2% for Pb, Ni & Cd respectively, and reached 83.4%, 57.9% and 92.5% for Pb, Ni & Cd at 60 min. Equilibrium was reached within 30 min for lead and cadmium with 81 % and 88.2% removal while the adsorbent required 60 min to reached equilibrium with nickel. Q_e values were very low and did not exceed 0.5 mg/L. Zayadi & Othman (2013) explained that the process of adsorption is effective at the beginning of the contact time because of the large number of active sites on the adsorbent surface, but after a certain time and with continuing the process of adsorption it will be difficult to occupy the remaining active sites. This phenomenon occurs because of the repulsive forces that reduce the effectiveness of the adsorbents during adsorption.

Table 3: Effect of contact time and depth of the adsorbent layer on the percentage removal of heavy metal ions

Run	Metal	Contact Time (min)	Depth of Layer (cm)	Ce (mg/L)	Qe (mg/L)	Removal % of the Ions
1	Pb	30	10	2.31	0.16	76.9
2		30	20	1.90	0.07	81.0
3		60	10	2.06	0.15	79.4
4		60	20	1.66	0.06	83.4
1	Ni	30	10	6.32	0.45	36.8
2		30	20	5.47	0.20	45.3
3		60	10	5.68	0.40	43.2
4		60	20	4.21	0.15	57.9
1	Cd	30	10	1.63	0.12	83.7
2		30	20	1.18	0.04	88.2
3		60	10	1.45	0.10	85.5
4		60	20	0.75	0.03	92.5

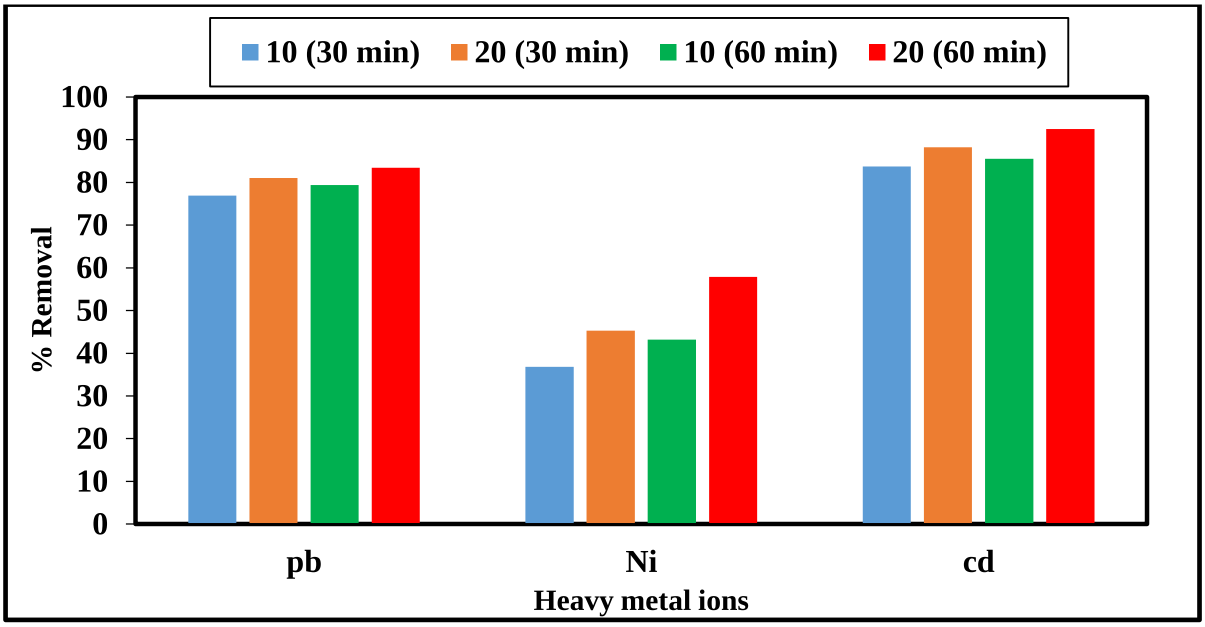

Figure 2: The percentage removal of ions with the depth of adsorbent layer 10 and 20 cm

4. Conclusions

1- Palm tree pollen shells (a waste) that collected from palm tree fields at the north-eastern of Basra, Iraq used as an inexpensive and readily available adsorbent for the removal of Pb (II), Ni (II) & Ni (II) from aqueous water without requiring any pre-treatment.

2- The experimental studies on adsorbents would be quite useful in developing appropriate technology for the removal of heavy metal ions from contaminated water or effluents.

3- This study gives evidence that the removal of heavy metal ions is unfavourable in the acidity and basicity mediums.

Recommendations

1- Investigate the possibility of removing other types of heavy metals using palm tree pollen shells.

2- Investigate the influence of other factors such as changing the initial concentration of aqueous solutions on the adsorption process.

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الملخص

في هذه الدراسة ، تم التحقق من العوامل المؤثرة على كفاءة امتزاز ايونات الرصاص والنيكل والكروم من المحاليل المائية باستخدام قنابة نورة النخيل في درجة حرارة 30 مئوية ± 1 . تم استخدام طريقتين للأمتزاز وهما الامتزاز بالدفعات والامتزاز المستمر. استخدمت النتائج المثلى التي تم الحصول عليها من الطريقة الأولى (حجم دقائق 600 ميكرون و أس هيدروجيني 7 للماء) في اختبارات الامتزاز المستمر. تم تسجيل أعلى نسبة ازالة لأيونات المعادن الثقيلة بعد مرور الماء المتأين عبر عمود الامتزازالمملوء بـ 20% من المادة المازة لمدة 30 دقيقة.

أظهرت الدراسة أيضًا امكانية استخدام قنابة نورة النخيل بكفاءة كمادة مازة متوفرة ورخيصة لإزالة أيونات المعادن الثقيلة.