



Removal of Pb (II) and Ni (II) Ions from aqueous solution by Sea Snail Shells

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Abstract

Studies on the removal of lead (II) and nickel (II) ions from aqueous solutions by adsorption on the surface shells of *Hexaplex kuesterianus* have been carried out with an aim to obtain information on treating effluents containing these types of heavy metals. Factors influencing the adsorption of Pb (II) and nickel (II) ions from aqueous solution have been investigated by following a batch adsorption technique at $30 \pm 1^\circ\text{C}$. The optimum results were found to be at 0.5g, 600 μm , 60min and 7 pH. The study also showed that snail shells can be used efficiently as an affordable adsorbent to remove heavy metal ions.

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Introduction

While recognizing that the industrial revolution transferred humanity to a very advanced stage, we cannot overlook the negative consequences that appeared as a result of that, such as increasing the levels of industrial pollution by heavy metals in water resources. The increase of heavy metals in wastewater is a major concern for their inability to biodegrade, as well as their toxicity that cause serious health problems after mixing with the rivers, which means the main source of the drinking water. In fact, the common heavy metal contaminants such as lead and nickel are becoming more prominent due to their routes of exposure and their toxic implications (Pehlivan and Altun, 2007; Oyaro *et al.*, 2007). The literature referred the main causes of lead poisoning are exposure to lead-based paint and using the lead pipes for drinking water. World Health Organisation (WHO) stated that the maximum permissible lead in drinking water is 0.01mg/L and 0.05mg/L for wastewater (Sahebi and Emtyazjoo, 2011, Chawla *et al.*, 2015). On the other hand, nickel is used in a wide variety of applications including metallurgical processes and electrical components, such as batteries (Cempel and Nickel, 2006). This metal enters the body via food and water. The maximum permissible limit for nickel in drinking water depending on WHO is 0.02mg/L and 0.05mg/L for wastewater (Elumalai *et al.*, 2017).

In order to study the possibility of reducing the concentrations of heavy metal ions in aqueous effluents to acceptable standards, a huge number of investigations have conducted during the last decades using different methods such as adsorption. Actually, adsorption techniques have become more important and popular due to their efficiency in the removal of pollutants and the possibility of using cheap materials available as successful adsorbents such as the waste materials from agriculture, wood and fisheries industry (Alternative Low-cost Adsorbent for Water and Wastewater Decontamination Derived from Eggshell Waste: An Overview). The study of (Annadurai *et al.*, 2003) suggested that banana and orange peel can be used separately as adsorbents to

remove Pb (II) and Ni (II) from water due to their large surface areas and pore sizes, in addition to having a mechanical force capable of maintaining porous structure during preparation. Continuously, Bernard *et al.* (2013) used the activated carbon that produced from low-cost substance and activated chemically by zinc chloride salts to remove lead ions from wastewater. The study included estimating the effects of changing different factors such as the amounts of the adsorbent material, pH of the aqueous solution, the contact time and speed of the rotor vibrator cycles on the amount of adsorbed. The best result was obtained at 1g, 350 rpm and 6 pH. 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, 0.5g 100mL; contact time, 2h).

This study is designed to provide information on the use of sea snail shells (*Hexaplex kuesterianus*) as an adsorbent to remove Pb (II) and Ni (II) ions. Parameters such as adsorbent dosage, particle size, contact time and pH were investigated at 32°C.

Materials and methods

Preparation of Adsorbent

Hexaplex kuesterianus were collected from Faw district at the south of Basra, Iraq. The soft tissues were removed and 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 in a mixer grinder to reduce the size, then washed several times with distilled water until a pH 7 was obtained. The adsorbents were dried in an oven at 105°C for 24hr and then sieved to obtain the size of 212, 400 and 600µm.

Preparation of Synthetic Solutions

In this practical study, the efficacy of sea snail shells for the removal of metal ions (lead and nickel) from the aqueous solutions was studied. The chemical materials were supplied by the University of Basara.

The metal solutions 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 concentration of 40 ppm of Pb (II) and 10 ppm of Ni (II).

Batch Adsorption Experimental Studies

Metal investigation was completed in the batch process. The adsorption studies were conducted at various levels of process parameters of pH 2-9, contact time 60-180min, metal ion concentration 40 ppm of Pb (II) and 10 ppm of Ni (II), the weight of sample 0.2-1g and particle size 213-600mm. ZHICHENG analytical model thermal shaker was used for the batch experiments. The pH measurements were performed with LABQUEST2 analyzer.

The experiments were carried out by contacting precisely weighted samples of Hexaplex kuesterianus shell powder with 100mL of Pb (II) or Ni (II) solutions in the 250ml leak proof corning reagent bottle. The initial pH of solutions was adjusted to the desired pH by adding 1mol/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, suspensions were passed through 0.45µm pore size filters. The residual metal was determined by an atomic absorption spectrophotometer (Varian Model 202FS). The adsorbed quantities of the metal ions were calculated from the concentration of solutions before and after adsorption based on the equation (1), (Ali *et al.*, 2016):

$$Q_e = (C_o - C_e) V/W \dots (1)$$

Where:

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

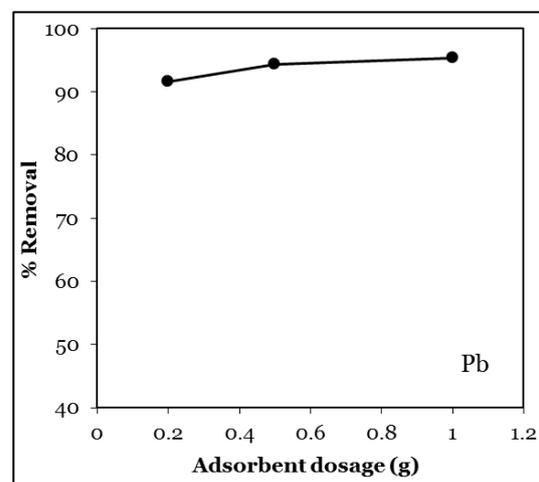
Results and dissection

Effect of Adsorbent Dosage

Removing Pb (II) and Ni (II) from aqueous solutions containing 40 ppm of Pb (II) and 10 ppm of Ni (II) was performed using varied adsorbent dosages 0.2, 0.5 and 1g under the specific conditions (particle size

of 600µm, initial pH of 7, contact time of 60min, 150 rpm shaking speed and at room temperature of 32°C). Table 1 shows increasing metal ions percentage removal with increasing adsorbent loading. It can be noticed that the removal of Pb (II) ions attained high (91.65%) even at a low adsorbent dosage of 0.2g. As shown in Fig. 2. the percentage removal of ions decreased after increasing the weight of mass from 0.5 to 1g. This may be attributed to the overlapping of adsorption sites due to overcrowding of adsorbent particles (Bernard *et al.*, 2013). On the other hand, the increase in adsorbent dosage to 0.5g has led to removing more than 70% of Ni (II) ions

The results in this work can be considered as being very good when compared to the results obtained using some types of activated carbons. For example, although (Heavy Metals Removal from Industrial Wastewater by Activated Carbon Prepared from Coconut Shells) reported that only 0.2g of activated carbon derived from coconut shells was enough to reach equilibrium with percentage removal of 100% of Pb (II), the carbonization and activation of sample with zinc chloride adds additional costs to the water treatment processes where the cost of adsorbents play a significant role in selecting the suitable adsorbent in practical applications. For nickel ions, the results in this work agree with results obtained by Thakur and Parmar (2013) that explained the percentage removal of Ni (II) increased rapidly with increase in the adsorbent dose up to 0.6g because of the greater availability of the exchangeable sites or surface area.



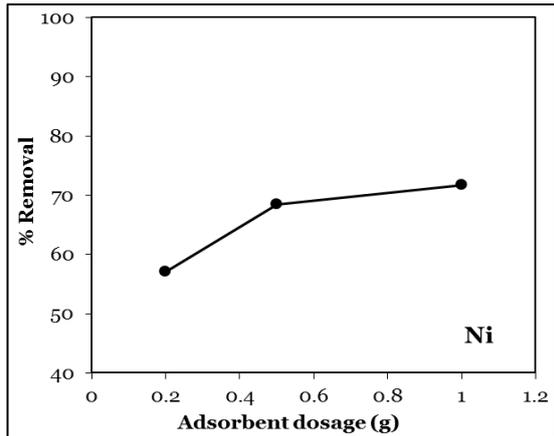


Fig. 1. The relationship between the percentage removal of Pb(II) and Ni (II) with adsorbent dosage.

Table 1. Effect of adsorbent dosage on the percentage removal of Pb (II), Cu (II).

Ion	Weight (g)	C _o (mg/L)	C _e (mg/L)	Q _e (mg/L)	Removal % of the Ions
Pb (II)	0.2	40	3.34	7.33	91.65
	0.5	40	2.24	7.55	94.4
	1	40	3.42	7.21	91.2
Ni (II)	0.2	10	4.3	0.94	57
	0.5	10	3.16	1.15	68.4
	1	10	2.83	1.43	71.7

As shown in Fig. 2, at the size 212µm, the removal percentage were 94.45 and 62.8% for Pb (II) and Ni (II) respectively, while the ions removal percentage decreased to 92.8 and 60.9% with increasing the size of adsorbent up to 400µm. The main reason of that is due to the fact that the adsorbents which have low particle size exhibit high surface area (Al-Shmery, 2013). Mondal (2008) confirmed that and referred that the specific surface available for adsorption is greater for smaller particles and hence present removal of Pb (II) ions increases as particle size decreases; for larger particles, the diffusional resistance to mass transport is higher and most of the internal surface of the particle may not be utilized for adsorption. However, just one sample (600µm) exhibited unexpected result, the removal of Ni (II) ions increased up to 68.4% after using this size of adsorbent. The particle size 600 µm selected as the optimum adsorbent size to remove both Pb and Ni metal ions in the work. Interestingly, while the equilibrium concentration of lead ions in aqueous solution (40 ppm) was 3.53 which represents high potential of snail shell in the adsorption of lead ions, the equilibrium concentration of nickel ions in aqueous solution (10 ppm) was just 3.16mg/L, and that represents medium potential of this adsorbent toward adsorption of nickel ions from aqueous solutions.

Effect of Size of the Adsorbent Particles

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) and Ni (II) from aqueous solutions were repeated using three particle sizes of adsorbents (212, 400, and 600µm) under the specific conditions (0.5g of adsorbent, initial pH of 7, contact time of 60min, 150 rpm shaking speed and at room temperature of 32 oC).

The results are shown in Table (2) indicate that the adsorption capacity increases with a decrease in the size of adsorbent.

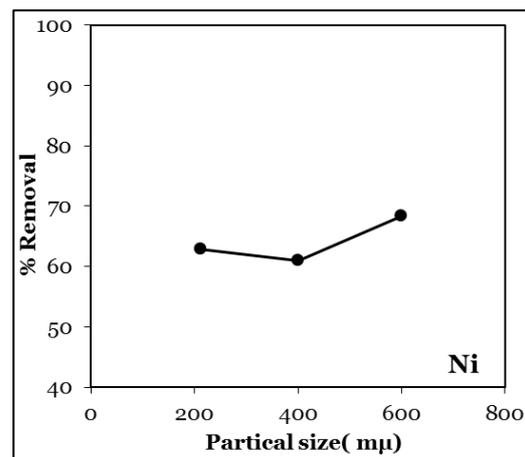
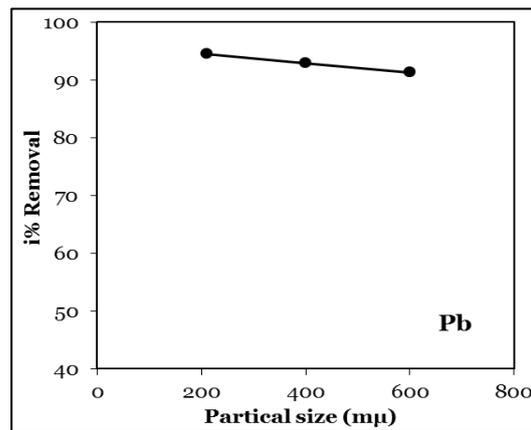


Fig. 2. The relationship between the percentage removal of Pb(II) and Ni (II) with the particle size of adsorbent.

Table 2. Effect of particle size on the percentage removal of Pb (II), Cu (II).

Ion	Particle size (m μ)	C ₀ (mg/L)	C _e (mg/L)	Q _e (mg/L)	Removal % of the Ions
Pb (II)	212	40	2.22	7.56	94.4
	400	40	2.89	7.42	92.8
	600	40	3.53	7.3	91.2
Ni (II)	212	10	3.72	1.26	62.8
	400	10	3.91	1.22	60.9
	600	10	3.16	1.37	68.4

Effect of Contact Time on Adsorption of Heavy Metals

The relationship between adsorption process time of the sea snail shells and the percentage removal of Pb (II) and Ni (II) ions from aqueous solution is shown in Fig. 3. The effect of contact time (30, 60, 120 and 180min) was studied under the specific conditions (0.5g of adsorbent, adsorbent particle size 600 μ m, initial pH of 7, contact time of 60min, 150 rpm shaking speed and at room temperature of 32 oC). The results presented snail shells was very effective to remove trace amount of Pb. The removal efficiency of sea snail ranged from 93.6-94.45% for Pb (II) compared with its ability to remove nickel ions that were in between 68.4-75.3%. The percentage removal of Pb (II) and Ni (II) metal ions reached equilibrium within 60min at 94.45% and 68.4% respectively. After increasing the contact time up to 180min, the percentage removal of Ni (II) ions increased slightly while the percentage removal of Pb (II) remained nearly constant. Therefore, the optimum adsorption process time is 60 min. These results are in agreement with the results obtained by Bernard *et al.* (2013) and Vijayakumaran *et al.* (2009) which they reported that about 60 min was enough for the Pb (II) and Ni (II) metal ions to reach equilibrium over different types of carbonaceous adsorbents such as coconut shells and morinda coreia bark. Meanwhile, at about 60min, the equilibrium concentration of lead ions and nickel in aqueous solutions was 2.22 and 3.16, respectively.

This represents a high potential of this absorbent or the removal of lead ions and medium potential for the removal of nickel ions.

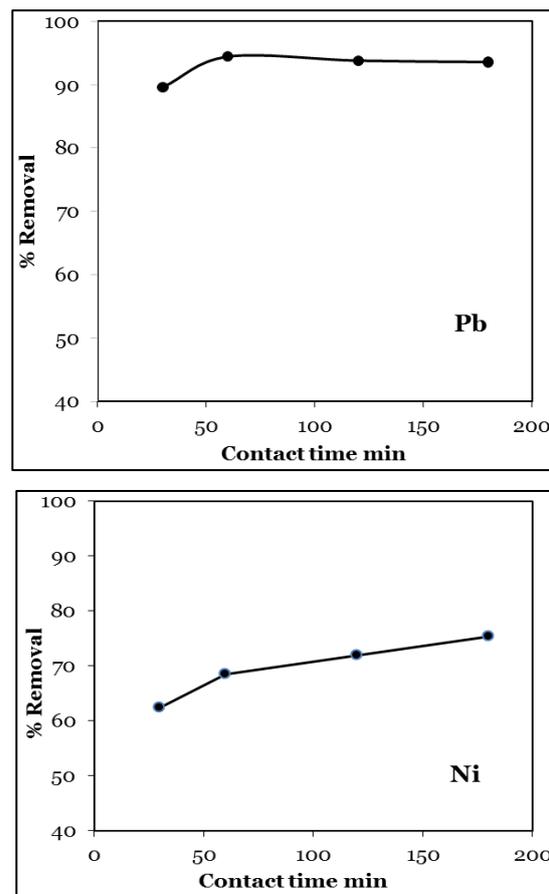


Fig. 3. The relationship between the percentage removal of Pb (II) and Ni (II) with time.

Table 3. Effect of contact time on the percentage removal of Pb (II), Cu (II).

Ion	Contact time (min)	C ₀ (mg/L)	C _e (mg/L)	Q _e (mg/L)	Removal % of the Ions
Pb (II)	30	40	4.16	7.17	89.6
	60	40	2.22	7.55	94.4
	120	40	2.47	7.54	93.8
	180	40	2.56	7.49	93.6
Ni (II)	30	10	3.76	1.25	62.4
	60	10	3.16	1.37	68.4
	120	10	2.81	1.44	71.9
	180	10	2.47	1.51	75.3

Effect of pH on the Adsorption of Heavy Metals

The pH of the aqueous solution is one of the imperative factors governing the adsorption of the metal ions. The effect of pH was studied from a range of 2 to 8 under the precise conditions (at an optimum contact time of 60min, 150 rpm shaking speed, with 0.5g of the adsorbents used, adsorbent particle size 200 μm and at a room temperature of 32°C). From Fig. 4 and Table 4, it was observed that the percentage removal of Pb (II) and Ni (II) ions increased up to 94.5% and 68.4% with increasing pH to 7. This suggest that, at low pH mediums, the compete between the H+ ions and the lead ions to the adsorption sites (negative charges on the surface) did not affect significantly on the percentage of removal (Arshadi *et al.*, 2014). However, this image has slightly changed after increase the basicity of an aqueous solution. The removal of lead ions decreased to 92.9% with raising pH to 8. on the other hand, at low pH medium (pH 2), the removal of Ni (II) was less than 50% due to the effect of basic medium on the adsorption of nickel ions.

The percentage of removal nickel ions increased after raising the pH up to 7. The results of these investigations are consistent with results obtained by Dowlatshahi *et al.* (2014) and Venkateswarlu *et al.* (2015) that explained the removal efficiency of Pb (II)

and Ni (II) increases gradually with increasing pH of aqueous solution up to 6-7.

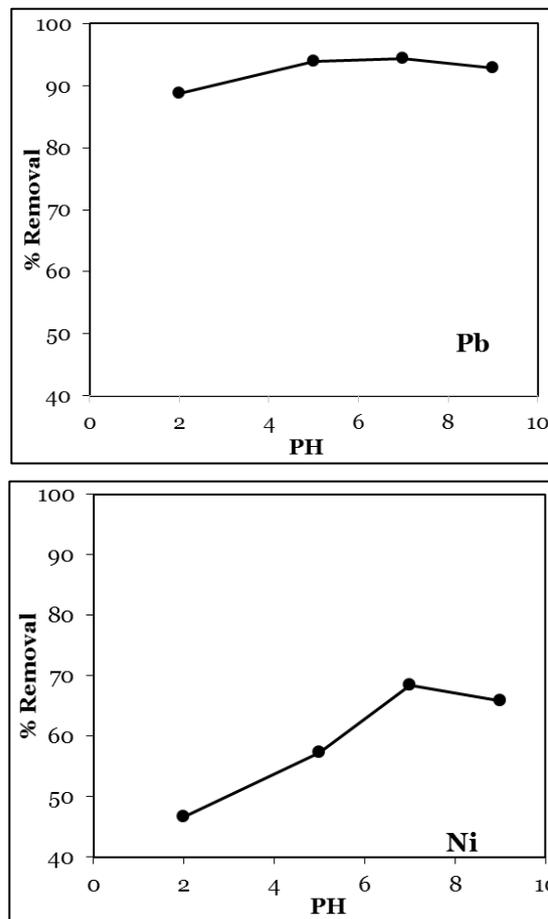


Fig. 4. The relationship between the percentage removal of Pb (II) and Ni (II) with PH.

Table 4. Effect of PH on the percentage removal of Pb (II), Cu (II).

Ion	PH	C _o (mg/L)	C _e (mg/L)	Q _e (mg/L)	Removal % of the Ions
Pb (II)	2	40	4.52	7.09	88.7
	5	40	2.46	7.51	93.9
	7	40	2.22	7.60	94.4
	8	40	2.81	7.43	92.9
Ni (II)	2	10	5.31	0.94	46.7
	5	10	4.27	1.15	57.3
	7	10	3.16	1.37	68.4
	9	10	3.41	1.32	65.9

Conclusions

1. Snail shells (a waste) is inexpensive and readily available adsorbent for the removal of Pb (II) and Ni (II) ions from aqueous water without requiring any pre-treatment.
2. The batch adsorption experiments showed that the optimum conditions for the maximum removal of lead

- and nickel ions by snail shells were at 7 PH, 60min contact time, 0.5g adsorbent dose and 600μm.
3. The experimental studies on adsorbents would be quite useful in developing an appropriate technology for the removal of heavy metal ions from contaminated water or effluents increasing basicity.

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

Recommendations

1. An awareness program should be launched to aware the workers against the Hazards of heavy metal contamination.
2. Investigate the possibility of removing other types of heavy metals using alternative materials such as marine and freshwater snail shells.
3. Determine the removal efficiency for heavy metals using dynamic adsorption system.

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