Effects of Egg shells for Different Heavy Metals Removal from Aqueous Solution

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Abstract Characteristics and efficiency of eggshells (ES) were investigated as a low-cost adsorbent in removal of different heavy metal ions from aqueous solution. Initial findings showed ES potential to be applied as an effective sorbent due to high concentrations of carbon and calcium and high porosity and availability of functional groups. Adsorption experiments were studied with varying pH, contact time, and ES concentration. Maximum percentages of heavy metal ions removal were recorded at optimum pH, contact time and adsorbent concentration. Evaluation of the isotherms and kinetics confirmed that ES has high value of adsorption capacity. This experiment demonstrated the ability of ES as an effective, sustainable, and low-cost adsorbent for removal of the heavy metal ions in different wastewaters.

Keywords: Adsorption, Eggshells, Heavy metals, Low-cost

1. Introduction

Adsorption has been recognized as a promising technique due to its ease of operation, simplicity of design, high efficiency, and comparable low cost of application in decoloration process (El-Bindary *et al*. 2016). Adsorption of different heavy metals has been studied using low cost adsorbents including agricultural wastes such as hazelnut shell, orange peel, banana peel, sunflower seed shells, apple pomace, bamboo dust, etc. Some of the advantages of using agricultural waste for wastewater treatment include simple technique, requires little processing, good adsorption capacity, selective of adsorption effluent, low cost, free availability, and easy regeneration (Liao *et al*. 2011; Mouni *et al*. 2011; Anirudhan and Sreekumari 2011; Depci *et al*. 2012; Saka 2012).

Lead (Pb^{+2}) is classified as a priority hazardous substance by various agencies including the Agency for Toxic Substances and Disease Registry (Bediako *et al*. 2016; Çelebi and Gök 2017). Since Pb^{+2} pollution in drinking water leads to important health problems for people, it is seen as significant environmental issue. Pb^{+2} is related to industrial activities. Activated carbon is usually used as the versatile material due to high surface area, micro porous structure, high adsorption capacity (Wasewar *et al*. 2010). However, activated carbon is expensive and there is a need for its regeneration after each adsorption experiment. In order to decrease the cost of adsorption, low cost forest wastes are presently considered promising adsorbents for adsorption (Ghazi *et al*. 2015; Kyzas *et al*. 2015). Recently, our laboratories have developed untreated ES as a potential adsorbent for the removal of Pb^{+2} from its aqueous solutions. ES are well known waste materials, which are everyday generated on a large scale from household, restaurants, food industries, bakeries, etc. (Daraei *et al*. 2013). The purpose of the present study is to investigate the optimum conditions for the removal of Pb^{+2} from its aqueous solutions using ES as a biosorbent. This paper includes results of the effects of pH, contact time, ES dosage, etc. on its removal along with adsorption isotherms.

2. Materials and Methods

2.1. Aqueous Solution

The Pb^{+2} simulated solution was prepared from $Pb(NO_3)_2$ (Merck). About 1.593 g of $Pb(NO_3)_2$ was weighed and a standard Pb^{+2} concentration of 1000 mg/L was prepared, and further working solutions of 100 mg/L was prepared as and when required.

2.1. Preparation of ES as an Adsorbent

The ES were collected and washed with distilled water several times to remove dirt particles and dried for three hours in an oven at 150 ºC and then allowed to cool at room temperature, subsequently it were crushed and then finally sieved into particle size of 0.5 mm. The sieved adsorbent was stored in an air-tight container. No other chemical modification was taken place. (Zahir Hussain and Mohamed Sheriff, 2014). As presented in Table 1, the chemical composition (CC) of the ES shows that calcium oxide was the most abundant component. Proximate analysis (PA) was conducted according to ASTM D 5832-95, ASTM D 3172-89 and ASTM D 2867-95 standards. (Mopoung *et al*. 2015; Freire and Holanda 2006; Bashir and Manusamy 2015).

Table 1. PA analysis and CC of ES adsorbent

PA (Wt.%)		CC	(Wt.%)
Moisture	0.5	C	21.1286
Ash	43.5	Na_2O	0.1046

Crude fibre	3.0	MgO	0.9261
Protein	1.35	P_2O_5	0.4149
Carbohydrate	51.7	CaO	76.9922

2.2. Analytical Methods

Before the start of the experiments, ES were dried and placed in ball mill and obtained crumbs were sifted to acquire the size of smaller than 100 µm. All chemicals were analytical grade, as they were purchased from Merck. The pH measurements were performed with LABQUEST2 digital meter. Adsorption experiments were performed in batch systems, using ES amount, pH and contact time as variables. The Pb^{+2} concentrations in the initial and effluent samples were analyzed using the Perkin Elmer Optima 2100 DV model inductively coupled plasma optical emission spectrometry (ICP-OES). The surface morphology of ES was investigated using a Fei Quanta FEG250 model field emission scanning electron microscope (SEM). The chemical composition of the ES sample was determined by X-ray fluorescence machine (Bashir and Manusamy 2015). The experiments were carried out by contacting precisely weighted samples of ES with 100 mL of Pb^{+2} solutions in the sealed 250 mL Erlenmeyer flasks. The suspensions were conducted on a thermal shaker at a shaking speed of 250 rpm at 20 °C in triplicate. After the specified time, suspensions were filtered through filter study 0.45 µm pore size membrane filters. The initial pH of Pb^{+2} solution was adjusted to the desired pH by adding 1 mol/L HCl or NaOH solutions. After adsorption, the mixtures were filtered and the filtrates were analyzed for Pb^{+2} content using an ICP-OES at 261.42 nm.

2.3. Pb^{+2} Adsorption Capacity

The experiments were performed at different process variables for the ES, the concentration of Pb^{+2} deposited onto ES surface utilizing the accompanying mathematical expression:

$$q_e\ (mg/g) = (C_0-C_e)*V/1000*w \quad (1)$$

Where, q_e is the amount of Pb^{+2} deposited on ES (mg/g), C_e is the initial solute concentration in the solution before adsorption (mg/L), C_o is the final concentration of solute in the solution after adsorption (mg/L), V is the volume of the metal solution (L) and w is the weight of the ES adsorbent. Adsorption system was quantified by calculating the adsorption percentage (E %) as defined by the Eq. 2:

$$\text{Adsorption (E) (\%)} = (C_0-C_e)/C_0 *100 \quad (2)$$

Adsorption experiments were performed in triplicate and the mean values of instances were submitted. In addition, blank examples were used to compare the results through all adsorption system. Data submitted are the mean values from the adsorption tests, error bars are indicated in the figure 1, 2, 3.

3. Results and Discussion

3.1. Effect of Contact Time for Pb^{+2}

The adsorption of Pb^{+2} has been investigated on ES as a function of time in the range of 1-150 minutes. The efficiency initially increased rapidly and the equilibrium was attained in 15 minutes at efficiency of 97%. The maximum Pb^{+2} removal which were found 97.35% at contact time of 10 minutes for ES (Figure 4).

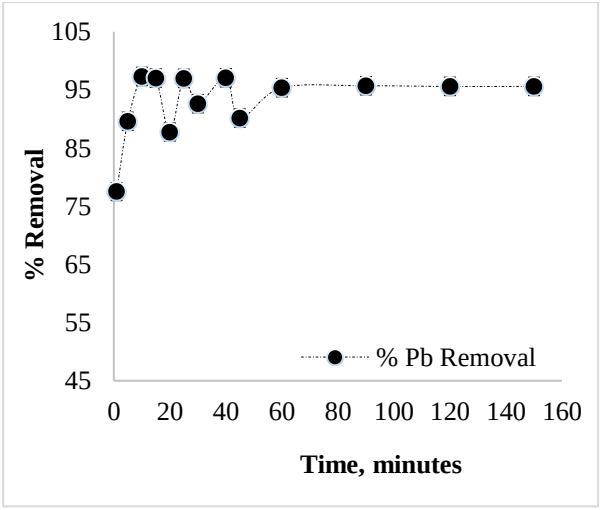

Figure 1. Effect of %Pb^{+2} using ES as an adsorbent.

3.2. Effect of pH on Pb^{+2}

The Pb^{+2} removal efficiency of ES at different pH values is shown in Figure 2. Values of pH >6 have not been studied, since it precipitated as $Pb(OH)_2$, being the process of entrapment actually a combination of adsorption and micro precipitation. It was found that Pb^{+2} uptake by ES was a function of the initial solution pH. Figure 2 shows that the maximum Pb^{+2} removal efficiencies that were found 94.43% at pH 3.0 at 100 mg/L of initial concentration for ES. Almasi *et al.* (2012) and Wolfova *et al.* (2013) also observed the same experimental results. The optimum initial pH value for Pb^{+2} adsorption by ES was determined to be 3.0.

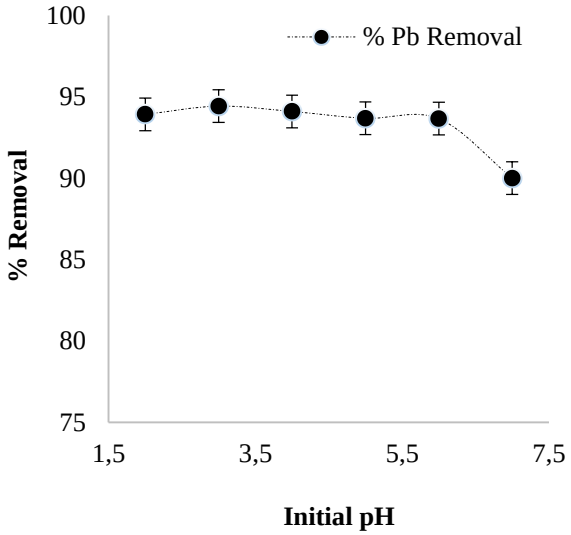

Figure 2. Effect of pH on the yield of Pb^{+2} using ES.

3.3. Effect of ES Amount

The adsorbent amount in aqueous solution is a momentous parameter in the adsorption works because it makes the capacity of an adsorbent for a given initial concentration of the adsorbate (Mouni *et al*. 2011). Effect of ES amounts on the elimination yields of Pb^{+2} are indicating in Figure 3. It was observed that the Pb^{+2} removal yield of the ES was a function of ES amounts in the aquatic solution. The amount of Pb^{+2} adsorbed increase from about 32.56% to 92.28% with an increase in ES amount from 0.1 to 2.5 g. The maximum adsorption efficiency of Pb^{+2} onto the ES was found to be 92.28% at the dose of 2.5 g/L ES. It can be explained as ES amount increased, more and more surface area available metal ions will be exposed to more active sites for binding (Kumar *et al*. 2011). As compared to some low-cost adsorbents in the previous literature, the organic waste used in our study is of relatively higher adsorption capacity and ranges within the most efficient and best adsorbent for Pb^{+2}. The surface physical morphology of ES characterized by SEM was determined in the laboratories of Aksaray University Scientific and Technological Research Center Laboratories (data not shown).

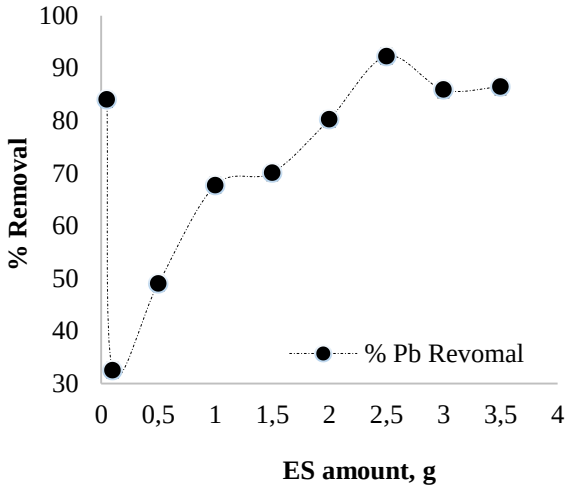

Figure 3. Effect of ES dose on adsorption of Pb^{+2}.

3.4. Comparison of Pb^{+2} Removal with Different Adsorbents Reported in Literature

A list showing the adsorption removal of different adsorbents for the adsorption of lead from aqueous solutions is given in Table 2. As it can be seen, the observed removal efficiencies of acorn shell for Pb^{+2} are comparable with other low-cost adsorbents**.**

Table 2. Comparison of adsorption removal of various adsorbents for Pb^{+2}

Adsorbent	Removal (%)	pH	Adsorbent Amount (g)	Pb^{+2} conc. (mg/L)	References
Almond Shell	68	6-7	0.5	200	(Pehlivan *et al*. 2009)
Antep pistachio	90	5.5	1.0	30	(Yetilmezsoy, Demirel 2008)
Groundnut shell	82.81	4.9	1.0	-	(Shukla, Roshan 2005)
Hazelnut shell	90	6-7	0.5	200	(Pehlivan *et al*. 2009)
Palm shell	-	3-5	-	10-700	(Issabayeva *et al*. 2008)
Pecan shell	-	5.5	4	100	(Vaghetti *et al*. 2009)
Pistachio shell	83	6-9	0.1	30	(Kazemipour *et al*. 2008)
Walnut Shell	95	4	10	100	(Wolfova *et al*. 2013)
Groundnut shell	98	5.1	2.2	152.5	(Janyasuthiwong *et al*. 2015)
ES	**95**	**3.0**	**2.5**	**100**	**This Study**

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