Removal of Heavy Metals from Simulated Water by Using Eggshell Powder

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Abstract Characteristics and efficiency of eggshell powder (ESP) 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 ESP 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 ESP has high value of adsorption capacity. This experiment demonstrated the ability of ESP as an effective, sustainable, and low-cost adsorbent for removal of the heavy metal ions in different wastewaters.

Keywords: Adsorption capacity, Eggshells, Heavy metals, simulated water

1.   Introduction

Aquatic ecosystems contamination especially with heavy metal ions is an environmental problem worldwide (Rai, 2008). Of all contaminant metals, cadmium is considered an extremely toxic heavy metal with acceptable levels one-tenth those of most of the other toxic metals (Drasch *et al.* 2004; Elkhatib *et al.* 2016). Cadmium (Cd) is recognized as one of the most harmful heavy metal pollutants in the environment due to its toxicity, non-degradability, bioaccumulation and mobility in natural water and soil ecosystems (Cao *et al.* 2017; Tetsuro *et al.* 2008). It could cause a high carcinogenicity and an endocrine disorders, as well as renal dysfunction and bone fracture (Ahmaruzzaman 2011). Cd pollution arises mainly from domestic sewage and the effluents of industries involved in electroplating, smelting, alloy manufacturing, pigments, plastic, cadmium-nickel batteries, fertilizers, pesticides, pigments and dyes, textile operations, and refining (Elkhatib *et al.* 2016; Chaney 2010; Cao *et al.* 2017). The main form of Cd in contaminated water is Cd^{+2} and the remediation technologies available to reduce Cd concentrations in contaminated water systems include ion exchange, solvent extraction, chemical precipitation, phytoextraction, ultrafiltration, reverse osmosis, electrodialysis, adsorption etc. (Purkayastha *et al.* 2014; Rao *et al.* 2016).

However, most of these technologies have shown limitations in removing the toxic contaminants from contaminated water to safe levels and they are costly, laborious, and time-consuming (Savage and Diallo 2005; Schwarzenbach 2006). Among these methods, adsorption was considered as one of the prospective process due to low-cost, simplicity of application and efficiency (Sun *et al.* 2016; Kocaoba 2009). For the adsorption process, the adsorbent was the key parameter. This study aims at investigating the feasibility of ESP adsorbent for cadmium removal from simulated waters. The contact time, pH, Weight of the ESP, temperature and their interactions, which are considered as the most critical parameters affecting the removal of Cd^{+2} from simulated waters. The aim of this study is the determination of optimum parameters within the operating conditions for cadmium removal from simulated waters.

2.   Materials and Methods

2.1. Simulated Effluent Preparation

The Cd solution was prepared from $3CdSO_4 \cdot 8H_2O$ (Merck). About 2.281 g of $3CdSO_4 \cdot 8H_2O$ was weighed and a standard Cd effluent concentration of 1000 mg/L was prepared, and further working solutions of 100 mg/L was prepared as and when required. After adsorption, the final effluent solution was analyzed by Perkin Elmer Optima 2100DV model inductively coupled plasma optical emission spectrometry (ICP-OES).

2.2. Batch Adsorption Experimental Studies

Metal investigation was completed in the batch process. The adsorption studies were completed in the exploratory conditions of various effective process parameters of pH 2-6, contact time 1-150 min, metal ion concentration 100 mg/L, the weight of the ESP 0.05-5 g. ZHICHENG analytical model thermal shaker was used for the batch experiments. Then it was analyzed using the Perkin Elmer Optima 2100DV model inductively coupled plasma optical emission spectrometry (ICP-OES). The pH measurements were performed with LABQUEST2 analyzer. The surface morphology of ESP was investigated using a Fei Quanta FEG250 model field emission scanning electron microscope (SEM). The chemical composition of the ESP sample was determined by X-ray fluorescence machine

(Bashir and Manusamy 2015). As presented in Table 1, the chemical composition of the ESP shows that calcium oxide (CaO) was the most abundant component. Thus, the ESP sample can be considered from a chemical viewpoint a pure relatively natural carbonate-based material (Bashir and Manusamy 2015).

Table 1. Chemical composition of ESP

Composition	Wt.%
C	21.128
Na_2O	0.105
MgO	0.926
P_2O_5	0.415
SO_3	0.326
K_2O	0.054
CaO	76.992
Fe_2O_3	0.013
SrO	0.039

The experiments were carried out by contacting precisely weighted samples of ESP with 100 mL of Cd^{+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 lead 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 Cd content using an ICP-OES (Perkin Elmer Optima 2100DV) at 261.42 nm.

2.3. Cadmium Adsorption Capacity

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

$$q_e \text{ (mg/g)} = (C_0 - C_e) * V / 1000 * w \qquad (1)$$

Where, q_e is the amount of Cd^{+2} deposited on ESP (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 ESP adsorbent. Adsorption system was quantified by calculating the adsorption percentage (E %) as defined by the Eq. 2:

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

Adsorption experiments were performed in triplicate and the mean values of instances were submitted. In addition, blank examples (with deionized water, without Cd^{+2}) were used to compare the results through all batch adsorption procedures. Data submitted are the mean values from the adsorption tests, standard deviation (≤5%) in figures. The experimental data were fitted to the kinetic, isotherm models (data not shown). The best-fit model indicates the most probable adsorption mechanism.

3. Results and Discussion

3.1. Determination of Contact Time for ESP adsorbent

The adsorption process time is the key parameter for the selection of adsorbent for the adsorption process. The batch adsorption experiments were conducted for 100 mg/L Cd^{+2} concentration with the function of adsorption process time and removal efficiency of ESP are demonstrated in Figure 1. The removal efficiency of Cd^{+2} increases gradually with increasing adsorption process times and reaches equilibrium at around 80 min, at this point the maximum amount Cd^{+2} is removed from the solution. Figure 1 depicts that the adsorption efficiency, increased from 48.88 to 75.99% at a contact time of 60 min with 100 mg/L Cd^{+2} concentration. At this optimum adsorption process time, the clump of the batch experiments was led to make sure that equilibrium is reached.
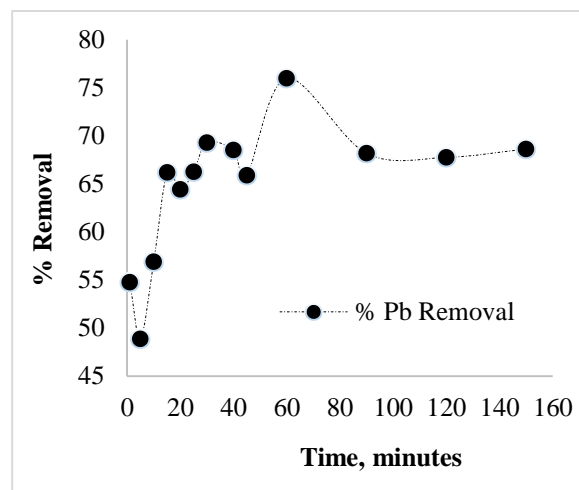

Figure 1. Effect of adsorption process time on % adsorption of Cd^{+2} using ESP as an adsorbent.

3.2. Effect of Hydrogen Ion Concentration (pH) on Cd^{+2}

The variation of pH is highly effected on the adsorption process for removal of Cd^{+2} from waste water using ESP as an adsorbent. The initial pH of solution is a significant control parameter for the evaluation of adsorption performances (Okafor *et al.* 2012). The effect of pH on adsorption of Cd^{+2} at 20 ^0C for constant concentration and time of adsorption 70 min is shown in Figure 2. It was observed that the pH of the solution varies from 2.0 to 6.0, the adsorption efficiency is very low because repulsion is taking place between solution and ESP adsorbent. The adsorption efficiency is slowly increasing with pH (3.0 to 6.0) of the solution, because the effluent solution is exposed to the negative charges and strongly attracting the Cd^{+2} ions with the adsorbent surface. The solution pH value is increased 3.0 to 5.0; leads undergo hydrolysis process forming a precipitation of $Cd(OH)_2$ and $Cd(CO_3)_2$, dominate at high pH where as Cd^{+2} and aqueous sulfate

species dominate at lower pH (<6). This subsequently leads to change the equilibrium conditions and the kinetics of the adsorption process. These studies were described that the potential of H^+ ions on the ESP surfaces is not metal specific. The maximum efficiency 64.04% is obtained at pH 5.0.
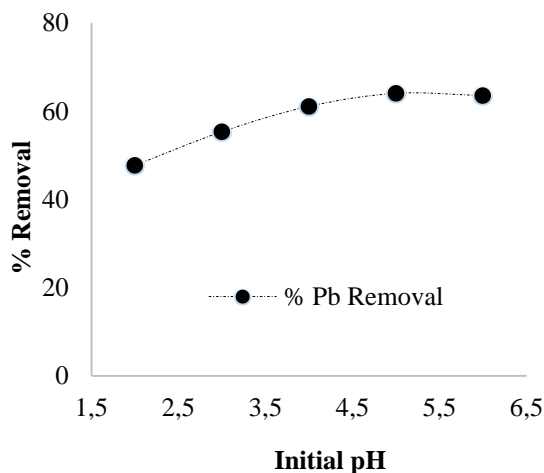
Figure 2. Effect of solution pH on the removal efficiency of Cd^{+2} using ESP as an adsorbent.

3.3. Effect of ESP 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 ESP amounts on the elimination yields of Cd^{+2} are indicating in Figure 3. It was observed that the Cd^{+2} removal yield of the ESP was a function of ESP amounts in the aquatic solution. The amount of Cd^{+2} adsorbed increase from about 23.82% to 95.93% with an increase in ESP amount from 0.05 to 5 g. The maximum adsorption efficiency of Cd^{+2} onto the ESP was found to be 95.93% at the dose of 3.5 g ESP. It can be explained as ESP amount increased, more and more surface area available metal ions will be exposed to more active sites for binding (Kumar *et al.* 2011).
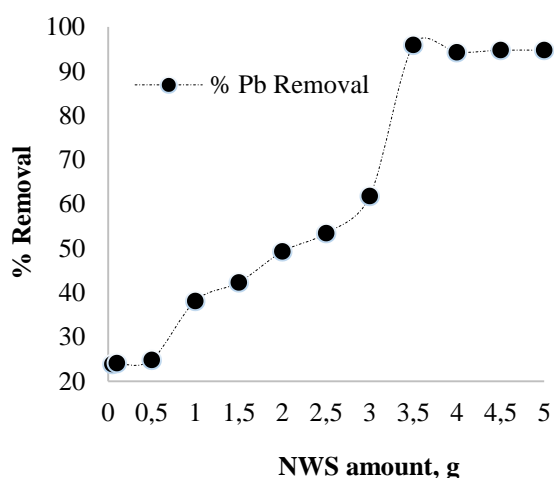
Figure 3. Effect of adsorbent dose on adsorption of Cd^{+2} by ESP.

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 Cd^{+2}. The surface physical morphology of ESP characterized by SEM was determined in the laboratories of Aksaray University Scientific and Technological Research Center Laboratories (data not shown).

4. Conclusions

The present experimental study results indicated that the ESP might be feasible successfully as an adsorbent of Cd^{+2} from aqueous solution. The adsorption of Cd^{+2} onto the ESP was found to be pH, contact time, and ESP amount depended. The optimum pH value for the experimental study was determined as 5.0. The maximum removal efficiencies by the ESP were obtained around 65-96% for Cd^{+2} under optimum conditions (pH=5.0, contact time=60 minute, ESP amount= 3.5 g, shaking speed= 250 rpm and 20 ^{0}C). It may be concluded that ESP could be used, as a practical, effective and low-cost, high capacity adsorption, and abundant source to remove Cd^{+2}. Future studies would be done on the effect of temperature, different isotherms and thermodynamic to better understand the adsorption of Cd^{+2} (data not shown).

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