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EFFECT OF OPERATIONAL CONDITIONS ON THE REMOVAL OF CADMIUM IONS FROM SIMULATED WASTEWATER USING COMPOSITE SORBENT

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ABSTRACT

This work is studied the effect of operational parameters on the efficacy of composite sorbent in the reclamation of simulated wastewater contaminated with cadmium ions. This sorbent was manufactured from precipitation of hydroxyapatite (resulted from reaction of calcium and phosphate that extracted from cement kiln dust and sewage dead biomass) on the remaining solids from extraction process. The effect of different parameters such as contact time between adsorbate and adsorbent (5-180 min), initial pH of the solution (2-7), adsorbent dosage (0.05-2 g/50 mL) for agitation speed of 200 rpm at 25ºC were studied. The best values of these parameters were 120 min, 5, and 0.4 g/50mL for contact time, pH, and adsorbent dosage respectively that achieved the removal efficiencies ranged from 69 to 99.3% due to variation of initial cadmium concentration from 10 to 300 mg/L.

Keywords: Cadmium, Adsorption, Wastewater, Hydroxyapatite.

Introduction

Discharging of industrial wastewaters containing different pollutants can lead to contaminate the environment and disorder in its ecosystem. Increasing and development of the alloy and leather industries, metal galvanizations and others result in significant increase of heavy metals ions concentration in the industrial wastewaters. In spite of low concentrations of these metals they are often considered as toxic compounds and their removal from wastewater is crucial issue. Accumulation of metals in human body can lead to severe disorders in the performance of kidneys, liver, sexual, brain and nerve systems (Cempel and Nikel, 2006; Debnath *et al*., 2019). Direct discharging of wastewater containing heavy metals like cadmium, lead, zinc, nickel …etc into municipal wastewater collection system will damage biological treatment units and produce active sludge which can destroy the agricultural products. Since heavy metals are not degradable through biological ways, they stored in the living tissues and enter the food chain of plants, animals and human beings. Therefore, with regard to the numerous disadvantages of heavy metals, their removal from industrial wastewaters is a very important environmental issue (Faisal and Ahmed, 2015; Faisal *et al*., 2020e; Faisal and Abd Ali, 2017; Rashid and Faisal, 2018; Sharma *et al*., 2014).

One of the most commonly used ways of heavy metal ions removal are, ion exchange, oxidation–reduction by zero-valent, or precipitation by apatite, and adsorption by clay soil wastes, natural zeolite, animal bones, sawdust, agricultural by-products, and grain rice are very cheap and easily available in the nature (Shareef, 2009). Several previous studies were conducted to remove metal ions from wastewater like cadmium by zeolite (Faisal and Hmood, 2015), lead onto sewage sludge (Sulaymon *et al*., 2015), zinc by zero valent iron (Faisal *et al*., 2015), lead with waterworks sludge (Faisal *et al*., 2020b), copper and cadmium by sand coated with iron oxide and humic acid (Abdul-Kareem and Faisal, 2020; Faisal *et al*., 2020a) and nickel on cement kiln dust (Faisal *et al*., 2020c)

Hydroxyapatite (HAP) has been applied in this regard; however, because of economic implications, alternative procedures to produce HAP from cheap and recyclable or waste materials have been pursued. The use of waste eggshells has been dominant (Ibrahim *et al*., 2015a) among the alternative procedures because of the fact that it is cheap, high calcium content and readily available. Synthetic hydroxyapatite (HAP) is a particularly attractive material which formed from calcium and phosphate. Number of methods have been used for HAP synthesis, such as solid-state reaction, Co-precipitation, hydrothermal reaction, sol–gel synthesis, microemulsion synthesis and mechanochemical synthesis (Han *et al*., 2004; Ibrahim *et al*., 2015b). The major idea of this study is finding the effects of operational conditions on the performance of material coated with HAP nanoparticles in the removal of cadmium from simulated wastewater. These particles are prepared by mixing of calcium and phosphate extracted from cement kiln dust and sewage sludge byproducts resulted from cement industry and activities of wastewater treatment plants; however, the

particles are planted on filter cake remaining from extraction process.

Materials and Methods

Materials

Cadmium was selected as a representative of contaminants. To simulate the water's contamination, a solution of $Cd(NO_3)_2.4H_2O$ (manufactured by HIMEDIA, India) with concentration of 1000 mg/L and this solution was kept at room temperature. The solution was used as stock solution to prepare any specific value of cadmium concentration and the pH of this solution was adjusted by adding 0.1 M of HCl or NaOH as needed.

Cement kiln dust and sewage sludge byproducts were collected from cement factory and wastewater treatment plant respectively. They are used to manufacture the hydroxyapatite nanoparticles using extraction procedure and these particles have been planted on the immobilized solid phase remaining extraction.

Batch experiments

Batch experiments were conducted to specify the best conditions for treatment process. These conditions included the contact time, initial pH, initial concentration of contaminants, and sorbent dosage. A series of 250 mL conical-flasks were employed and each flask was filled with 50 mL of cadmium solutions which have an initial concentration of 50 mg/L. 0.1 g of adsorbent was added to the solutions in the flasks. The solution in each flask was kept stirred on a high-speed orbital shaker at 200 rpm for 3 hours. A fixed volume (20 mL) of the solution was withdrawn from each flask, and filtered using filter paper type (Wattmann No. 1 and Teknik No.1) to separate the solid particles. A fixed volume (10 mL) of the clear solution was pipetted out for analysis to determine the concentration of the remaining cadmium. The measurements were carried out using Atomic Adsorption Spectroscopy (AAS). Tests were investigated with different values of initial metal concentration (50-300 mg/L), different amounts of dosage (0.05-2 g/50mL) and finally different values of pH and contact time.

Results and Discussion

Effect of contact time

For batch experiments, contact time should be fixed at an appropriate value to ensure attaining equilibrium concentrations. Figure 1 shows the variation of relationship correlated between the removal efficiency and contact time upon mixing 0.1 g of HAP planted on filter cake material with 50 mL of contaminated solution under experimental condition of 25ºC, initial concentration (C_o) 50 mg/L, initial pH 5 and agitation speed of 200 rpm. This figure demonstrates that the removal percentage of cadmium is significantly increased with increasing of contact time. It is clear that the rate of sorption is greater at the initial stage and gradually drops in due course indicating a gradual blinding of sorption sites on the adsorbent surface. Within 2 h, about 69.5% of cadmium, was removed. While the residual concentrations of this chemical is being kept relatively constant beyond the 2 h contact time with insignificant changes up to 3 h (Ahmed *et al*., 2020; Faisal and Naji, 2019).

The high rate of adsorption can be attributed to the existence of adequate numbers of the reactive binding sites on the sorbent surface and the tendency of decreasing rate with elapsed time may have resulted due to further occupation of the active sites by cadmium particles. Therefore, the sorption results conform with the outcomes of previous studies, like Faisal *et al*. (2020) who analyzed the interaction pattern between Iraqi bentonite and cadmium. Accordingly, the contact time of 2 h can be adopted for carrying out subsequent sorption experiments as it seemed sufficient to attain the equilibrium state.

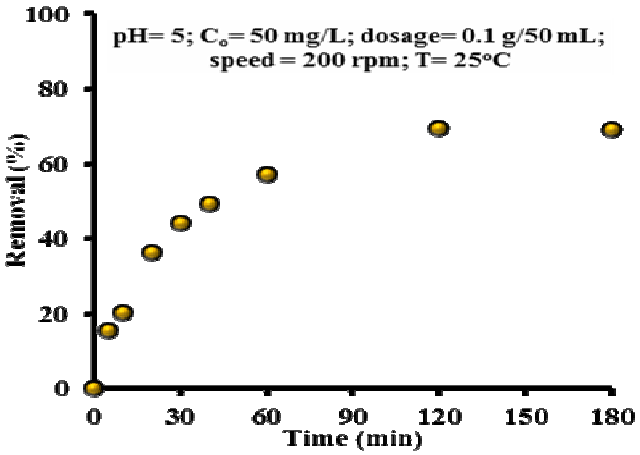

Fig. 1: Contact time effect on the removal efficiency of cadmium.

Effect of initial concentration

Other experiments were carried out to study the effect of various initial concentrations (C_o) of cadmium on sorption efficiency. These experiments were conducted using C_o ranging from 10 to 300 mg/L with addition of 0.1 g/50 mL of adsorbent and shaken for 2 h at 200 rpm with initial pH of 5. Figure 2 presents the removal efficiencies for cadmium as a function of C_o at equilibrium state. The results indicate a higher removal efficiency at the lower values of C_o while displaying a decreasing pattern at the upper range of the C_o up to 300 mg/L. Such variations can be interpreted as due to saturation of the sorbent's active sites that interact with cadmium. Conclusions also point out the rapidly increased amount of sorbed contaminant onto unit mass at equilibrium in the lower range of C_o.

The sorption quantities of metal ions are growing gradually with an increase of the initial concentration, providing an improvement of driving force for the combination of these species and the adsorption sites. Thus, the removal rate declines with the rise of initial concentration. The hydroxyapatite was highly dependent on protonation and deprotonation by H^+ and OH^- in the aqueous solution. The hydroxyapatite surface possesses two different reactive sites, hydroxyl functional groups, Ca-OH and P-OH (Othmani *et al*., 2013). Therefore, different interactions occur between these functional groups with the ionic or polar groups of the contaminant species.

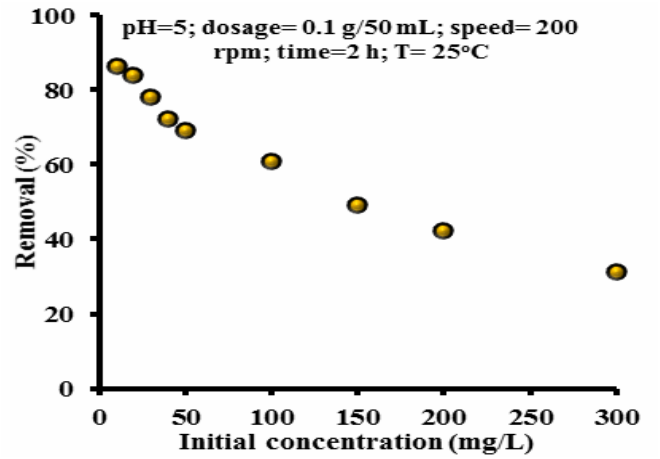

Fig. 2: Effect of initial concentration on removal efficiency of cadmium.

Effect of sorbent dosage

The dependence of cadmium adsorption on the amount of adsorbent dosage was experimented using a range of adsorbent amounts (0.05 to 2 g). Each dosage was added and continuously mixed with 50 mL of aqueous contaminant solution in a batch tests the following conditions: T= 25ºC, C_o= 50 mg/L, initial pH= 5, agitation rate= 200 rpm and contact time= 2 h. Figure 3 illustrates the efficiency of removing the contaminant as a function of varying amounts of sorbent. The obtained data demonstrate increasing removal efficiency with increasing the dosage of the adsorbent within the adopted range. From figure 3, the removal efficiency has reached its highest level when using a dose of 0.4 g of adsorbent, and after that dosage the removal efficiency was remained fix at this value, so a dose of 0.4 g was adopted for the rest of the experiments. This trend of relationship was expected as a common sense of that the higher dosage of sorbent in a solution, the greater availability of active sites.

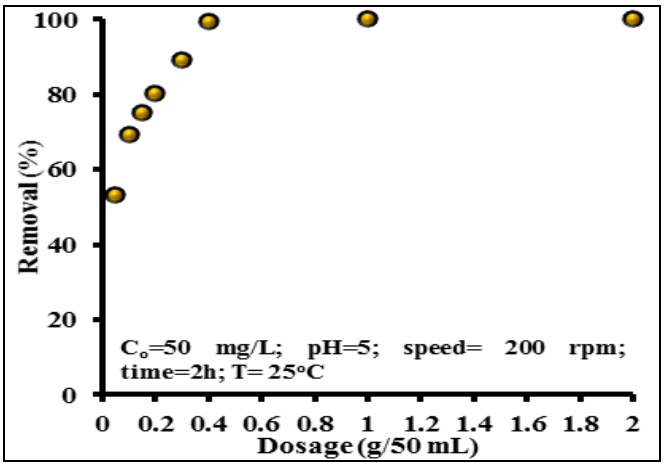

Fig. 3: Effect of sorbent dosage on the removal efficiency of cadmium.

Effect of initial pH

The effect of pH on the sorption of cadmium ions onto HAP planted on the filter cake was studied at room temperature by varying the pH of aqueous solution - adsorbent suspension. The results are plotted in Figure 4 showing an increased removal efficiency with increasing pH values within the experimented range of 2.0 to 7.0 for C_o of 50 mg/L, contact time of 2 h and agitation rate of 200 rpm and 0.4 g. The plots show that increasing sorbent dosage at certain pH will accelerate attainment of equilibrium status. In order to avoid precipitation of cadmium metal on the adsorbent, the tests were carried out at pH 7. It is evidence that the increasing pH values within the experimental range of (2-7) led to increasing cadmium removal due to a decrease in hydrogen ions liberated in the aqueous solution.

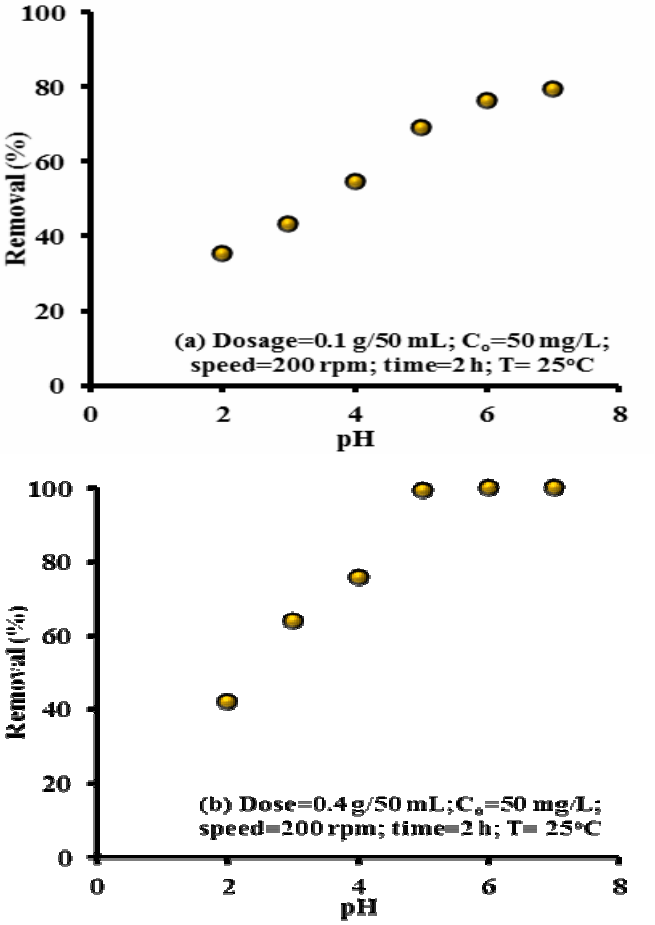

Fig. 4: Effect of pH on the removal efficiency of cadmium for sorbent dosage of (a) 0.1 g/50 mL and (b) 0.4 g/50 mL

Conclusions

Results proved that the prepared sorbent produced from precipitation of hydroxyapatite nanoparticles onto immobilized solid phase has a good ability in the removal of cadmium ions from simulated wastewater. This work represents a good application for concepts of sustainability because the preparation procedure based on using solid wastes (i.e. cement dust and sewage sludge) resulted from industrial activities. The best operational parameters required to achieve the maximum removal efficiency (>90%) were pH=5, time=120 min, and sorbent dosage= 0.4 g/50mL for initial metal concentration=50 mg/L and agitation speed of 200 rpm; however, the increase of initial concentration to 300 mg/L will be accompanied with decrease of removal efficiency to be 69% at the same mentioned best conditions.

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