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Investigation of Cadmium Adsorption by using of Peganum Harmala Seeds, Pine and Cypress Cone as Adsorbent from Aqueous Solutions

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ABSTRACT

In the present study, adsorption cadmium was studied by PHS, PC and CC in aqueous environment. Before batch adsorption study, adsorbent was dried by sunlight or oven, and then powdered adsorbent. Next effect of initial pH, contact time, agitation speed, adsorbent dose and cadmium initial concentration was investigated on adsorption cadmium. Finding study showed that cadmium adsorption on solution was dependent initial pH, contact time, agitation speed and initial cadmium concentration and adsorbent concentration, and also results implies that the best adsorption capacity (mg/g) cadmium for each three adsorbent in initial pH=10; and the highest efficiency adsorption cadmium for each three adsorbent in contact time=10 min obtained, saturation capacity adsorption adsorbents, the reason decrease efficiency adsorption in times greater than 10 min, agitation speed 100 rpm for PHS and agitation speed 150 rpm for PC and CC was better adsorbed cadmium; for each three adsorbent the best adsorption in adsorbent dose 10 g.L⁻¹ and in initial concentration cadmium 400 mg.L⁻¹ for each three adsorbent the highest adsorption cadmium observed. Study showed the best adsorption cadmium or removal it in fit to the process.

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INTRODUCTION

Nowadays, various metals are discharged from many sources into the environment. The sources of trace metals are associated with human activities. Cadmium (Cd) like as the other heavy metals can be introduced in significant amounts that effects on human health [1]. Cadmium, which is very toxic, can cause serious damage to the kidneys and bones. Itai-itai disease, renal damage, emphysema, hypertension and testicular atrophy are all harmful effects of cadmium [2]. The major sources of cadmium are industrial waters such as metal plating, cadmium-nickel batteries, phosphate fertilizer, mining, pigments, stabilizers and alloys [3]. The methods used to remove cadmium ions are chemical precipitation, adsorption, ion-exchange, reverse osmosis (RO), electro dialysis, electrochemical reduction, electrocoagulation, etc. Adsorption process is the most frequently applied method to industrial effluent treatment. A lot of studies on this process have been carried out [4]. Consequently, interest is growing in the use of sorbents made from low-cost renewable materials and agricultural wastes [4]. These materials are alternative adsorbents for heavy metals removal such of cadmium from aqueous environment. Several natural adsorbents, including algal biomass [5-9], peat moss [10-11], bark [12-15], and sugar beet pulp [16], have been investigated for their ability to removal cadmium from water. Adsorption of cadmium from aqueous solutions can take place via two mechanisms, ion exchange and complexation. In the ion-exchange mechanism, cadmium binds to anionic sites by displacing protons from acidic groups or existing alkali or alkali earth metals {e.g., sodium (Na) or calcium (Ca)} from anionic sites at high pH (8,10-11). This mechanism explains the release of light metal ions during heavy metal uptake experiments. In the complexation mechanism, cadmium sequestration is viewed as the coordination of cadmium to surface functional groups. Cadmium adsorption is considered a complex formation where cadmium is designated as the central atom and surrounding groups as the ligand(s) [9]. However, in both cases, the extent of cadmium but adsorption from aqueous solutions is strongly influenced by the chemistry and surface morphology of the sorbent.

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Methodology:

2.1 Materials used and sample preparation:

In this study powdered Peganum Harmala Seeds (PHS), pine cone (PC) and cypress cone (CC) were used as adsorbents. PHS with hull were collected from plain surround in Birjand city, South Khorasan Province, Iran, and then were dried by sunlight and powdered, and sieved to a uniform particle size (60 mesh). PC and CC collected from parks in Birjand city, At first, washed thoroughly with double distilled water to remove foreign materials, and then were dried in lab at 80 °C by oven for 24 hr and powdered, and then sieved to a uniform particle size (60 mesh).

2.2. Adsorption experiments:

This study was investigated in batch system. Batch adsorption studies were performed in 100 ml Erlenmeyer flasks inside an incubator container. The contents of all Erlenmeyer flasks were mixed thoroughly using magnetic stirrers with a fixed setting to achieve a constant speed. A stock solution of 1000 mg/L Cadmium was prepared by dissolving {Cd(NO₃)₂} in 1000 ml double distilled water. Required concentrations of Cadmium standards were prepared by appropriate dilution of the above stock cadmium standard solution. For every examination, at first 50 ml of samples with determinate concentration was added into the Erlenmeyer flask. For regulating the pH range, it was used the HCl or NaOH, 1 N addition of adsorbent were maintained throughout the experiments. Then having added the determinate dose of adsorbent was added into the Erlenmeyer flask and was shaking immediately in regulated speed by shaker. After desired contact time, the samples were filtered through Whatman No. 42 filter paper. The filtrates were analyzed for residual cadmium concentration. The main process parameters considered were pH 2- 12 (2-3-4-5-6-7-8-9-10-11-12), initial cadmium concentration 25–400 mg/L (25-50-100-200-400 mg/L), adsorbent dose 0.5-10 g/L (0.5-1-2-3-4-6-10 g/L), contact time 2-120 min (2-5-10-15-20-30-40-60-80-120 min) and agitation speed 0-300 rpm (0-50-100-150-200-300 rpm). For being sure about the results' accuracy, every sample was examined two times and the average number was reported as result.

2.3. Analytical method:

At the end of each step, the supernatant liquids were filtered and the residual cadmium concentrations were measured by atomic absorption spectrophotometer T80+UV/VIS Spectrophotometer at 540 nm wavelength.

The spectrophotometer was calibrated by a series of standard solutions, which were prepared for each run from 1000 mg/l cadmium reference solutions [17].

The pH was measured by a pH meter Knick 765. At the end of the experiment, data were analyzed by Microsoft Excel software.

RESULTS AND DISCUSSIONS

3.1. The effect of initial pH:

The effect of initial pH on cadmium adsorption was studied in the pH ranges from 2 to 12. The results from these experiments are presented in figure 1. As shown in figure 1 adsorption capacity in pH 2 for PHS, CC and PC were 8.43 mg/L, 8.9 mg/L and 8.9 mg/L respectively and by increasing pH from 4 to 10 the adsorption capacity was increased too, so the adsorption capacity in pH 10 for PHS, CC and PC were 19.35 mg/L, 23.45 mg/L and 21.7 mg/L respectively. Therefore the high adsorption capacity occurred in pH equal to 10 and by increasing pH from 10, adsorption capacity decreased for tree adsorbent.

The low adsorption of cadmium at lower pH may be due to the positively charged sorbent and sorbent species, which leads to an electrostatic repulsion interaction [18-19]. Besides this, a higher concentration of H⁺ in the solution competes with cadmium ion for adsorption sites, resulting in the reduced uptake of cadmium ions [18-19]. With increasing pH, the concentration of H⁺ decrease but the cadmium ions concentrations remain constant [18-19]. Therefore, a competition in the adsorption process between H⁺ and cadmium ions becomes more evident for values below 4 [18-19].

3.2. The effect of contact time:

Figure 2 represented the effect of contact time (2 to 180 min) on cadmium adsorption in experimental conditions as follow: (adsorbent dose: 4 g/L; initial concentration cadmium: 100 mg/L; initial pH=10 for each three adsorbent; agitation speed 100 rpm for PHS and agitation speed 150 rpm for pine cone and cypress cone).

The high adsorption capacity for each three adsorbents achieved in contact time equal 10 min, but by contact time increasing the adsorption capacity was constant. This phenomenon is due to saturation the adsorbents pores in first time as adsorption process [18].

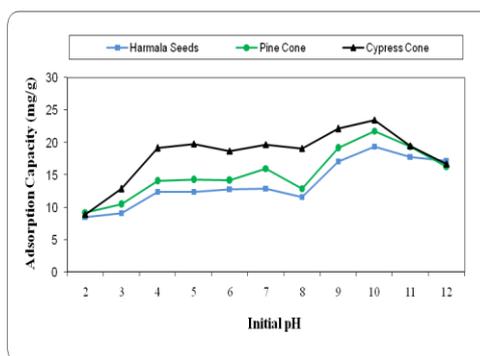


Fig. 1: Effect of initial pH (2 to 12) in adsorption Cd^{2+} [adsorbent dose=4 g.L⁻¹; Initial Cd^{2+} concentration=100 mg.L⁻¹; contact time=10 min; agitation speed: 100 rpm for PHS and 150 rpm for PC and CC].

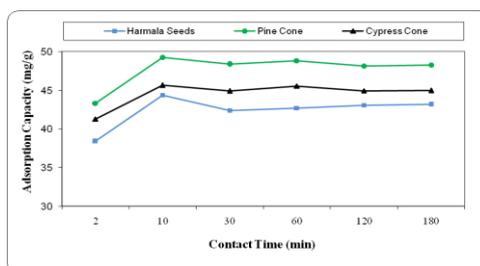


Fig. 2: Effect of contact time (2 to 180 min) in the adsorption Cd^{2+} [adsorbent dose=4 g.L⁻¹; Initial Cd^{2+} concentration =100 mg.L⁻¹; initial pH=10 and agitation speed: 100 rpm for PHS and 150 rpm for PC and CC].

3.3. The effect of agitation speed:

Figure 3 represented the effect of agitation speed (0 to 300 rpm) on cadmium adsorption in experimental conditions as follow: (adsorbent dose: 4 g/L; initial concentration cadmium: 100 mg/L; initial pH=10; contact time=10 min for each three adsorbent).

Results indicated that adsorption capacity is increased with agitation speed increasing, however the most cadmium adsorption for PHS achieved in agitation speed equal 100 rpm and for PC and CC adsorbent were occurred 150 rpm. But with increase from these optimum agitation speeds for all adsorbents adsorption of cadmium was decreased. The result of this phenomenon can be described as follow: the binds complex between metal ions and adsorbents in higher agitation speed will be break and the capacity adsorption will be decreased as its consequence [20].

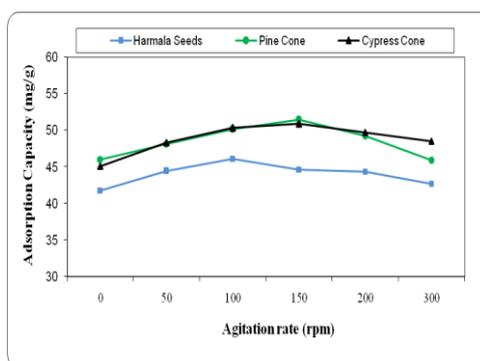


Fig. 3: Effect of agitation speed (0 to 300 rpm) in the adsorption of Cd^{2+} [adsorbent dose=4 g.L⁻¹; Initial Cd^{2+} concentration =100 mg.L⁻¹; initial pH=10 and contact time=10 min for three adsorbent].

3.4. The effect of adsorbent dose:

The effect of adsorbent dosage (0.5 to 10 g/L) on cadmium adsorption with experimental conditions (initial concentration cadmium: 100 mg/L; contact time: 10 min.; initial pH=10 for each three adsorbent and agitation speed 100 rpm for PHS and agitation speed 150 rpm for PC and CC) is presented in figure 4. As can be seen, the

cadmium adsorption for three adsorbents was increased from 0.5 g/L (82, 87 and 90% for CC, PHS and PC respectively) to 2 g/L for CC and PC (96 and 94% respectively) and 3g/L for PHS (97%), but by increasing the adsorbent dosage from optimum condition there is not significant effect on cadmium removal efficiency. Because by adsorbent dosage increasing, the available site for cadmium adsorption is increased, and therefore the cadmium adsorption increased too. But by passing of optimum dosage the cadmium ions are constant and available sites for binding with cadmium ion increased, therefore the removal cadmium efficiency will be negligible [21-25].

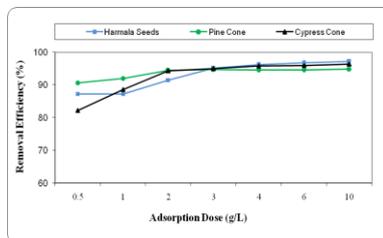


Fig. 4: Effect of dose adsorbents (0.5 to 10 g/L) for the adsorption of Cd²⁺ [Initial Cd²⁺ concentration =100 mg.L⁻¹; contact time=10 min; pH=10 for three adsorbent and agitation speed: 100 rpm for PHS and 150 rpm for PC and CC.

3.5. The effect of initial cadmium concentration:

Effect of initial cadmium concentration (25 to 400 mg/L) on cadmium adsorption with experimental conditions (adsorbent dose: 2 g/L for PC and CC and 3g/L for PHS; contact time: 10 min; initial pH=10 and agitation speed 100 rpm for PHS and agitation speed 150 rpm for PC and CC) is shown in figure 5.

This figure represented that adsorption capacity increased with cadmium concentration increasing. The most adsorption capacity achieved in 400 mg/L for each three adsorbents but the removal efficiency decreased by cadmium increasing (results is not shown),

This happens because more accessible and easier cadmium for absorption by adsorbents was occurred [26-27].

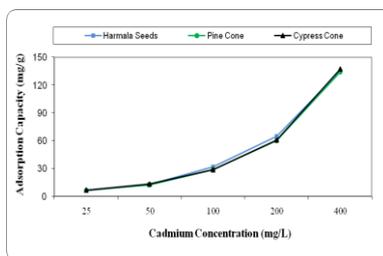


Fig. 5: Effect of initial cadmium concentration (25 to 400 mg.L⁻¹) for Cd²⁺ adsorption [adsorbent dose: 2 g/L for PC and CC and 3g/L for PHS; contact time: 10 min; initial pH=10 and agitation speed 100 rpm for PHS and agitation speed 150 rpm for PC and CC].

Conclusion:

In this study, we used from three low-cost adsorbents (PHS, PC and CC) for cadmium removal from aquatic environments. The effects of the different operational parameters are investigated on cadmium removal. The following conclusions can be achieved from the experimental results in this work:

The results show that the adsorbents derived from PHS, PC and CC can be fruitfully employed for the removal of cadmium and other heavy metals from wastewater.

PHS, PC and CC are a potential adsorbent for metal ions such as cadmium. The main features of these adsorbents are its availability in large quantities, low cost, and a good ability for binding metal ions.

In this study, effects of the contact time, initial pH, adsorbent dose and temperature was investigated, Their findings shown that higher efficiency of cadmium adsorption and removal in agitation speed and initial pH upper, lower temperature, and upper adsorbent dose have positive effect on the uptake of cadmium by the PHS, PC and CC as adsorbents.

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