Experimental study of Cd(II) ions elimination by bionanocomposite hydrogel based on starch-g-poly(acrylic acid) reinforced with cellulose nanofibers in a fixed bed column

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Abstract
In the present study, continuous adsorption of bio-nanocomposite hydrogel for removing Cd(II) ions from aqueous solution using a fixed-bed column was investigated. The bio-nanocomposite hydrogel was synthesized based on starch grafted poly (acrylic acid) (St-g-PAA) reinforced by cellulose nanofibers (CNFs). The effect of operating conditions of pH, initial concentration, and flow rate on process efficiency were investigated by using a three level Box-Behnken design (BBD) comprising 15 experiments. The gained data was employed to develop a polynomial model to optimize Cd(II) ions removal efficiency. The model specifies, the optimum Cd(II) ions removal efficiency at 82.45%, for operating conditions of pH=5, initial concentration of 10 mg/L, and flow rate of 5 mL/min, while under these conditions the efficiency was measured at 82%.

Keywords: Starch hydrogel, Adsorption process, Cadmium ions, Fixed- bed column, BoxBehnken design

Introduction
Heavy metal ions are major pollutants released in environment and cause serious health concerns on human and wildlife. Cd(II) as a heavy metal ion, is highly hazardous to human beings causing many health problems in several organs such as kidney, lung, and liver [1]. This has an extremely long biological half-life that essentially initiating a cumulative toxin [2]. The main source of Cd(II) ion pollutant in water are metal, cement, pigment and plastics production, petrochemical complexes [3], coatings [4], phosphate fertilizer, mining, and battery industries [5]. Various techniques are available for the removal of heavy metal ions. These are chemical precipitation, ion exchange, electrochemical treatment, membrane technologies, photo catalysis, solvent extraction, and reverse osmosis [6]. Removal of metal ions from solution by these techniques are not only costly but also produce waste by-products [7]. Among the technologies, adsorption is considered as one of the most suitable techniques for treatment of waste water containing Cd(II) ions [8]. Application of adsorption techniques for large scale wastewater treatment usually employ continuous operations, such as fixed bed units. These can treat large volumes of contaminated water in a shorter time period. These units can be easily scaled up from laboratory to pilot unit, and the process is easy to monitor and operate.

Continuous adsorption processes using fixed bed columns are effective processes for cyclic adsorption/desorption as they depend on driving force of concentration gradient. This in turn allows for efficient utilization of the adsorbent efficiency and results in higher quality of effluents [9]. Different adsorbents such as clays, zeolites [10], resin [11] and activated carbon [12] have been successfully applied for the removal of metal ions from waste water. However, bio-adsorbents have unique properties such as biodegradability, low- cost, and abundant availability [7].

Biohydrogels are typical examples of bio-adsorbents with the three-dimensional hydrophilic networks contained chemical and/or physical cross-linking. These have the ability of adsorbing and retaining large amounts of water or biological fluids without dissolution [13]. Hydrogels derived from biopolymers can be produced from a wide range of materials including gums, collagen, cellulose, alginate, carrageenan, and chitosan. Hydrogels based on starch are attractive due to their biodegradability and successful application in removal of organic and inorganic pollutants from aqueous solutions [7,14]. The adsorption capability and mechanical performance of hydrogels can be improved by incorporating reinforcement materials such as cellulose nanofibers (CNFs) [15].

In recent years, experimental softwares have usually to optimize number of experiments and reduces reagent and utility consumption. The most common designs for organized experiments are based on Central Composite Design (CCD) and Box-Behnken Design (BBD) from response surface method (RSM) [16]. Application of experimental design facilitate analizing of gained data.

Several studies have been reported on application of hydrogels for the adsorption of contaminants from water [17-19]. But, only a few of them were investigated in fixed-bed column systems [9,20]. In the present study, Starch-g-Poly (acrylic acid) CNFs reinforced (St-g-P(AA)/ CNFs) hydrogel beads were synthesized and used as adsorbents in a fixed-bed column for removal of Cd(II) ions from aqueous solution. The parameters influencing on the Cd(II) ions removal efficiency, such as pH, initial concentration, and flow rate of contaminent solution were investigated. Furthermore, the Box-Behnken design was used to estimate optimum values of the effective parameters on an efficient removal of the Cd(II) ions through the adsorption column.

Experimental

Provided Materials used in this study were corn starch (Qazvin Glucosan Iran company),
CNFs (Nano Novin Polymer Company, Iran), N, N'- methylene bisacrylamide (MBA), potassium persulfate, acrylic acid (AA), cadmium nitrate tetrahydrate, hydrochloric acid, and sodium hydroxide (Merck, Germany). In all experiments, deionized water was used to prevent ions competition on adsorption process.

In order to prepare St-g-P(AA)/ CNFs hydrogel, at first 1 g of starch was mixed with 30 mL deionized water in a four-neck reactor until gelatinized at 85-95˚C. The mixture temperature was slowly cooled down to 60˚C. Then, 1wt.% potassium persulfate was added as a primer to the reactor solution. After 10 min, a solution containing 2 g CNFs, 10 mL of deionized water, 3.65 g AA and 1wt.% MBA cross linker, was added to the reactor contents. The reaction was performed at temperature of 70˚C for a period of 3 hr. At all stages, a mechanical stirrer at rate of 300 rpm was used to homogenize the mixture [21].

A solution containing Cd(II) ions at concentration of 500 mg/L was prepared and the other solutions were obtained by dilution. To adjust pH of solutions hydrochloric acid (1M) and sodium hydroxide were used. The concentration of Cd(II) ions was measured by atomic absorption spectroscopy (Buck Scientific Company VGP-210).

In this study, a Plexiglass® tube with 30 cm height and 5 cm inner diameter was used to design the fixed-bed column system. In order to prevent blockage of the column by swollen hydrogels, trays with a distance of 5 cm were inserted into the column and 0.2 g of hydrogel were placed on each tray. The solution containing Cd(II) ions was pumped through the top of the column and samples were taken from the bottom of the column at the specified time intervals. All tests were carried out at ambient temperature, 25˚C.

The Cd(II) ions removal efficiency for various samples were calculated by Equation 1:

$$R(\%) = \frac{C_0 - C_e}{C_0} \times 100 \qquad (1)$$

Where C_0 is the initial concentration and C_e is the equilibrium concentration of Cd(II) ions of the solutions during the process.

In this study, Box-Behnken design response level method was used to develop a quadratic model and evaluate the effect of independent variables on cadmium ions removal efficiency, as well as predict the optimum response value. The total of 15 experiments were performed. The intended variables and levels are shown in Table 1. All of the results were incorporated into the Box–Behnken design by using Design-Expert software (version 11.0.3.0)

Table 1. Independent variables level and their experimental values in Box-Behnken design

		Levels		
Variables	Symbol	-1	0	+1
pH	A	4	5	6
Initial concentration (mg/L)	B	10	30	50
Flow rate (mL/min)	C	5	10	15

Results and discussion

The experimental runs were performed and based on the gained data, a quadratic mathematical model was obtained to represents the effect of three independent variables (A, B, and C) on the response values of Cd(II) ions removal efficiency, Equation 2.

$$\text{Ion Removal Efficiency } (\%) = -585.13 + 269.12A - 0.76B - 2.54C + 0.07AB + 0.27AC + 0.01BC - 26.74A^2 \qquad (2)$$

The adequacy of a fitted-response surface model was statistically evaluated based on the coefficient of determination (R^2) and the ANOVA results. A model F-value of 265.35 and a very low probability value (less than 0.0001) implies the significant fitted model. The P-value of B^2 and C^2 are 0.93 and 0.73 respectively. Therefore, they are insignificant in the derived model as their values are greater than 0.1. The "lack of fit" of P-value is 0.3598 that shows it is insignificant comparing to the pure error. The R^2 value was 0.998 that indicate the models could be successfully implement to predict the Cd(II) ions removal efficiency within the experimental range.

Considering the significance of the obtained model, it can be used to predict the optimal values. The optimum percentage of Cd(II) ions removal and the operating conditions are presented in Table 2.

Table 2. The optimized process variables and removal efficiency based on the model

Flow rate (mL/min)	Initial concentration (mg/L)	pH	Ions removal efficiency (%)
5	10	5	82.45

For validation, duplicate confirmatory experiments were conducted using the optimized parameters and the Cd(II) ions efficiency was obtained at 82.02%.

The combined effects of independent variables on Cd(II) ions removal efficiency are represented in figure 2.

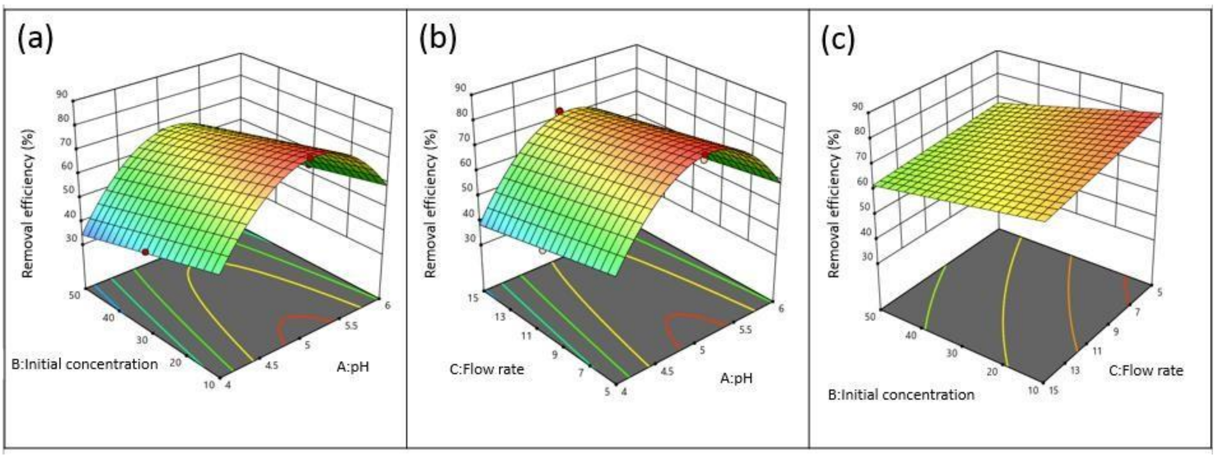

Figure 2. Cadmium ions removal efficiency under various operational conditions (a) pH and initial concentration, flow rate= 5 mL/min (b) pH and flow rate, initial concentration = 10 mg/L (c) initial concentration and flow rate, pH=5.

Figures 2a and 2b showed the variation of Cd(II) ions removal efficiency upon variation of pH from 2 to 6. As shown, the removal efficiency of Cd(II) ions was increased by changing from acidic to alkaline medium and the maximum removal efficiency was occured at pH = 5. In the low pH value, there is a strong competition between the C(II) and H^+ ions. As the pH increases, Cd(II) ions have more chance to be adsorbed on the adsorbent sites due to less competition. On the other hand, by increasing pH value, some -COOH groups are converted to -COO groups and more adsorption sites are formed. Experiments were not carried out at pH higher than 6 due to formation of cadmium hydroxide that may results be inconclusive [8]. The initial concentration of the solution containing Cd(II) ions affects the adsorption rate. As illustrated in Figures 2a and 2c, by increasing the inlet initial Cd(II) ions concentration the removal efficiency of Cd(II) ions was decreased. As a certain amount of hydrogel adsorbent in the fixed bed column

have specific active sites, the chance of Cd(II) ions adsorption on the active sites is enhanced by decreasing the concentration of Cd(II) ions [22].
As shown in Figures 2b and 2c, by increasing the inlet flow rate the removal efficiency was decreased. At low flow rate, the Cd(II) ions have more time to travel along the column for adsorption, hence the removal efficiency is increased [22].

Conclusions

In this study, bio-nanocomposite hydrogel was synthesized based on starch grafted poly (acrylic acid) reinforced by CNFs to employ as an adsorbent for removing Cd(II) ions from aqueous solutions using a fixed bed column. The experimental design procedure based on Box-Behnken design was performed to evaluate the effect of independent variables (pH, initial concentration, and flow rate) on Cd(II) ions removal efficiency. The results indicate by either of increasing pH, or decreasing of Cd(II) ions concentration or flow rate enhance the removal efficiency. Based on a developed model, the optimum percentages removal for Cd(II) ions was 82.45% at pH of 5, initial concentration of 10 mg/L, and flow rate of 5 mL/min. By performing an experiment under this operating condition, the removal efficiency was 82.02% that confirm the model.

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