



Study of Co(II) adsorption from aqueous solution using protein granules produced from chicken feather

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Abstract

Background: Co(II) constitutes a part of vitamin B₁₂, hence, it is necessary for human health. However, at concentrations higher than the permissible limits, humans and animals suffer adverse chronic effects. It is necessary to reduce the concentration to a permissible level. In the present study, pre-purification and thermal modification of chicken's feather increased their porosity and they were used to adsorb Co(II) ions from aqueous solutions.

Methods: Chicken feather was procured from a slaughter house, washed with detergent and dried at laboratory temperature. To increase the porosity and remove the organic pollutants attached to the feather, feathers were heated in the oven for 1 hour at 165°C. Some batch experiments were conducted to optimize the parameters affecting the adsorption process, such as solution pH, initial concentration of Co(II) and contact time, at a constant agitating speed and temperature.

Results: The p*H*_{zpc} of chicken's feather granules obtained was 5.3. The results showed that a time of 60 minutes, pH value of 9 and initial concentration of 10 mg/l were the optimum conditions for Co(II) removal by the adsorption process. Increasing the initial concentration of Co(II) from 10 to 50 decreased the removal efficiency from 52% to 26%. The pseudo-first order kinetic model provided the best correlation ($R^2 = 0.998$) for adsorption of Co(II) on chicken's feather granules.

Conclusion: The increase in electrostatic repulsion forces between positive charges of Co(II) ions decreased the removal efficiency at higher concentrations of Co(II) ions. The maximum efficiency of Co(II) adsorption was obtained at pH= 9, which is higher than the p*H*_{zpc} of the adsorbent.

Keywords: Adsorption, Chicken feather, Co(II), Protein.

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Introduction

Heavy metals are produced from different industrial activities and regarded as the main cause of water pollution (1,2). They accumulate in microorganisms, aquatic plants and animals, and finally enter the environment and the human food chain, resulting in health problems (3). Cobalt is a common toxic metal which contaminates the environment remarkably (4). It constitutes a part of vitamin B₁₂ and consequently, its presence in the food chain is necessary for human health. However, at concentrations above the permissible limits, humans and animals suffer chronic adverse effects (5). The Environment Preservation Agency (EPA) has determined 5 ppb as the maximum allowable amount of Co(II) in drinking water (6). Different technologies, such as electro-dialysis, ion exchange, reversed osmosis, ultrafiltration, chemical precipitation and adsorption have been used for the removal of metal

ion, which have low cost in performance (7-9). Among the different technologies for purification, absorption is regarded as a fast, cheap and efficient method. Recently, the use of industrial and agriculture wastes have increased, as reported by some researches (10). Chicken feather is a natural and cheap adsorbent. It was previously used to provide creatinine nanoparticles which had a good efficiency in the removal of pollutants. In addition, using the waste of feather as an adsorbent, is an environment – friendly method and cleans subsequent contamination from the environment. It has been proven that the redundancy of chicken's feather which is insoluble has non-toxic creatinine and has great ability to adsorb inorganic pollutants (11,12). In previous studies, chicken's feather was used to remove aquatic pollutants such as heavy metals including As, Cd, Cr, Cu, Zn, etc (13,14). Zhou et al (15) conducted a study to adsorb oil from aquatic solutions



using a creatinine porous foam made of chicken's feather. Their results showed that the modified adsorbent had a great adsorption capacity for the removal of oil products. Eslahi et al (16) estimated the feasibility of producing nanoparticles from feather wastes after modification with ultrasonic and enzymatic hydrolysis. Their results showed that the particle size decreased after ultrasonic hydrolysis. In this research, the thermal stability of feather nanoparticles increased with enzyme hydrolysis during ultrasonic hydrolysis. In 2013, Pandima Devi and Muthukumaran (17) used chicken's feather as an adsorbent in the removal of color from water. In their study, adsorption capacity was determined with regard to conditions of pH, contact time, temperature, adsorbent amount and adsorbate concentration. The data were consistent with Freundlich and Langmuir isotherm. Yang et al (18) modified feather with tannic acid 5% and used it to remove metal cations from aqueous solutions. Their results indicated that the fiber of the feather modified with tannic acid had a high adsorption for metal cations. They concluded that it can be used as metal ion adsorbent from aqueous solutions (18). In the present study, pre-purification and thermal modification of chicken's feather increased its porosity and were used to adsorb Co(II) from aqueous solutions.

Methods

This descriptive study was carried out in 2015 in the Chemistry Laboratory of the Health School, in Shahid Sadooghi University of Yazd. All chemicals used for the tests were of analytical purity grade, and purchased from the Merck Company. The following equipment were used for this study namely a distillation device, analytic sensitive scale of 0.0001 g accuracy model HR200 of A & D Japan, pH-meter model MI 151 of Wagtech, orbital shaker (GFL 137) and atomic absorption spectrophotometer model 20 AA Varian.

Preparation of adsorbent

Chicken's feather was procured from the slaughter house, washed with detergent and dried under the laboratory temperature. To increase their porosity and to remove the organic pollutants attached to the feather, the dried feathers were heated in the oven for 1 hour at 165°C. The protein granules were obtained after grounding the feather and then, the ground feathers were sized with standard sieves of 60 and 100 meshes (250 and 149 μ diameter). To remove organic materials, the separated granules were rinsed with ethanol 20% and distilled water. After drying, the granules were kept in desiccators for the next tests.

Adsorption experiments

To investigate pH_{zpc} , 50 ml of the 0.1M NaCl solution was introduced to 8 flasks of 250 ml and the pH was adjusted in the range of 2-12 by 0.1M NaOH or HCl solutions, 0.1 g adsorbent was added to each flask. The suspension was shaken for 24 hours and the final pH was recorded

after filtration.

The parameters affecting the process, such as pH of solution, initial concentration of Co(II) and contact time for Co(II) adsorption, were optimized by batch adsorption. For adsorption tests, first, a stock solution of 50 mg/L Co(II) was prepared from cobalt nitrate salt and the required concentrations were provided with dilution of stock solution by distilled water. To determine the effect of contact time, the experiments were carried out at a contact time of 30, 60, 90, 120 and 180 minutes, while all other parameters were kept constant. To determine the effect of pH on the adsorption efficiency of Co(II) using protein granules of the feather, all the parameters were kept constant and pH was varied in four levels of 3, 5, 7 and 9 by a buffer solution. Then, 0.1 g of adsorbent was added and was in contact with the pollutant for a fixed time, so that the process of adsorption could take place. In the next stage, to examine the effects of initial concentration on the adsorption efficiency, all the parameters were kept constant and the initial Co(II) concentration was varied by 10, 20, 30, 40 and 50 mg/L.

For all the tests, to have a good contact of adsorbent with Co(II) in the suspension and to control the temperature, each sample was agitated by an orbital shaker at 150 rpm in a 250 ml flask. After a desired contact time, the flasks were removed from the shaker and the adsorbent was separated from the suspension by a Whatman filter. The clear solution was analyzed to get the remaining Co (II) concentration by using an atomic absorption spectrophotometer. The following formula was used to calculate the adsorption efficiency and capacity:

$$\%RE = \frac{(C_0 - C_e)}{C_0} \times 100 \quad (1)$$

$$q = \frac{(C_0 - C_e)}{m} \times V \quad (2)$$

Where C_0 and C_e , are the initial and final concentrations of Co(II) (mg/l) respectively, V is volume of suspension (L), m is mass of adsorbent, q is adsorption capacity and RE is removal efficiency (3).

Results

The pH_{zpc}

pH_{zpc} is the pH at which adsorbents have a net zero surface charge. Figure 1 shows the plot between pH_{final} and $pH_{initial}$ for determining pH_{zpc} . The results indicated that the pH_{zpc} for chicken's feather granules was 5.3. Chicken's feather granules becomes more positively charged when pH is less than pH_{zpc} and more negatively charged when pH is above pH_{zpc} .

The adsorption experiments were conducted in a stepwise manner. In each stage of the test, regarding a variable, other conditions were constant and the next stages were examined with optimum parameters being constant from

previous stages.

The effect of contact time on adsorption efficiency

Figure 2 shows the effect of contact time on the removal efficiency of Co(II) in aqueous solution. The efficiency of granules of chicken's feather to remove Co(II) increased with an increase in contact time. The removal efficiency increased from 52% to 59% with the increase of contact time from 30 to 180 minutes.

Regarding the obtained results, the equilibrium time of 60 minutes for the Co(II) adsorption on the modified chicken feathers was chosen as the optimum contact time and it was constant in the next experiments.

In order to investigate the adsorption characteristic, kinetic constants of adsorption were determined by pseudo-first order and pseudo-second order equations based on the solid phase adsorption. Table 1 shows equations and parameter values of the linearized forms of the pseudo-first order and pseudo-second order model for adsorption of Co(II) onto granules of chicken's feather.

According to the coefficient regression of kinetic investigation, the high correlation coefficient ($R^2=0.998$) was shown in the pseudo-first order model.

The Effect of pH on adsorption efficiency

Figure 3 shows the effect of solution pH on Co(II) removal with chicken's feather by a batch adsorption process. To investigate this, the adsorption equilibrium was studied under four pH levels of 2, 5, 7 and 9 at a constant time of 60 minutes.

As can be seen in Figure 3, increase in pH had a remarkable effect on the removal efficiency. Hence, increasing the pH from 3 to 9 enhanced the absorption efficiency from 0% to 52%.

The effect of initial Co(II) concentration on adsorption efficiency

The effect of initial concentration on the removal efficacy shown in Figure 4 indicates that an increase in the initial concentration of Co(II) caused a decrease in the removal

rate. Also, an increase in initial concentration from 10 to 50 mg/L, decreased the removal efficiency from 52% to 26% at contact time of 60 minutes.

Discussion

By increasing the contact time, the efficiency of Co(II) removal increased and the removal of Co(II) increased from 54% to 59% when the time increased from 30 to 180 minutes. Figure 2 shows that the rate of adsorption was high at the initial time (<60 minutes) and decreased gradually while the adsorption rate had a constant trend, which is probably due to the large number of empty sites available on the adsorbents at the initial stage. Over time,

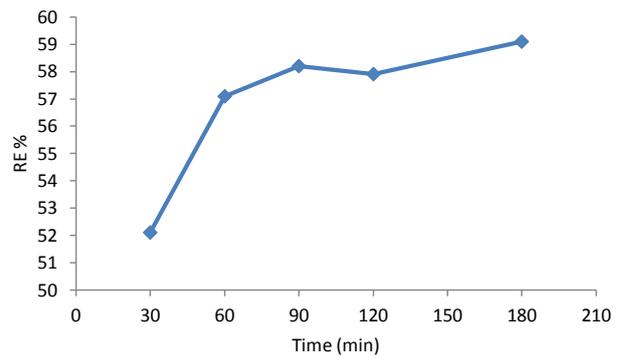


Figure 2. Effect of contact time on Co(II) removal at $C_0 = 5$ mg/l, pH = 9, m = 0.1 g.

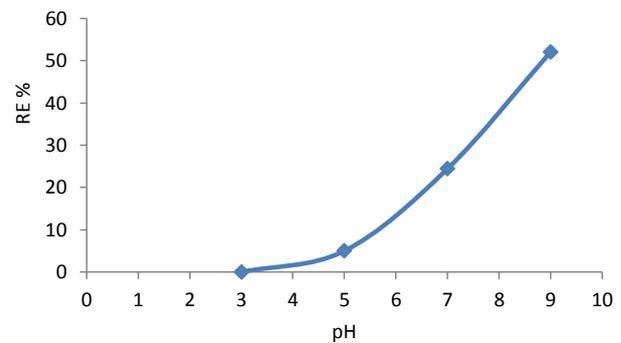


Figure 3. Effect of pH on Co(II) removal at $C_0 = 5$ mg/l, m = 0.1 g.

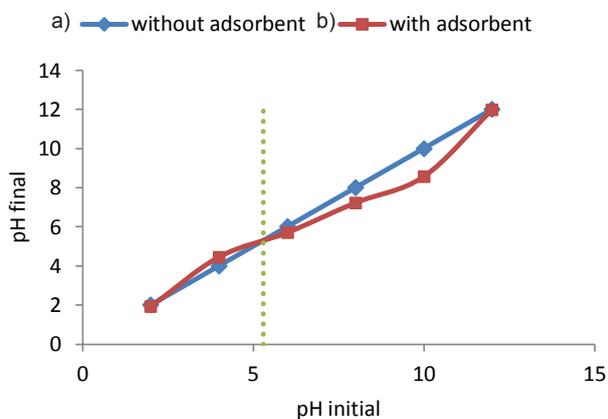


Figure 1. The plot of pHf vs pHi; a) without adsorbent, b) with adsorbent.

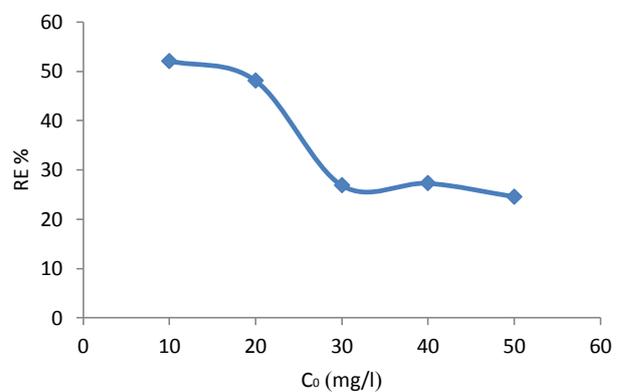


Figure 4. Effect of initial concentration on Co(II) removal at pH = 7, m = 0.1 g.

Table 1. Parameter values using pseudo-first order and pseudo-second order model for adsorption of Co(II) onto protein granules of chicken's feather

Linear equation	Pseudo-first order			Pseudo-second order		
	$t/q_t=1/q_e \cdot t + 1/K_2 q_e^2$			$\ln(q_e - q_t) = \ln q_e - K_1 t$		
Metal ion	q_e	K_1	R^2	q_e	K_2	R^2
Co(II)	3.05	5.6×10^{-2}	0.998	1.11	5.6×10^{-2}	0.947

the accumulation of Co(II) ions on empty sites resulted to less number of active sites and increased the number of adsorbed particles from the solution, which led to a decrease in the adsorption rate of Co(II) from the solution. At the initial stage of the process, the concentration gradient increased between adsorbed material in the solution and surface adsorbent. This led to the increase of Co(II) adsorption in the initial stages. At times higher 60 minutes, the concentration decrease led to a decrease in the adsorption rate. These findings are consistent with those of Olgun and Atar (19) on copper and cobalt removal from aqueous solution by B wastes.

According to the results of kinetic investigations, the correlation coefficients in these models were more than 0.90 and the experiment data showed a good fit for the two models. Nevertheless, the maximum correlation coefficient was detected in the pseudo-first order model. So, the adsorption process followed the pseudo-first order model and this shows that the rate of adsorption depend on one component in the reaction. On the other hand, the adsorption rate was related to the concentration of Co(II) in the solution.

The results showed that variations of solution pH had a direct relationship with the removal efficiency. The maximum removal efficiency of Co(II) was obtained at pH = 9. According to Figure 1, the zero point charge (pH_{zpc}) of adsorbent was specified to be 5.3, then, at pH lower than pH_{zpc} , the surface charges became positive. It increased electrostatic repulsion force between Co(II) ions and adsorbent. So, the removal efficiency of Co(II) decreased at lower pH. At higher values of pH, greater than pH_{zpc} , due to OH⁻ attraction by the adsorbent, the adsorbent had negative charge which produced a powerful electrostatic force with positive ions of Co(II) and adsorbent. Therefore, Co(II) removal increased at higher values of pH. These findings are consistent with those of Abbas et al (3) on kinetic studies of cobalt absorption on apricot stone activated carbon and those of Yu et al (20) on the effect of pH, ion strength and fulvic acid on sorption and desorption of cobalt from aquatic solution by bentonite.

The rate of absorption was determined at five initial Co(II) concentration levels of 10, 20, 30, 40 and 50 mg/L. As can be seen in Figure 4, the greatest value of Co(II) removal was in the concentration of 10 mg/L. Increasing the initial concentration of Co(II) from 10 to 50 mg/L decreased the removal efficiency from 52% to 26%. At lower concentrations of Co(II), adsorption took place at empty sites

on the adsorbent surface, due to the short length of diffusion path and presence of enough active sites, while in higher concentrations of Co(II), these empty sites became saturated and greater adsorption required penetration in deeper areas of adsorbent passing from a relatively long path which decreases the efficiency of adsorption. With increase in electrostatic repulsion forces between charges of Co(II) ions, the adsorption and removal efficiency decreased. In higher concentrations, some Co(II) ions were adsorbed on the surfaces of granules of feather; therefore, these ions made the great spaces around granules of adsorbent to become filled and increased the spatial prevention for other ions. These findings are consistent with those of Ahmadpour et al (21) on the removal of cobalt from aquatic solutions by almond green hull and those of Al-Shahrani (22) on the purification of waste water contaminated with cobalt using active bentonite.

Conclusion

Porous protein granules, the name for the residual chicken's feather remaining after slaughtering, was extracted and left as a waste product in an industrial poultry slaughterhouse. It was converted to an adsorbent and used for the removal of aqueous Co(II) from wastewater. The adsorption of Co(II) ions increased with an increase in solution pH and decreased with the initial concentration of Co(II) ions.

The results showed that the protein granules derived from a slaughterhouse can be effectively employed for decreasing the Co(II) concentration in wastewater. The results show that the removal efficiency of the porous granules derived from chicken's feather for Co(II) is comparable or more than the other available adsorbents. Also, it is a waste generated in the slaughter industry and can be easily available. Therefore, the cost of the porous granules prepared from chicken's feather would be cheaper than the commercially available adsorbents.

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Ethical issues

This study was approved by the ethical committee of Shahid Sadoughi University of Medical Science.

Competing interests

The authors declare that they have no competing interests.

Authors' contributions

The study was directed by MF who performed all the experiments. MHSN is the first author and guided on the experimental methods and drafted the manuscript. All authors have read and approved the final manuscript.

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