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# Application of almond green hull for the removal of cobalt ion from aqueous solution

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**Abstract** The presence of heavy metals in the environment is of important concern due to their toxicity and health effects on human and other living creatures. Cobalt is one of the usual toxic heavy metal present in the waste water of nuclear power plants and many other industries. The standard level of cobalt in drinking water is 2 $\mu gL^{-1}$ but values up to 107 $\mu gL^{-1}$ have been also reported. Many different adsorbents have been used for the removal of cobalt. In the present investigation, almond green hull, an agriculture solid waste, was used for the adsorption of Co(II) from aqueous solutions. The efficiency of this adsorbent was studied using batch adsorption technique under different experimental conditions such as adsorbent dose, initial metal-ion concentration, contact time, adsorbent particle size, and chemical treatment. Optimum dose of adsorbent for maximum metal-ion adsorption were 0.25 g for 51.5 $mgL^{-1}$ and 0.4 g for 110 $mgL^{-1}$ concentrated solutions, respectively. Also, the adsorption of Co(II) on almond green hull followed pseudo second-order kinetics. Adsorption isotherms were expressed by Langmuir and Freundlich adsorption models. The Langmuir adsorption model fits the experimental data reasonably well compared to the Freundlich model. Maximum adsorption capacity of this new sorbent was found to be 45.5 $mgg^{-1}$. The present study revealed that such a low cost material may be used as an efficient adsorbent for the removal of cobalt from wastewater streams.

Keywords: Almond Green Hull, Agricultural Waste, Sorbent, Cobalt, Pesudo-Second-Order.

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## Introduction

Heavy metals are frequently present in the aquatic streams by different industrial wastewaters. The presence of these metals in environment is of importance concern due to the toxicity and health effects on the human and living creatures. There are various methods for the removal of heavy metals including: chemical precipitation (Mauchauffée and Meux, 2007), reverse osmosis (Mohsen-Nia et al., 2007), ion exchange (Verma et al., 2008), and adsorption (Meena et al., 2008). Cobalt is one of the usual toxic heavy metal affecting the environment and present in the waste water of nuclear power plants and many other industries such as mining, metallurgical, electroplating, paints, pigments and electronic (Manohar et al., 2006). The standard level of cobalt in drinking water is 2 $\mu gL^{-1}$, but values up to 107 $\mu gL^{-1}$ have been reported (EPA). Different sorbents used for the removal of cobalt ions are: industrial waste (Bhatnagar et al., 2007), sepiolite (Kocaoba and Akyuz, 2005), pre-treated arca shell biomass (Dahiya et al., 2008), ETS10, and ETAS 10 (Choi, 2006). In the present study, a new low cost materials i.e. almond green hull was used for the removal of Co (II) from aqueous solution. Almond green hull is an agricultural crop residue from almond fruit that is not usually used by animals and human.

## Materials and methods

Cobalt chloride was obtained from Merck in analytical grade. Stock solutions were prepared by dissolving cobalt chloride in the de-ionized water. The sorbent i.e. green hull of almond was first washed with distilled water to remove soluble impurities. Then, sample was dried in an electric oven for 20 hours at 180°C. Dried sample was ground and chemical treatment was then carried out with the solution of hydrogen peroxide (2%) + ammonia (2%).

Adsorption of Co (II) from the solution was studied by batch technique using this new adsorbent. The general method used for this study is described as follows: 0.25 g of sorbent with particle size of 325 (44 micron) was contacted with 50 ml of the 50 mgL$^{-1}$ Co (II) solution in a reactor and mixed with the stirrer (720 rpm) for a specified time. The reactor was a jar cell with a double cylindrical jacket in which the temperature was controlled by circulating water through the jacket and stirring speed was kept 720 rpm to maintain the sorbent particles in suspension. The sorbent and solution were separated from each other by filtration after each run. The Co (II) ion concentrations in the solutions were determined by atomic absorption spectrophotometer (Varian, spectra-110-220/880 Australia Pty. Ltd.) equipped with a Zeeman atomizer.

## Results and discussion

### *Characterization of sorbent (almond green hull)*

Chemical and thermal treatment processing could affect adsorption capability of sorbent for the removal of cobalt ions as these treatments result in some functional groups on the solid surface. The surface functional groups can be quantitatively measured by the Boehm’s titration.
The data obtained from the Boehm method are presented in Table 1. As shown in the Table, the amount of acidic and basic group is as follow: phenolic > basic > lactonic> carboxylic groups.

**Table 1.** Surface acidity and basicity of used almond green hull by Boehm`s method.

| Surface basicity (mmolg$^{-1}$) | Carboxylic groups (mmolg$^{-1}$) | Lactonic groups (mmolg$^{-1}$) | Phenolic groups (mmolg$^{-1}$) |
|---|---|---|---|
| 1.165 | 0.39 | 0.45 | 1.26 |

### *Effect of temperature and contact time*

Figure 1 shows the effect of operation time at different temperatures on the adsorption of Co (II) for a fixed adsorbent dose of 0.25 g and particle size of 44 micron (mesh 325). The initial concentration was 51.5 mgL$^{-1}$ for all cases. The experimental data show that the amount of Co (II) adsorption increased by increasing time. This is due to thw higher contact between the sorbent surface and cobalt ion. The amount of Co (II) ion adsorbed onto the adsorbent are increased rapidly during the initial time of 1 minute at 25°C (97.22% of removal efficiency). Subsequently, the adsorption amount rises gradually and reaches almost equilibrium after about 3 min time for Co (II).

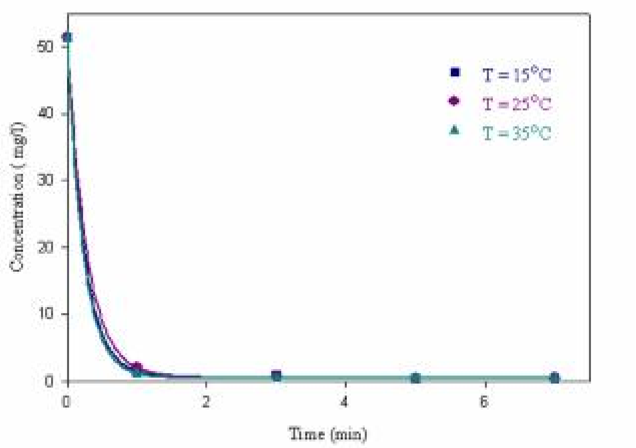


**Figure 1.** Effect of contact time on adsorption of Co(II) at different temperatures (stirring speed= 720 rpm; sorben amount t =0.25g ; Co= 51.5mg $L^{-1}$, mesh No= 325).

*Effect of initial concentration and sorbent amount*

The effect of initial concentration at different levels ranging from 17.8 to 110 $mgL^{-1}$ and constant sorbent amount of 0.25 g and particle mesh number of 325 can be seen in Figure 2. It is found that removal efficiency of Co (II) increased with increasing sorbent/sorbate ratio especially at very early adsorption time of 1 minute or the absolute amount of Co (II) adsorbed per unit weight of the ground almond green hull decreased. Sorption efficiency and adsorbed amount per unit weight for Co (II) removal at 17.8, 51.5, and 110 $mgL^{-1}$ concentration and 1 minute time are 98.5% (3.50 $mgg^{-1}$), 97.22% (10.01 $mgg^{-1}$), and 75.5% (16.60 $mgg^{-1}$), respectively. The results show that the removal of Co (II) ions is concentration dependent. At higher initial concentrations, the ratio of available adsorption sites to cobalt molecules is less and binding site saturate more rapidly.

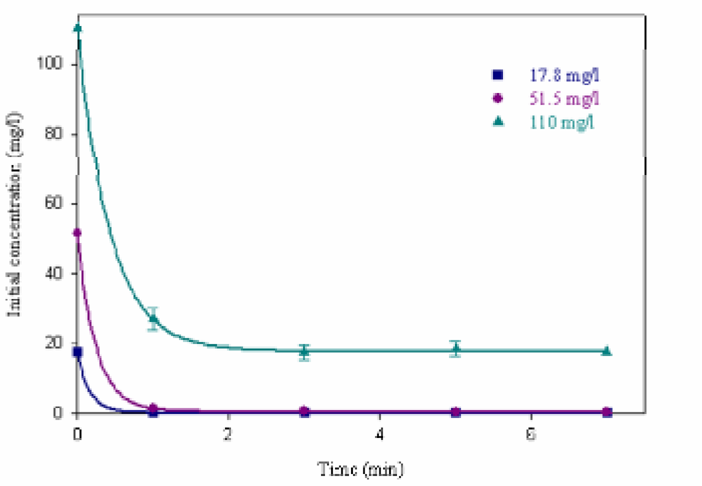


**Figure 2.** Effect of initial concentration on adsorption of Co(II) (stirring speed= 720 rpm; sorben amount t =0.25g ; T=25°C, mesh No. = 325).

The effect of initial concentration for different amounts of sorbent in the removal of Co (II) is shown in Figure 3. The sorbent amount was 0.25 and 0.4 g for both initial concentrations of 51.5 and 110 $mgL^{-1}$. The unadsorbed ion is decreased with increasing sorbent for a fixed initial concentration due to the greater surface area available for adsorption.

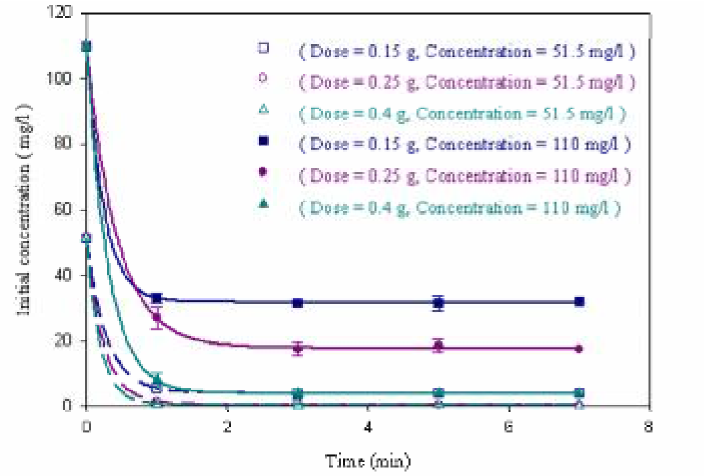


**Figure 3.** Effect of initial concentration on adsorption of Co(II) with different adsorbent amount (stirring speed= 720 rpm; T=25°C, mesh No= 325).

*Kinetic study*

In order to investigate the mechanism of adsorption, kinetic models are generally used to test the experimental data. Pseudo-second-order equations can be used assuming that measured concentrations are equal to surface concentrations.

The pseudo-second-order kinetic model is expressed as:

$$dq/dt = k_{2,ads}(q_e - q_t)^2 \qquad (1)$$

Where $k_{2, ads}$ (g/mg. min) is the rate constant of the second-order adsorption.

$$t/q_t = 1/k_{2,ads}q_e^2 + t/q_e \qquad (2)$$

The equation constants can be determined by plotting $t/q_t$ against t.
The values of different parameters determined from pseudo-second-order kinetic model for the cobalt ions along with their corresponding correlation coefficients are presented in Table 2. The correlation coefficients for the second-order kinetic model are nearly equal to 1 and the theoretical values of $q_e$ also agree very well with the experimental values. This suggests that the adsorption of cobalt follows the second-order kinetic model.

**Table 2.** Comparison among adsorption rate constants, $q_e$ estimated and coefficients of correlation (D) associated to the pseudo-second-order kinetic model.

| T (°C) | $K_{2,ads}$ ($gmg^{-1} min^{-1}$) | $q_e$ ($mgg^{-1}$), Exp. | $q_e$ ($mgg^{-1}$), Cal. | D (%) | $R^2$ |
|---|---|---|---|---|---|
| 15 | 3.52 | 10.20 | 10.25 | 0.49 | 0.9999 |
| 25 | 3.65 | 10.22 | 10.26 | 0.39 | 0.9999 |
| 35 | 3.79 | 10.24 | 10.27 | 0.29 | 0.9999 |

*Adsorption isotherm*

The Langmuir and Freundlich equations are commonly used for describing adsorption equilibrium of water and wastewater treatment applications.

The linear form of Langmuir isotherm is given by the following equation:

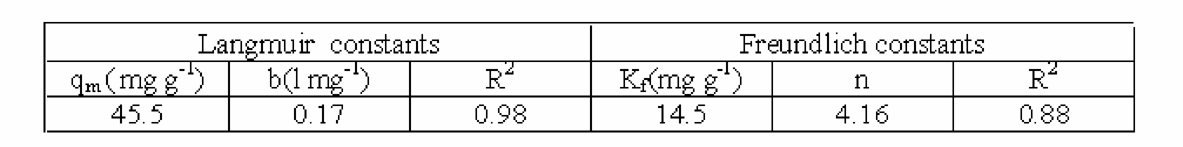
$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{bq_m C_e} \tag{3}$$

Where $q_e$ is the amount adsorbed at equilibrium ($mgg^{-1}$), $C_e$ the equilibrium concentration ($mgL^{-1}$), b a constant related to the energy or net enthalpy of adsorption ($Lmg^{-1}$), and $q_m$ is the Langmuir constant related to maximum adsorption capacity. The Langmuir constants, b and $q_m$ were calculated and these values are given in Table 3. The adsorption data is also analysed by Freundlich model. The logarithmic form of Freundlich model is given by following equation:

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \tag{4}$$

Where $q_e$ is the amount adsorbed at equilibrium ($mgg^{-1}$), $C_e$ is the equilibrium concentration of the adsorbate ($mgL^{-1}$) and $K_f$ and n are Freundlich constants related to adsorption capacity and adsorption intensity, respectively. The Freundlich parameters are given in Table 3.
The sorption isotherms were determined at fixed temperature (25°C) for a concentration range of 24.5-134 mg $L^{-1}$. All solutions contained a fixed mass of 0.05g of adsorbent.

**Table 3.** Freundlich and Langmuir adsorption constants associated to adsorption isotherms of cobalt on almond green hull.



| Langmuir constants | | | Freundlich constants | | |
|---|---|---|---|---|---|
| $q_m$ (mg $g^{-1}$) | b(l $mg^{-1}$) | $R^2$ | $K_f$(mg $g^{-1}$) | n | $R^2$ |
| 45.5 | 0.17 | 0.98 | 14.5 | 4.16 | 0.88 |

The good correlation coefficients showed that Langmuir model is more suitable than Freundlich model for adsorption equilibrium of cobalt.

## Conclusion

The current study emphasizes the ability of almond green hull to adsorb Co (II) from aqueous solutions. In the batch mode studies, the adsorption was dependent upon the initial metal-ion concentration and adsorbent particle size. The adsorption process followed pseudo-second-order kinetics and obeyed Langmuir adsorption isotherm. The adsorptive capacity of almond green hull for cobalt is comparable with other sorbents. Low cost of this sorbent with its rapid adsorptive ability would offer a promising technique for industrial wastewaters cleanup.

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