Rapid removal of cobalt ion from aqueous solutions by almond green hull

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ABSTRACT

Almond green hull, an agriculture solid waste, was chemically treated and used for the adsorption of Co (II) from aqueous solutions. The efficiency of this new adsorbent was studied using batch adsorption technique under different experimental conditions such as sorbent amount, initial metal-ion concentration, contact time, adsorbent particle size, and chemical treatment. Optimum dose of sorbent for maximum metal-ion adsorption were 0.25 g for 51.5 mg l^{-1} and 0.4 g for 110 mg l^{-1} solutions, respectively. High removal efficiencies of Co (II) were occurred in the first 1 min of sorbent contact time. The adsorption of Co (II) on almond green hull was also observed to follow the 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. The maximum adsorption capacity of this new sorbent was found to be 45.5 mg g^{-1}. The present study revealed that such a low cost material could be used as an efficient sorbent for the removal of cobalt from wastewater streams.

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1. Introduction

Heavy metals of different industrial wastewaters are frequently remained in the aquatic streams. The presence of these heavy metals in the environment is of importance concern due to their toxicity and health effects on the human and living creatures. Therefore, elimination of toxic heavy metals is attended by many researches. There are various methods for the removal of heavy metals such as chemical precipitation [1], reverse osmosis [2], ion exchange [3], coagulation [4], and adsorption [5–11]. Cobalt, one of the common toxic metals affecting the environment, is present in the waste water of nuclear power plants and many other industries such as mining, metallurgical, electroplating, paints, pigments and electronic [12]. High levels of cobalt may affect several health troubles such as paralysis, diarrhea, low blood pressure, lung irritation and bone defects [13]. The standard level of cobalt in drinking water is 2 μg l^{-1}, but values up to 107 μg l^{-1} have been reported [14].

One of the adsorbent which is widely used for the removal of cobalt and other heavy metals is activated carbon [15,16]. The application of this adsorbent is limited on the commercial considerations, due to the relative high cost associated with its preparation. Other sorbents used for the removal of cobalt ions are: Al-pillared clay [12], industrial wastes [17], sepiolite [18], funji [19], pre-treated arca shell biomass [20], brown seaweed [21] lignocellulosics [22], marine green alga [23], coir pith [24], zeolite [25], ion exchange resin [26], magnetic chitosan nanoparticle [27], ETS10, and ETAS10 [28]. Among them, low cost sorbents were especially investigated and their technical feasibility for heavy metal removals from the contaminated streams has been reviewed [29].

In the present study, an agriculture waste material, i.e. almond green hull was examined as a new sorbent for the removal of Co (II) ion from aqueous solutions. Almond trees are abundance in the world and almond hull is an agriculture crop residue that cannot be used by animals and it is usually burnt. The annual production of almond (with hard shell) is about 108,000 ton in Iran. Almond green hull is estimated to be about 0.25–0.6 wt% of whole almond fruits depending upon their various types. Therefore, about 36,000–160,000 ton of this waste material, being generated in the agriculture sections of the country, can be used for waste water treatments annually. To the best of our knowledge, this material was not used before for this kind of application. Utilization of almond green hull not only provide a low cost and easily available sorbent for the removal of heavy metals such as Co (II), but also it would help the environmental pollution.

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2. Materials and methods

2.1. Materials

Cobalt chloride of analytical grade was obtained from Merck. Stock solutions were prepared by dissolving cobalt chloride in de-ionized water. The green hull of almond was first washed with the distilled water to remove soluble impurities. Then, it was dried in an oven for 20 h at 180 °C. Dried sample was powdered, sieved (in two ranges of <44 to <250 μm), and then treated with the solution of hydrogen peroxide (2%) and ammonia (2%) for 30 min. Chemical treatment was used to extract soluble organic compounds of the shell and enhance chelating efficiency [30].

2.2. Boehm's titration

Chemical and thermal treatment processing would affect adsorption capability of sorbent for the removal of metal ions as they result in some functional groups on the solid surface. These surface functional groups are quantitatively measured by the Boehm's titration. In this method 0.5 g sorbent is placed in a series of flasks, each containing 50 ml of 0.05 N sodium bicarbonate, sodium carbonate, sodium hydroxide and hydrochloric acid, respectively. Flasks are sealed and shaken for 24 h, after which, the solutions are filtered. Then 10 ml of each solution is pipetted to a flask and titrated with 0.05 N sodium hydroxide and/or hydrochloric acid, depending on the original solution used. The amount of acidic groups on the sorbent is calculated under the assumption that NaOH neutralizes carboxylic, lactonic, and phenolic groups; Na_2CO_3 neutralizes carboxylic and lactonic groups; and $NaHCO_3$ only neutralizes carboxylic group. The number of surface basic sites is calculated from the amount of HCl reacted with the sorbent. The reaction between reagents and acidic oxygenated-functional groups on the surface is based on the difference in acid/base strength. The strength of acidic and basic groups is as follow: carboxyl > lactone > phenol [31].

2.3. Batch adsorption

Batch adsorption technique was used out for the study of Co (II) adsorption from solutions. The effect of contact time (0–7 min), temperature (15, 25 and 35 °C), concentration (18, 50 and 110 mg l^{-1}), particle size (mesh no. 325 and 60), and adsorbent
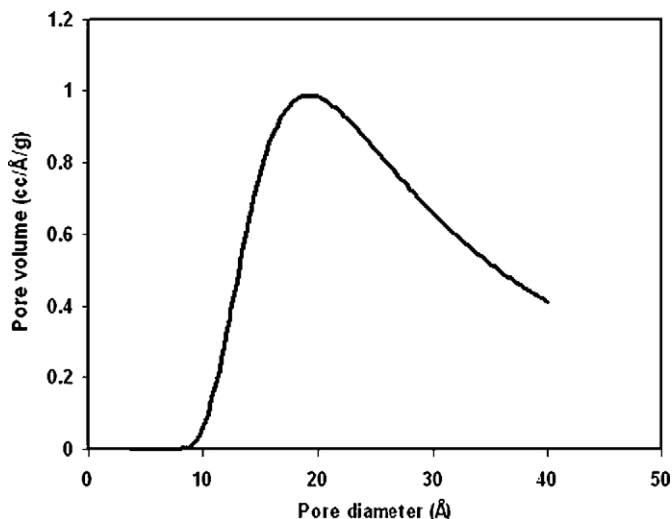

Fig. 1. Pore volume distribution of walnut green hull adsorbent.

dose (3, 5 and 8 g l^{-1}) were studied. In typical experiment, 0.25 g sorbent with mesh no. 325 (particle size <44 micron) was contacted with 50 ml of the 50 mg l^{-1} Co (II) solution in a reactor and mixed with stirrer (720 rpm) in a predetermined time. The reactor was a jar cell with a double cylindrical jacket in which the temperature was controlled by the circulating water through the jacket. Stirring speed of 720 rpm was selected to maintain the sorbent particles in suspension. The sorbent and solution were separated 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.

The uptake of metal ions in solution was calculated by the difference in their initial and final concentrations. Each experiment was repeated twice and average values are given as the results. The obtained data were employed to calculate the equilibrium metal uptake capacity according to the Eq. (1).

$$q_e = \frac{v(C_0 - C_e)}{m} \tag{1}$$

where q_e (mg g^{-1}) is the equilibrium amount of metal in the adsorbed phase, C_0 and C_e are the initial and equilibrium concentrations of metal ion (mg l^{-1}) in the aqueous solution, v is volume of the solution (l), and m is the sorbent dose (g) in the mixture.

3. Results and discussion

3.1. Sorbent characteristics

The structural characteristics of the treated walnut green hull with particle size of <44 μm were measured as: BET surface area of 186 m^2 g^{-1}, pore volume of 0.0562 cm^3 g^{-1}, average pore diameter of 19.2 Å, and density of 1.2 g cm^{-3}. Pore volume distribution of the sorbent is shown in Fig. 1.

Results obtained from the Boehm's method are presented in Table 1. It is seen that the amount of acidic and basic groups are as follows: basic > phenolic > lactonic > carboxylic.

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

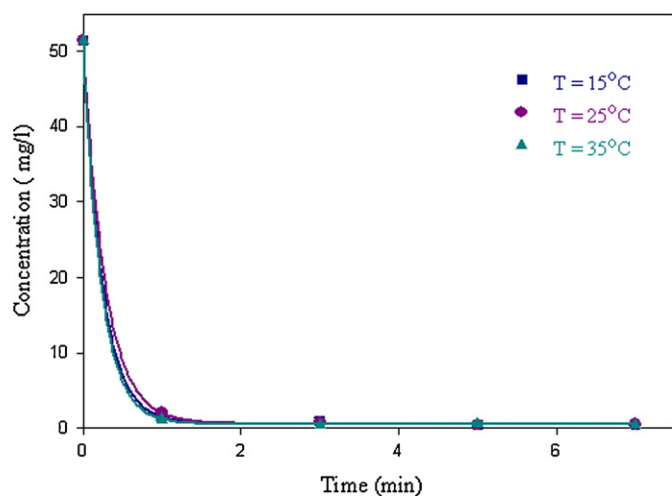| Surface basicity (mmol g^{-1})	Carboxylic groups (mmol g^{-1})	Lactonic groups (mmol g^{-1})	Phenolic groups (mmol g^{-1})
1.165	0.39	0.45	1.26

Fig. 2. Effect of contact time on adsorption of Co (II) at different temperatures (stirring speed = 720 rpm; sorbent amount = 0.25 g; Co Concn. = 51.5 mg l^{-1}, mesh no. = 325).

3.2. Effect of temperature and contact time

Fig. 2 shows the effect of operating time on the adsorption of Co (II) at different temperatures for a fixed sorbent dose of 0.25 g and particles with mesh no. 325. The initial concentration was 51.5 mg l^{-1} for all cases. The experimental data indicate that Co (II) ion adsorption increased by increasing time. This is due to the higher contact between the sorbent surface and cobalt ion. It is interesting that the amount of Co (II) adsorbed onto the adsorbent are increased rapidly during the initial contact time of 1 min at 25 °C and achieved to 97.22% of removal efficiency. Subsequently, the adsorption is improved gradually and reached nearly to equilibrium after 3 min. The short time needed for adsorption to reach equilibrium could be attributed to the high adsorption efficiency of almond green hull and readily available adsorbing sites (surface functional groups) on the adsorbent surface.

The results also indicate that there is not a significant difference among the amounts of Co (II) adsorbed at different temperatures. This is another reason for the great potential between Co (II) and almond green hull and independency of the sorption process to the temperature.
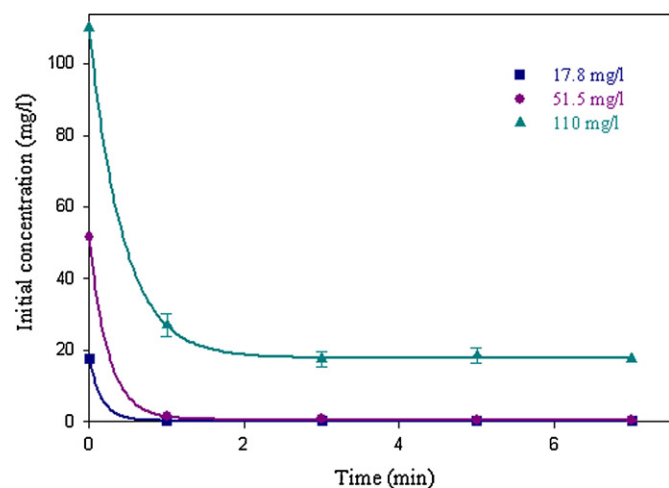

Fig. 3. Effect of initial concentration on adsorption of Co (II) (stirring speed = 720 rpm; sorbent amount = 0.25 g; T = 25 °C, mesh no. = 325).
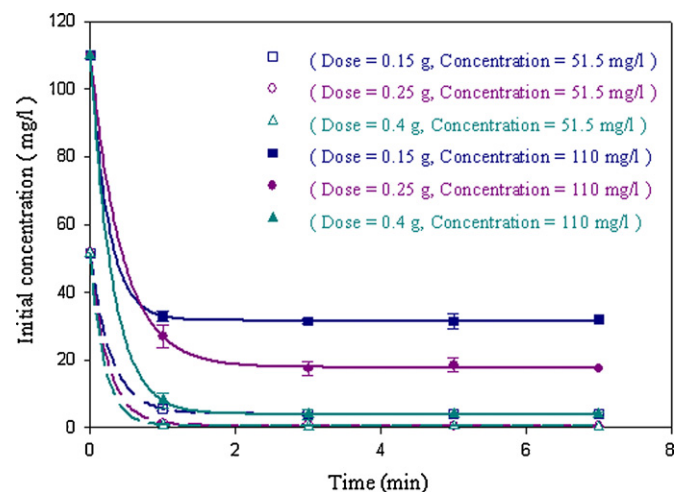

Fig. 4. Effect of initial concentration on adsorption of Co (II) with different doses of adsorbent (stirring speed = 720 rpm; T = 25 °C, mesh no. = 325).

3.3. Effect of initial concentration and sorbent amount

The effect of initial concentration at different levels ranging from 17.8–110 mg l^{-1} and constant dose and size of sorbent (0.25 g and mesh no. 325) can be seen in Fig. 3. It is found that the removal efficiency of Co (II) was increased with enhancing sorbent/sorbate ratio, especially at short time of 1 min, but the absolute amount of Co (II) adsorbed per unit weight of almond green hull was decreased. Sorption efficiency and adsorbed amount per unit weight of Co (II) removal at 17.8, 51.5, and 110 mg l^{-1} concentrations and 1 min time are: 98.5% (3.50 mg g^{-1}), 97.22% (10.01 mg g^{-1}), and 75.5% (16.60 mg g^{-1}), respectively. The equilibrium times are found to be the same for all different concentrations studied. Similar results are also reported by researchers for a variety of adsorbate–adsorbent systems [12,32]. The results show that Co (II) ions removal is concentration dependent. At higher initial concentrations, the ratio of available adsorption sites to cobalt molecules is less and binding sites can saturate more rapidly.

The effect of initial concentration on the removal of Co (II) for different doses of sorbent is shown in Fig. 4. The sorbent dose was 0.25 and 0.4 g for both initial concentrations of 51.5 and 110 mg l^{-1}. The unadsorbed ions are decreased by increasing sorbent dose for a fixed initial concentration due to the greater surface area available for adsorption. It is found that there is an optimum dose of sorbent for any initial concentration which gives maximum removal.

3.4. Effect of mesh size

Effect of mesh size for the removal of Co (II) at 5 min contact time and 0.25 g sorbent is shown in Table 2. The results indicate that the ion removal enhanced with decreasing the adsorbent particle size. By assuming spherical shape for particles, it can be shown that the surface area per volume is higher for smaller particles. Improving surface area would increase binding sites and contact surfaces, which results in higher mass transfer and more rapid sorption.

Table 2
Effect of adsorbent particle size cm the removal of cobalt ion (initial concentration = 51.5 mg l^{-1}, t = 5 min, amount of sorbent = 0.25 g, T = 25 °C).

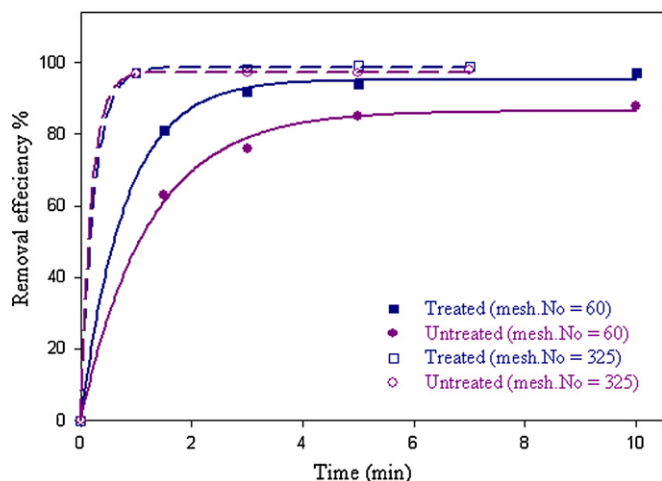|	Mesh no. (size)			
	60 (250 μm)	100 (149 μm)	170 (88 μm)	325 (44 μm)
Concentration (mg l^{-1})	4.10	1.33	0.64	0.38

Fig. 5. Effect of chemical treatment on adsorption of Co (II) with different adsorbent particle sizes (stirring speed = 720 rpm; T = 25 °C, sorbent dose = 0.25 g).

3.5. Effect of chemical treatment

As mentioned before, the chemical treatment was carried out for extracting soluble organic compounds and enhancing chelating efficiency. Effect of chemical treatment is shown in Fig. 5. As seen in this figure, removal efficiency is higher for the treated sorbent with mesh no. 60 (<250 μm), but it is remain the same for treated and untreated sorbents with mesh no. 325 (<44 μm). It is suggested that for smaller particles increasing the surface area are predominant as a consequence of high affinity of these particles toward cobalt ions.

3.6. Kinetic study

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

The pseudo-first-order rate Lagergren model is [33,34]:

$$\frac{dq}{dt} = k_{1,ads}(q_e - q_t) \tag{2}$$

where q (mg g^{-1}) is the amount of adsorbed metal ion on the adsorbent at time t and $k_{1,ads}$ (min^{-1}) is the rate constant of the first-order adsorption. The integrated form of Eq. (2) is:

$$\log(q_e - q_t) = \log\ q_e - \frac{k_{1,ads}t}{2.303} \tag{3}$$

q_e, the equilibrium sorption uptake, is extrapolated from the experimental data at time $t = \infty$. A straight line of $\log (q_e - q_t)$ versus t suggests the applicability of this kinetic model. Then, q_e and $k_{1,ads}$ can be determined from the intercept and slope of the plot, respectively.

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

$$\frac{dq}{dt} = k_{2,ads}(q_e - q_t)^2 \tag{4}$$

where $k_{2,ads}$ (g mg^{-1} min^{-1}) is the rate constant of the second-order adsorption.

$$\frac{t}{q_t} = \frac{1}{k_{2,ads}q_e^2} + \frac{t}{q_e} \tag{5}$$

The equation constants can be determined by plotting t/q_t against t.

It is found that the q_e values obtained by first-order kinetic model differ from those measured experimentally, suggesting

Table 3
Comparison among adsorption rate constants, q_e estimated and coefficients of correlation (D) associated to the pseudo-second-order kinetic model.

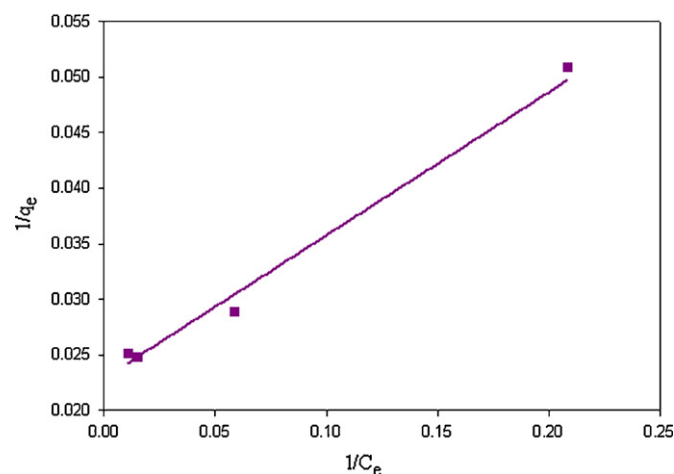| T (°C)	$k_{2,ads}$ (g mg^{-1} min)	Experimental, q_e (mg g^{-1})	Calculated, q_e (mg g^{-1})	D (%)	R^2
15	3.52	10.20	10.25	0.49	0.9999
25	3.65	10.22	10.26	0.39	0.9999
35	3.79	10.24	10.27	0.29	0.9999

Fig. 6. Langmuir isotherm for adsorption of cobalt ion (stirring speed = 720 rpm; T = 25 °C).

the adsorption is not a first-order reaction. The values of different parameters determined from the pseudo-second-order kinetic model along with their corresponding correlation coefficients are presented in Table 3. The correlation coefficients of the second-order model are nearly equal to 1 and the theoretical values of q_e agree very well with the experimental values. This finding suggests that the adsorption of cobalt follows the second-order kinetic model.

3.7. Adsorption isotherms

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:

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{bq_mC_e} \tag{6}$$

where q_e is the amount adsorbed at equilibrium (mg g^{-1}), C_e the equilibrium concentration (mg l^{-1}), and q_m and b (l mg^{-1}) are the Langmuir constants related to maximum adsorption capacity and energy of adsorption, respectively. When $1/q_e$ was plotted against $1/C_e$, straight lines with slope $1/bq_m$ was obtained (Fig. 6), which show that the adsorption of cobalt followed the Langmuir isotherm. The Langmuir constants, b and q_m, were calculated and their values are given in Table 4.
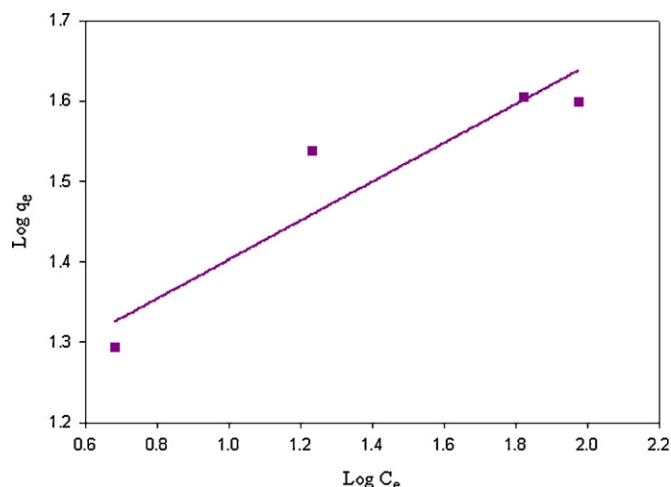
Table 4
Freundlich and Langmuir adsorption constants associated to adsorption isotherms of cobalt on almond green hull.

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

Table 5
R_L values far adsorption of cobalt onto almond green hull at 25 °C.

Co (II) initial concentration (mg l^{-1})	24.5	51.6	106.5	134
R_L	0.19	0.102	0.052	0.042

Fig. 7. Freundlich isotherm for adsorption of cobalt ion (stirring speed = 720 rpm; T = 25 °C).

R_L value indicates the type of isotherm. Values between 0 and 1 for this parameter indicate favorable adsorption [24].

$$R_L = \frac{1}{1 + bC_0} \tag{7}$$

The results are presented in Table 5. R_L values for cobalt ion were found to be between 0 and 1 for all concentrations at 25 °C, indicating favorable adsorption.

The adsorption data was also analysed by Freundlich model. The logarithmic form of Freundlich model is given by following equation:

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \tag{8}$$

where q_e is the amount adsorbed at equilibrium (mg g^{-1}), C_e is the equilibrium concentration of adsorbate (mg l^{-1}) and K_f and n are Freundlich constants related to adsorption capacity and adsorption intensity, respectively. The plots of $\log q_e$ against $\log C_e$ for the adsorption data of cobalt is given in Fig. 7. The Freundlich parameters are also given in Table 4.

Table 6
Comparison of maximum adsorption capacity of almond green hull with different adsorbents for Co (II).

Adsorbent	q_m (mg g^{-1})	References
Kaolinite	0.919	[35]
ETS10	0.93	[28]
ETAS10	0.94	[28]
Area shell biomass	11.53	[20]
Coir pith	12.82	[24]
Synthetic HAP	20.19	[36]
Montrnorinilite-K	20.45	[37]
Magnetic chitosan nanoparticle	27.4	[27]
Sterified coir pith	34.13	[38]
Al-PILC	33.61	[12]
Almond green hull	45.5	(Current article)
CeraliteIRC-50	58.8	[22]
Chitosan	76.34	[37]
SAC	153.85	[15]
PGBS-COOH	166.7	[15]

The sorption isotherms were determined at fixed temperature (25 °C) for a concentration range of 24.5–134 mg l^{-1}. In all different solutions a fixed dose of adsorbent (0.05 g) was used. The good correlation coefficients showed that Langmuir model is more suitable than Freundlich for adsorption equilibrium of cobalt.

Values of the adsorption capacity of other adsorbents from the literature are given in Table 6 for comparison. It is clear from this table that the adsorption capacity of almond green hull for Co (II) is comparable with the other adsorbents.

4. Conclusion

The current study highlighted the ability of almond green hull to adsorb Co (II) from aqueous solutions. In the batch mode of studies, adsorptions are found to depend on the initial metal-ion concentration and the 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 ion is comparable to the other high quality sorbents. Low cost and rapid adsorptive ability of this sorbent would offer a promising technique for industrial wastewaters cleanup.

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