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The removal of Cr (III) and Co (II) ions from aqueous solution by two mechanisms using a new sorbent (alumina nanoparticles immobilized zeolite) — Equilibrium, kinetic and thermodynamic studies

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ABSTRACT

The removal of Cr (III) and Co (II) from various samples of ionic solutions was investigated using several sorbents such as alumina nanoparticles (Al_2O_3 NPs), NaX zeolite granules and a new sorbent: alumina nanoparticles immobilized zeolite (ANIZ), in batch mode. The effects of various operating parameters were studied in order to optimize the removal conditions. Results showed that the removal capacity of zeolite has been significantly improved (Cr (III): 31.76%, Co (II): 17.2%) after the immobilization of Al_2O_3 NPs. Langmuir, Freundlich, Temkin and Dubinin–Radushkevich (D–R) equations were examined to describe the isotherm models and their constants were evaluated. The kinetic data were analyzed using Pseudo first order, Pseudo second order, Elovich and intraparticle diffusion models. The equilibrium data showed excellent correlation for both Langmuir and Freundlich isotherm models and the Pseudo second-order model was fitted to experimental results better than the other kinetic models. Thermodynamic analyses of the equilibrium data suggested that the removal reactions were spontaneous [$-\Delta G°$, $kJ \cdot mol^{-1} = 29.37$ to 43.69 for Cr (III); and 33.54. to 41.61 for Co (II)] and the spontaneity increased with increasing temperature.

1. Introduction

Heavy metals are widely distributed in the environment and are biologically significant due to their toxicity. The removal of heavy metals from industrial wastewater has become a very important environmental issue [1,2]. Cr (III) and Co (II) are considered as toxic metal ions present in effluent of many industries such as metallurgy, mining, electroplating, tanning and paint industries. These ions cause detrimental effects on human health and the environment. Therefore, various methods such as: reduction [3,4], precipitation [5–7], ion exchange [8–10], adsorption [11–14], solvent extraction [15,16], membrane separation [17,18], electrochemical treatment [19,20] and reverse osmosis [21,22] are utilized for the removal of heavy metal ions from wastewater. Among these methods adsorption and ion exchange methods have significant advantages. The adsorption process is shown to be economically feasible alternative way for the removal of heavy metals from aqueous solutions and it is effective in removing trace components from a liquid phase and may be used either to recover the component or simply to remove a noxious substance from an industrial effluent [23–27]. The use of adsorption method for removal of heavy metal ions becomes more effective if nano scale materials are used as the adsorbent. Nano scale adsorbents such as: TiO_2, MnO_2, Fe_2O_3, Zno, CeO_2, and Al_2O_3 are used as adsorbent for removal of heavy metal ions [28,29]. Among the nano scale adsorbents, alumina nanoparticles have particular importance. Alumina nanoparticles with a high surface area have a high adsorption capacity and have been used for reducing different contaminants in water [30–32].

Ion exchange is attractive because of the relative simplicity of the application [33–35]. Different types of zeolites can be used for this purpose. One of the unique properties of zeolites is their ability to exchange cations, which are located at specific sites at their channel cage system, by various cations from solutions. Zeolites are used for their special adsorption properties due to their unique surface chemistries and crystalline pore structures [36–40].

In this study the removal of Cr (III) and Co (II) has been investigated by alumina nanoparticles, NaX zeolite granules and alumina nanoparticles immobilized zeolite (ANIZ) in batch mode. ANIZ was prepared by immobilization of alumina nanoparticles onto the NaX zeolite granules by a physical as well as a sol–gel method. The preparation and characterization of ANIZ have been reported in the previous paper [41]. The removal capacity of Cr (III) and Co (II) was compared for three sorbents. The equilibrium data were applied to the Langmuir, Freundlich, Temkin

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Table 1
Isotherm models used to analyze equilibrium data.

Model	Non-linear form	Equation number	Ref.
Langmuir	$q_e = \frac{k_L \cdot q_{,max \cdot C_e}}{(1+k_L \cdot C_e)}$	2	[42]
Freundlich	$q_e = k_F C_e^{\left(\frac{1}{n}\right)}$	3	[43]
Temkin	$q_e = B \cdot \ln(K_T C_e)$	4	[44]
Dubinin–Radushkevich (D–R)	$q_e = q_D \cdot e^{-B_D\left[RT\ ,\ln\left(1+\frac{1}{C_e}\right)\right]^2}$	5	[44]

Table 2
Models used to analyze kinetic data.

Model	Linear form	Equation number	Ref.
Pseudo-first order	$\ln(q_e - q_t) = \ln(q_e) - k_{p1} t$	6	[45]
Pseudo-second order	$\frac{t}{q_t} = \frac{1}{k_{p2} q_e{}^2} + \frac{t}{q_e};\ \ V_0 = \frac{1}{k_{p2} q_e{}^2}$	7	[45]
Elovich	$q_t = \beta \cdot \ln(\alpha\beta) + \beta \cdot \ln(t)$	8	[45]
Intraparticle diffusion	$q_t = C + k_{int} \cdot t^{0.5}$	9	[45]

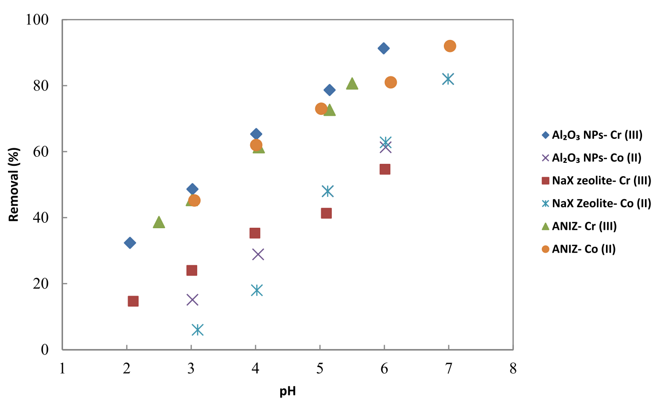

Fig. 1. Effect of pH on the removal of Cr (III) and Co (II); T = 25 °C, t = 240 min, C_0 = 50 mg/L.

and Dubinin–Radushkevich (D–R) isotherm models and the kinetic data were studied by Pseudo first order, Pseudo second order, Elovich and intraparticle diffusion models in order to determine the removal behavior.

2. Experimental

2.1. Materials and methods

NaX zeolite (pore size = 1 nm, particle size = 1.5–2.5 mm, specific surface area = 480 m^2/g, bulk density = 610–640 kg/m^3) with the Si/Al ratio equal to 1.25 was purchased from Zeochem company. Alumina nanoparticles (purity > 99%, particle size = 20 nm, specific surface > 160 m^2/g) were purchased from Nano Pars Lima company. Methods for the preparation of ANIZ have been discussed in the previous paper [41]. The alumina content of the prepared ANIZ by the physical and sol–gel methods was 82.98 $mg \cdot g^{-1}$ and 95.85 $mg \cdot g^{-1}$ respectively. The immobilized Al_2O_3 NP size on the surface of the zeolite was approximately 30–50 nm. Cr (III) and Co (II) stock solutions (1000 g/cm^3) were prepared by dissolving $Cr(NO_3)_3 \cdot 9H_2O$ (Merck, Germany) and $Co(NO_3)_2 \cdot 6H_2O$ (Merck, Germany) in the de-ionized water.

2.2. Removal experiments

Removal experiments of Cr (III) and Co (II) were carried out by alumina NPs, NaX zeolite and ANIZ in batch mode. The kinetic and equilibrium experiments were carried out in the optimum pH and sorbent dosage. Removal behavior of the prepared ANIZ was studied, using different initial concentrations of Cr (III) and Co (II) solutions. For equilibrium and kinetic studies, 50 mL of the solutions was poured in the polyethylene erlenmeyer flask. The pH of solutions was adjusted by adding either 0.1 M NaOH or 0.1 M HNO_3 solutions. The suspensions were shaken (250 rpm) at 25 °C for 240 min. The solid/liquid phases were separated by filtration. The removal percentage was calculated according to Eq. (1).

$$\text{Removal } (\%) = \frac{(C_0 - C)}{C_0} \times 100 \tag{1}$$

where C_0 and C_e are the initial and the final concentration of Cr (III) and Co (II) ions in solution phase, respectively.

2.3. Isotherm models used

The equilibrium data of the removal experiments has been modeled using equations listed in Table 1.

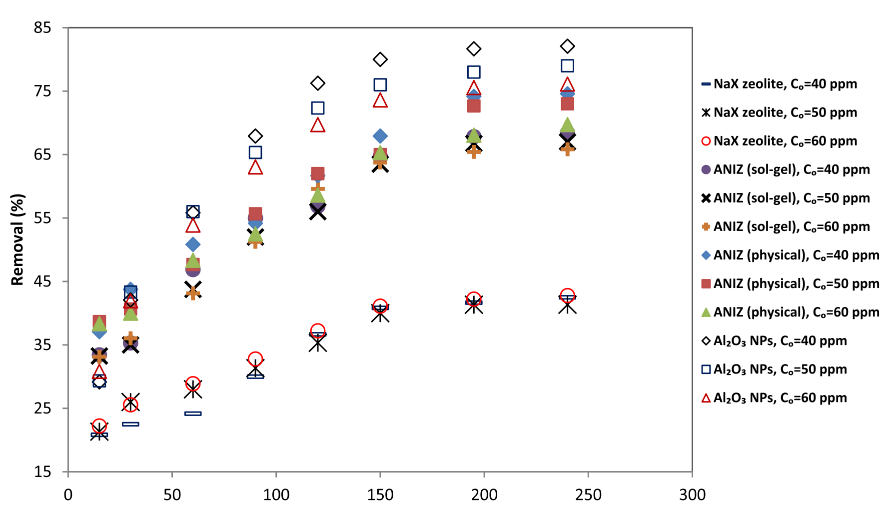

Fig. 2. Effect of contact time on the removal of Cr (III) ion; T = 25 °C, pH = 5.