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Research paper

Comparative and competitive adsorptive removal of Ni^{2+} and Cu^{2+} from aqueous solution using iron oxide-vermiculite composite

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ABSTRACT

In this study, iron oxide-vermiculite composite (Iovc) with a high specific surface area (SSA) was prepared to remove Ni^{2+} and Cu^{2+} from aqueous solution. It was characterized by X-ray diffraction (XRD), X-ray fluorescence (XRF), Fourier-transform infrared (FTIR), and scanning electron microscopy (SEM). The effects of initial pH of the solution, contact time and adsorbent concentration on the adsorption efficiency were investigated systemically. Equilibrium adsorption isotherms were measured for the single component by using various models. The homogenous adsorption of Ni^{2+} and Cu^{2+} was confirmed in the single system by Langmuir and Koble–Corrigan models. For the binary adsorption of Cu^{2+} and Ni^{2+} ions have been analyzed by using non-modified Langmuir, modified Langmuir, extended Langmuir, extended Freundlich and Sheindorf–Rebuhn–Sheintuch (SRS) models. The competitive extended Langmuir model described well the competitive adsorption of Ni^{2+} and Cu^{2+}. Maximum adsorption capacities for Ni^{2+} and Cu^{2+} in the binary system are 101.3 and 59.7 mg/g, respectively.
In the kinetic study, the experimental data fitted well the pseudo-second-order kinetics for Ni^{2+} and Cu^{2+} adsorption data. Furthermore, calculated thermodynamic parameters, ΔG°, ΔH° and ΔS° of adsorption showed that the adsorption of Ni^{2+} and Cu^{2+} was feasible, spontaneous and an exothermic process.

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1. Introduction

Due to the rapid development of industries, heavy metal wastewaters are widely discharged into the environment. They are non-biodegradable and tend to accumulate in living tissues, causing various diseases and disorders (Badawy et al., 2010). Ni^{2+} and Cu^{2+} compounds are common environmental pollutants arising from many industrial activities such as metal plating, mining, metallurgy, tanneries, electroplating, and painting. (Papandreou et al., 2007). Several noxious effects have been attributed to Ni^{2+} in living systems, e.g. serious lung and kidney problems aside from gastrointestinal distress, pulmonary fibrosis and skin dermatitis (Borba et al., 2006). Furthermore, Cu^{2+} exceeding its critical level might bring about mucosal and central nervous system irritation, kidney and liver dysfunction, anaemia and gastrointestinal diseases (Paulino et al., 2006).

Therefore, heavy metal (like nickel and copper) ions contaminating wastewater must be treated before releasing into environment. These methods include the chemical precipitation, chemical oxidation and reduction, ion exchange, liquid–liquid extraction, reverse osmosis, electrochemical treatment, and adsorption. These methods have been found to be limited, such as expensive equipment requirement, continuous replenishment of chemicals, time-consuming and easy to produce secondary pollution (Hajeeth et al., 2013; Kumar et al., 2013; Xin et al., 2012).

Among the aforementioned methods, adsorption process is generally considered to be a simple, low operation cost, improved selectivity for specific metal ions and the removal of heavy metal ions from waste industry effluents (Gök et al., 2008). There are many reports on various adsorbents such as resins (Rao et al., 2010), agricultural wastes (Sharma and Kothiyal, 2013), organic/inorganic composites (Longenberger and Mills, 1995), activated carbon (Fouladi Tajar et al., 2009), zeolite (Shawabkeh, 2009), bio-sorbent (Gupta and Rastogi, 2008), modified silica gel (Gupta and Rastogi, 2008), and clays (Hamidpour et al., 2010), which have been employed for the adsorption of toxic heavy metal ions from wastewater, such as Ni^{2+} and Cu^{2+}. Clays are widely used in adsorption of heavy metals from industrial wastewater and water solution. Table 1 shows a summary of different clays to adsorb diverse heavy metals.

Vermiculite (Vmt) is hydrated magnesium aluminum silicate mineral $[(Si_3Al)Mg_3(OH)_2O_{10}Mg_{0.5}\cdot nH_2O]$ that is the category of 2:1 clays formed by alteration of biotite and iron-bearing phlogopite micas. Vmt consists of an octahedral coordinated layer of magnesium, iron or aluminum as the basic structural unit, which is sandwiched between two tetrahedral coordinated layers of silicon in which all ions are surrounded by four oxygen (Alexandre-Franco et al., 2011). This

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Table 1
Concise summary of Cu^{2+} and Ni^{2+} adsorption on clays.

Clay	Heavy metal	q_m (mg/g)	Kind of investigation	References
Immobilized-bentonite	Cu^{2+}	114.70	Effect of pH and initial Cu^{2+} ion concentration, reusability	Alexandre-Franco et al. (2011)
Na-activated bentonite	Ni^{2+}	2.77	Equilibrium, kinetics, thermodynamics	Vieira dos Santos and Masini (2007)
Acid-activated montmorillonite	Cu^{2+}	32.2	Isotherm, kinetic and thermodynamic studies	Emmerich (1999)
ZrO–montmorillonite	Ni^{2+}	22.0	Optimum condition, isotherm and kinetic studies	Srivastava et al. (2006)
Montmorillonite	Cu^{2+}	7.61	Isotherm and kinetic studies	Angove et al. (1997)
	Ni^{2+}	12.88		
Kaolinite	Ni^{2+}	0.90	Optimum condition and isotherm studies	Mall et al. (2005)
	Cu^{2+}	1.22		

structure has caused a high layer charge density, high cation exchange capacity (CEC) (Vieira dos Santos and Masini, 2007), ability to retain plant available water and large number of exchange sites (Emmerich, 1999).

Given that industrial wastewater can contain many metals, it is necessary to focus on the simultaneous adsorption of two or more metals and also to quantify the interference of one metal with the adsorption of the other. The equilibrium adsorption isotherm equations proposed for single-component adsorption have been extended and modified to represent the binary and multi-component adsorption equilibrium (Srivastava et al., 2006). However, Vmt has not yet been studied very well for removing heavy metal in binary systems (particularly for removing Ni^{2+} and Cu^{2+} from aqueous solution).

The main objectives of this study include: (I) to modify raw Vmt by iron oxide in order to improve maximum adsorption capacities of Ni^{2+} and Cu^{2+} in the single and binary systems, (II) the applicability of non-competitive adsorption isotherm models in single system containing Ni^{2+} and Cu^{2+} ions, (III) to examine the multi-component adsorption isotherm equations to the competitive adsorption equilibrium of the metals in the binary system, and (IV) to determine thermodynamic parameter and find mechanism of sulfate adsorption onto modified Vmt.

2. Experimental methods

2.1. Materials

The sample of Vmt obtained from the eastern area of Azerbaijan in northwestern Iran was used without any chemical pretreatment. The sample was prepared under 150 μm size. Nickel nitrate hexahydrate ($Ni(NO_3)2\cdot6H_2O$), copper sulfate monohydrate ($CuSO_4\cdot9H_2O$), iron (II) sulfate heptahydrate ($FeSO_4\cdot7H_2O$), iron (III) nitrate heptahydrate ($Fe(NO_3)_3\cdot9H_2O$), sodium hydroxide (NaOH) and hydrogen chloric acid (HCl), sulfuric acid (H_2SO_4) and nitric acid (HNO_3) were procured from Merck Company.

2.2. Preparation of adsorbent

The Iovc was synthesized from a dispersion of 6 g Vmt in 60 mL solution of 1.5 mmol/L $FeSO_4\cdot7H_2O$, 6 mmol/L $Fe(NO_3)_3\cdot9H_2O$ (molar ratio 1:4) and 30 mL ethylene glycol. NaOH solution (60 mL, 0.056 mol/L) was added dropwise to precipitate the iron oxides. After the addition of NaOH solution, the mixture was adjusted to pH 11.0 and stirred for 2 h. The mixture was filtrated and the products were washed several times with water. Then the composites were dried at room temperature for 24 h and then at 70 °C for 4 h. Finally, Iovc (black precipitates(, molar ratio (Fe^{2+}:Fe^{3+}) 1:4, was ready to use.

2.3. Characteristics of adsorbents

The raw Vmt and modified Vmt (particle size of −150 μm) were characterized for their physical and chemical properties of mineralogical phases, crystallinity and morphology by XRD, XRF, FTIR and SEM analyses. The identification of the structure and mineralogical phases of adsorbents have been done by X-ray diffraction (XRD) analyses in a Philips X-ray diffractometer using CuKα radiation. The composition of samples was examined by Philips X-ray fluorescence (XRF) using X-ray diffractometer X unique II (80 kV, 40 mA, calibrated with a Si-standard). In order to find functional groups of raw and modified Vmt Fourier transform infrared (FTIR) was recorded with a Shimadzu IR instrument using KBr pellets from 4000 to 400 cm^{-1} range. The morphologies of raw Vmt and Iovc were observed by a direct measurement on scanning electron micrographs (SEM, Seron Technology, AIS2100). The concentration of Cu^{2+} and Ni^{2+} solutions after adsorption was determined by using atomic absorption (AA) spectrometry of unicam 939. The pH values were measured by using a digital pH meter (Sartorius pp-15, Germany).

2.4. Batch adsorption studies

All the experiments were carried out in 100 mL aqueous solution of the known concentration of Cu^{2+}, Ni^{2+} in single and binary systems, and in 250 mL glass containing 1 g of Iovc.

This glass was agitated at a constant shaking rate (with orbital shaker) of 500 rpm at room temperature. The initial pH values of solution (in the range of 2–8) were adjusted with the hydrogen chloric acid and sodium hydroxide. For optimization of contact time to achieve maximum adsorption yields in pH_0 4.5, batch adsorption experiments were realized at various times from 5 to 90 min. Experimental of pH (in the range of 2–8) and contact time (5 to 90 min) were done with 500 mg/L of Cu^{2+} and Ni^{2+} concentration.

2.5. Equilibrium studies

In order to perform equilibrium studies in a single system, the Langmuir, Freundlich, Temkin, Dubinin–Radushkevich (two-parameter), Khan, Koble–Corrigan, Toth, and Redlich–Peterson (three-parameter) models have been used to describe the equilibrium characteristics of Ni^{2+} and Cu^{2+} adsorption. The competitive adsorption as non-modified competitive Langmuir and the extended Freundlich and Langmuir, modified Freundlich and Langmuir equations have been applied to describe the equilibrium characteristics of multi-component adsorption. These models are described in Table 2.

In order to carry out adsorption isotherm study for a single system, the initial Ni^{2+} and Cu^{2+} concentrations were varied from 200 to 1000 mg/L for 10 g/L Iovc. In the binary system for each initial concentration of Cu^{2+} solution (200, 400, 600, 800 and 1000 mg/L), the Ni^{2+} concentration was changed from 200 to 1000 mg/L (200, 400, 600, 800 and 1000 mg/L). In all cases, the pH_0 and contact time of the solution were maintained at 4.5 and 30 min, respectively. This pH_0 and contact time were found to be the optimum on the basis of batch tests carried out to determine the effect of pH_0 and contact time, respectively, on the adsorption capacity of Iovc for metal ions.

2.6. Kinetic studies and thermodynamic studies

To identify the mechanism of the adsorption process, pseudo-first order, pseudo-second order, and intra-particle diffusion models have

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