Chemical Engineering Journal 148 (2009) 68–79

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Saw dust and neem bark as low-cost natural biosorbent for adsorptive removal of Zn(II) and Cd(II) ions from aqueous solutions

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ARTICLE INFO

Article history:
Received 16 November 2007
Received in revised form 12 June 2008
Accepted 4 August 2008

Keywords:
Saw dust
Neem bark
Low-cost
Adsorption
Zinc(II)
Cadmium(II)
Kinetics
Isotherm
Adsorption capacities
Functional groups
Metal binding process

ABSTRACT

The ability of saw dust and neem bark as low-cost natural adsorbents were investigated for adsorptive removal of Zn(II) and Cd(II) ions from aqueous solutions. Various physico-chemical parameters such as pH, initial metal ion concentration, and adsorbent dosage level and equilibrium contact time were studied. The optimum pH for adsorption was found to be 5 for Zn(II) and 6 for Cd(II). Kinetics data were best described by pseudo-second-order model. Mass transfer coefficients were also determined for individual adsorbents for removal of Zn(II) and Cd(II) ions from aqueous solutions. The equilibrium adsorption data were fitted to Langmuir and Freundlich isotherm models for Zn(II) and Cd(II) adsorption respectively. The adsorption capacities (q_{max}) for individual metal ions in terms of monolayer adsorption were compared with the other reported values. The sorption energy calculated by using Dubinin–Radushkevich isotherm for different system indicated that the adsorption process is physical in nature. The thermodynamic equilibrium constant and the Gibbs free energy were determined for each system and results indicated the spontaneous nature of the adsorption process. FT-IR studies were carried out to understand the type of functional groups in saw dust and neem bark responsible for metal binding process.

1. Introduction

The discharge of heavy metals into the watercourse is a serious environmental problem, which affects significantly the demand of quality water supply. Increasing concentration of these metals in the water constitutes a severe health hazard due to their toxicity, persistent in nature and non-biodegradability particularly when it exceeds the permissible limits [1,2]. Heavy metals do not degrade into harmless end products in the metabolism and they are accumulated in the food chain water–plants–animals–humans [3] thereby posing the greatest threat to the living organisms.

Cadmium is introduced into the water from smelting, metal plating, cadmium–nickel batteries, phosphate fertilizers, mining, pigments, pigments, stabilizers, alloy industries and sewage sludge [4]. The harmful effects of Cd(II) include acute and chronic metabolic disorders, such as itai-itai disease, renal damage, emphysema, hypertension and testicular atrophy [5]. Symptoms of zinc toxicity include loss of appetite, nausea, irritability [6]. The routes of entries of zinc into the environment include mining, purifying zinc, lead and cadmium ores, steel production, coal burning and burning of wastes. Zinc is present in high concentration in wastewater of pharmaceuticals, galvanizing, paints and pigments, insecticides, cosmetics, etc., that causes severe problem to the environment. The permissible limit (mg/L) for Zn(II) and Cd(II) in wastewater, given by CPCB are 5 and 2 mg/L respectively [7]. The permissible level for Zn(II) and Cd(II) in drinking water, given by EPA and IS: 10500 are 5 and 0.01 mg/L respectively [8,9]. Therefore it seems to be utmost important to remove the aforesaid metals from water and wastewater before its transport and cycling into the natural environment.

Generally, the various techniques employed for the effective removal of heavy metals from aqueous solution are the reduction and precipitation, coagulation, flotation, adsorption, ion-exchange and reverse-osmosis or electrodialysis, etc. [10–13]. However in many instances, these methods do not work effectively. For instance, precipitation method for heavy meal removal produces voluminous sludge that must be treated and disposed off normally at higher cost. Ion-exchange and reverse-osmosis, even though effective and efficient, are expensive due to high operational and maintenance cost hence only, few industries can think of it. Adsorption onto activated carbon is considered as an effective technique that was extensively used in the last few years [14,15]. But considering the cost economics, recent research has focused on the development of low-cost readily available alternatives using

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doi:10.1016/j.cej.2008.08.002

Nomenclature

b	Langmuir constant (L/mg)
C	concentration of metal ion after certain period of time (mg/L)
C_a	concentration of metal ion on the adsorbent at equilibrium (mg/L)
C_e	concentration of metal ion in solution at equilibrium (mg/L)
C_{final}	final concentration of metal ion in solution (mg/L)
$C_{initial}$	initial concentration of metal ion in solution (mg/L)
C_0	initial concentration of metal ion in solution (mg/L)
C_t	concentration of metal ion after time t (mg/L)
E	mean sorption energy (kJ mol^{-1})
F	amount adsorbed per gram of adsorbent at time/amount adsorbed per gram of adsorbent at equilibrium
ΔG^0	Gibbs free energy (kJ mol^{-1})
K_2	pseudo-second-order rate constant of adsorption [(mg/g) min]
K_{ad}	Lagergren rate constant (min^{-1})
K_c	thermodynamic equilibrium constant
K_f	measure of adsorption capacity (mg/g)
K_{id}	intra-particle rate constant [(mg/g) min$^{1/2}$]
K_{bq}	the constant obtained by multiplying q_{max} and b
M	mass of the adsorbent per unit volume (g/L)
m	amount of adsorbent added in gram
n	Freundlich constants, intensity of adsorption
q	amount adsorb per gram of the adsorbent (mg/g)
q_e	amount adsorb per gram of the adsorbent at equilibrium
q_m	equilibrium adsorption capacity (mg/g) using model
q_t	experimental value of amount of metal ion adsorb (mg/g of adsorbent) at any time t (min) from experiment
q_{tm}	adsorption capacity (mg/g) at any time t (min), using model
q_{max}	maximum adsorption capacity (mg/g)
q_{exp}	experimental values of equilibrium adsorption capacity (mg/g)
q_t	amount (mg) adsorb per gram of adsorbent at time t (min)
r^2	correlation coefficient
R_L	separation factor
S_s	external surface area of the adsorbent per unit volume (m^{-1})
t	time (min)
V	volume of the solution in mL
X_m	maximum adsorption capacity (mmol/g)

Greek letters

β	mass transfer coefficient (m/s)
λ	constant related to energy (mol^2/kJ^2)
ε	Polanyi potential (kJ^2/mol^2)

various agricultural, industrial, natural/biological waste materials including synthetic, modified model adsorbents. Several contributions have made in this area utilizing number of materials like olive stone carbon [16], sunflower stalks [17], spent grain [18], carboxy methyl cellulose [19], almond-shell carbon [20], sugarcane baggase [21], oak saw dust [22], black locust [22], cassava waste [23], baggage fly ash [24], wheat bran [25], *Aspergillus niger* [26], bone char [27], olive pomace [28], carrot residues [29], red seaweed [30], tree fern [31], sugar beat pulp [32], grape stalk waste [33], maize bran [34] and different low cost adsorbents [35].

Present study deals with a series of batch adsorption experiments to assess the potentiality of saw dust and neem bark for removal of Zn(II) and Cd(II) from aqueous solutions. The effects of adsorbent concentration, pH, contact time and initial metal ion concentration on the adsorption capacity were investigated. The rate kinetics and equilibrium parameters were determined to understand the mechanism of adsorption. Adsorption isotherm models and thermodynamic parameters were also investigated to know the adsorption characteristics.

2. Materials and methods

2.1. Adsorbents

Saw dust and neem bark were used as low-cost natural biosorbent.

Neem bark was collected from a local neem tree near Kolkata, West Bengal, India.

Saw dust of teakwood origin was collected from a saw mill at Dum Dum near Kolkata, West Bengal, India.

2.2. Pretreatment of the adsorbents

Saw dust and neem bark after collection were thoroughly washed with distilled water to remove muddy materials. Then saw dust and neem bark were soaked in 0.1 N NaOH to remove lignin based color materials followed by 0.1 N H_2SO_4 [35]. Finally it again washed with distilled water several times and dried in an air oven at 105 ± 5 °C for 6 h and cooled to room temperature in desiccators.

The adsorbents after drying to constant weight were sieved to obtain particle size of 250–350 μm prior to use for adsorption studies. The analysis was carried using a Particle Size Distribution analyzer (Model 117.08, MALVERN instruments, USA). The results of particle size distribution are presented in Table 1.

2.3. Reagents and equipments

All the necessary chemicals used in the study were of analytical grade and obtained from E. Merck India Limited, Mumbai, India.

Characterization of the adsorbents was carried out by surface area analysis, Bulk density, Scanning Electron Microscope (SEM) and FT-IR studies. The surface area of the both the adsorbents was measured by BET (Brunauer–Emmett–Teller nitrogen adsorption technique). The density of the adsorbents was determined by specific gravity bottle. The moisture content determination in the sample of saw dust and neem bark were carried out with a digital microprocessor based moisture analyzer (Mettler LP16). Scanning electron microscopic (SEM; Model S415A, Hitachi, Japan) studies was also conducted to observe the surface texture and porosity of the adsorbent. FT-IR (FTIR RX-1, PerkinElmer, USA) spectrometer was employed to determine the type of functional groups in saw dust and neem bark responsible for metal adsorption.

HACH-DR-4000 UV–visible Spectrophotometer and Atomic adsorption spectrophotometer (VARIAN SPECTRA AA 55) were used for determination of Zn(II) and Cd(II) content respectively in standard and treated solution. The pH of the solution was measured with a 5500 EUTECH pH Meter using FET solid electrode calibrated with standard buffer solutions.

2.4. Preparation of Zn(II) and Cd(II) standards

The stock solution containing 1000 mg/L of standard Zn(II) and Cd(II) were prepared by dissolving 4.395 g of AR grade $ZnSO_4 \cdot 7H_2O$.