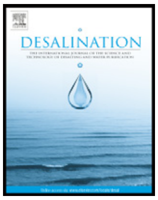
Desalination 273 (2011) 330–342

Contents lists available at ScienceDirect

Desalination

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



Equilibrium modeling of single and binary adsorption of Cd(II) and Cu(II) onto agglomerated nano structured titanium(IV) oxide

Sushanta Debnath, Uday Chand Ghosh *

Department of Chemistry, Presidency College, 86/1 College Street, Kolkata 700073, India

ARTICLE INFO

Article history:
Received 27 October 2010
Received in revised form 15 January 2011
Accepted 17 January 2011
Available online 3 March 2011

Keywords:
Cadmium(II)
Copper(II)
Kinetics
Isotherm
Bi-component
Nanostructured titanium oxide

ABSTRACT

Adsorption reactions of Cd(II) and Cu(II) with nanoparticle agglomerates of titanium(IV) oxide (NHTO) were investigated from single and bi-component systems at optimized pH 5.0. Kinetic data of metal ion removal reactions described the pseudo-second order equation very well. Both Langmuir and Redlich–Peterson models described the equilibrium data well ($R^2 > 0.95$). Values of the monolayer adsorption capacities ($mg \cdot g^{-1}$) of Cd(II) (49.50 to 60.24) and Cu(II) (42.02 to 52.63) were high, and that increased with increasing temperature on the reactions. Thermodynamic analyses of the equilibrium data suggested that the removal reactions were spontaneous [$-\Delta G^0$, $kJ \cdot mol^{-1} = 24.31$ to 32.73 for Cd(II); and 19.62 to 27.38 for Cu(II)]. Spontaneity of the reactions increased with increasing temperature. Langmuir monolayer adsorption capacity of either Cd(II) or Cu (II) was less in presence of each other than that of single component systems. The mean adsorption energy estimation suggested that the interaction between either of the metal ions with NHTO was columbic type. About 71 to 75% of adsorbed metal ions could be recovered as the metal oxide from their solutions, which were obtained by the desorption reaction with 0.1 M HCl.

1. Introduction

Discharge of industrial effluent with excess heavy metal ions contaminates the surface water and soils, and that poses significant threat to the ecology of flora and fauna and human health [1–3]. Heavy metal ions such as Cd(II) and Cu(II) are dangerously toxic to the public health for their high mobilization ability via complex formation through surface soil onto the groundwater. The Water Supply (Water Quality) Regulations 2000 of United Kingdom [4] suggested that the maximum allowed concentration (MAC) limit is 0.005 and 2.0 $mg \cdot L^{-1}$ in drinking water for Cd(II) and Cu(II), respectively. The Cd(II) is extensively used in manufacturing Ni–Cd cells, metal plating, metallurgical alloying, fertilizers, mining, etc. Another major source of surface water contamination with Cd(II) and Cu(II) is urban and agricultural storm water runoffs. Chronic exposure in Cd(II) leads to severe kidney damage in mammals and humans [5–8]. Major sources of Cu(II) contamination in soil as well as water are mining, fertilizer manufacturing, petroleum refineries, paints and pigments, steel works, foundries, electroplating and electrical equipment, brass industries, etc. Trace copper is essential element for the healthy growth of animals and plants. The recommended dietary allowance (RDA) of Cu(II) for an adult male is 3.0 $mg \cdot kg^{-1}$ of the body weight [9]. Inhibition of iron intake takes place with Cu(II) deficiency, which can produce anemia like symptoms [10]. However, continuous exposure to Cu(II) above RDA is fatal to both vegetations and creatures. Varieties type of health disorders encountered for the chronic Cu(II) poisoning [11].

There are different methods such as surface adsorption, chemical precipitation, ion-exchange, nano-filtration, membrane separation, reverse osmosis, etc. for the treatment of heavy metal contaminated surface and ground water. Among them, surface adsorption has been found to be most popular for easy operation, low cost and production of less sludge volume requires small space for disposal. Adsorption of Cd(II) for the removal was investigated using sugar beet pulp [12], iron ore slime [13], macro fungus biomass [14], algal biomass [15], wheat straw [16], tartrazine modified activated carbon [17], aluminum oxide [18] and cation exchange resin [19]. On the other hand, adsorption of Cu(II) for the removal was investigated using wheat straw [16], fish bone [20], tree fern [21], amino-functionalized magnetic nanoparticles [22], chitosan immobilized on bentonite [23], grape stalks waste [24], natural zeolite [25], and valonia tannin resin [26]. However, low adsorption capacities of the most materials, though cheap, limit their practical applications. Despite ion-exchange resin has given promising results, yet low thermal stability and high production cost have restricted its practical utility in the third world countries like India. Aiming to develop the reusable and cost effective adsorbent materials, synthetic hydrous oxides/mixed oxides of some polyvalent metals such as Sn(IV), Zr(IV), Fe(III) and Ti(IV) were investigated in removing As(III), As(V), Cr(VI), Pb(II) and fluoride from the contaminated water [27–33]. Among them, hydrous Ti(IV) oxide has got special attention for its multivariate activities. Titanium(IV) oxide has got special attention for photo oxidative and surface active

---

* Corresponding author. Tel./fax: +91 3322413893.
E-mail addresses: sushanta.debnath@yahoo.com (S. Debnath), ucghosh@gmail.com (U.C. Ghosh).

0011-9164/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.desal.2011.01.043

properties, which had been exploited for dye contaminated waste water treatment [34]. All these had encouraged to use hydrous Ti(IV) oxide for the investigation of metal ions removal from the aqueous solutions.

Thus, this manuscript reports herein some physicochemical aspects of Cd(II) and Cu(II) adsorption from the single and bi-component aqueous solutions for their removal by the synthetic nano-particles agglomerate of hydrous Ti(IV) oxide (NHTO).

2. Materials and methods

2.1. Instruments

Transmission electron micrographic (TEM) image was recorded on a FEI Tecnai S Twin transmission electron micrograph operating at 200 kV. Scanning electron microscopic (SEM) image (Tescan Vega, U.K.; model LSU+) was recorded spraying the sample on a carbon tape. The BET surface area and the pore-size distribution of NHTO were recorded on a Quantachrome Autosorb 1C BET surface area and pore size analyzer. An ELICO (India) made pH meter (model LI 127) was used for pH analysis. Atomic absorption spectrophotometer (model AAnalyst 200, Perkin Elmer) was used for analyzing metal concentration in solutions. Fourier Transform Infrared (FTIR) spectrophotometer (JASCO 680 Plus) was used for recording FTIR spectra.

2.2. Stock solutions

The stock solutions (1000 $mg \cdot L^{-1}$) of Cd(II) and Cu(II) were made separately by dissolving (in 1.5% nitric acid) an appropriate amount of cadmium(II) chloride and copper(II) chloride (guaranteed reagents), which were procured from E. Merck (India), Mumbai. The solutions of desired concentrations were prepared by diluting each stock with distilled water for the experiments. The exact concentration of each test solution was analyzed by the atomic absorption spectrophotometer (AAS) against the standard [35] before and after conducting experiments.

2.3. Synthesis of NHTO

Synthesis and characterization of NHTO were described in our previous work [36]. The outline of NHTO synthesis is the ingestion of 30 mL $TiCl_4$ slowly into 1.0 L distilled water with constant stirring. The curd-like white precipitate including liquid was treated with aqueous 0.1 M ammonia solution to raise pH of the supernatant to 4.8 (±0.2). The precipitate was aged for 6 days with the mother liquid, filtered and washed three times with deionised water until free from chloride. The solid mass, dried in an air-oven at 50° to 60 °C was ground and screened through a set of sieves for the size of agglomerates ranged in 0.29 to 0.36 mm for conducting experiments.

2.4. Experimental procedures

Adsorption experiments were carried out in a series of well capped polyethylene bottles (capacity: 250 mL). In each bottle, 0.1 g NHTO was placed with 50 mL of metal ion solution of initial concentration C_o ($mg \cdot L^{-1}$). The reaction mixtures in bottles were agitated (speed, $S_T = 300 \pm 10$ rpm) by a thermostatic rotary shaker at a fixed temperature ($T \pm 1$ °C) and pH for desired time duration. Once the agitation period was over, each reaction mixture was centrifuged. The metal concentration remaining in centrifugate was analyzed [39]. Adsorbed amount of the metal ion per unit mass of NHTO (q_{ad}, $mg \cdot g^{-1}$) was calculated by Eq. (1).

$$q_{ad} = \frac{w_i - w_r}{m} \tag{1}$$

where w_i and w_r are the initial and residual amounts of each metal ion (mg) added and remained in solution, respectively; m is the mass (g) of NHTO added for the experiment with metal solution.

For assessing the influence of initial solution pH (pH_i) on the adsorption reactions, experiments were conducted at pH_i ranged in 2.0 to 9.0 at T = 30 °C by the procedure described above taking C_o of the metal ions 10.0 $mg \cdot L^{-1}$. The time of agitation employed was 2.0 h. The blank experiments were also conducted at identical conditions without adding NHTO with metal solutions in bottles for the corrections.

For the assessment of influence of T and C_o on the adsorption reactions with NHTO, the experiments were carried out separately taking $C_0 = 2.5$, 5.0 and 10.0 $mg \cdot L^{-1}$ at T = 15°, 30° and 45 °C. The liquid phases were separated from the solids by centrifugation immediately after the over of agitation time (1.0 h) and, each centrifuged liquid was analyzed for the residual metal concentration.

Experiments for the reaction kinetics were carried out by agitating ($S_T = 300 \pm 10$ rpm) the reaction mixture taking at optimum pH. Here, 500 mL of each metal ion solution of $C_o = 2.5$, 5.0 and 10.0 $mg \cdot L^{-1}$ at pH 5.0 separately was mixed with 1.0 g NHTO taken into 1.0 L glass beakers, and agitated at adjusted T = 15°, 30° and 45 °C. At a regular time intervals, a suitable aliquot after centrifugation was analyzed for the residual metal concentration. Amount of the metal ion (mg) adsorbed per unit g of NHTO was calculated by the relation (Eq. 1).

Equilibrium isotherm experiments for the adsorption reactions of metal ions with NHTO were investigated at $pH_i = 5.0$ and $C_o = 25$ to 300 $mg \cdot L^{-1}$ by agitating ($S_T = 300 \pm 10$ rpm) for an hour at T = 15°, 30°, 45° and 60 °C.

The solution compositions that used for the adsorption reactions from binary systems of Cd(II) and Cu(II) for their removal by NHTO were:

Concentration of initial metal ion solution (C_0, $mg \cdot L^{-1}$)								
Cd(II)	25.0	50.0	75.0	100.0	125.0	150.0	200.0	300.0
+Cu(II)	300.0	200.0	150.0	125.0	100.0	75.0	50.0	25.0

Here, 0.1 g NHTO was added with 50 mL solutions of metal ions mixture (pH = 5.0), and agitated ($S_T = 300 \pm 10$ rpm) for 1.0 h at T = 30 °C. The concentration of the metal ion remaining in solution was analyzed.

2.5. Kinetic models used

The kinetics of the removal reactions had been modeled using Eqs. (2–6) given below:

Equations	Non-linear form of the equation	Equation number	Reference
Pseudo-first order	$q_t = q_e\,[1 - \exp(-k_1 t)]$	2	[37]
Pseudo-second order	$q_t = \dfrac{t}{(1/k_2 q_e^2) + (t/q_e)}$	3	[38]
Intraparticle diffusion	$q_t = k_{id} t^{0.5} + C$	4	[39]
Pore diffusion coefficient (D_p)	$D_P = \dfrac{0.03 r_o^2}{t_{0.5}}$	5	[40]
Film diffusion coefficient (D_F)	$D_F = \dfrac{0.23\, r_o \delta C_s}{C_L t_{0.5}}$	6	[41]

where q_t and q_e are adsorption capacities ($mg \cdot g^{-1}$) at any time, t (min) and equilibrium, respectively; k_1 (min^{-1}), k_2 ($g.mg^{-1} \cdot min^{-1}$) and k_{id} ($g \cdot mg^{-1} \cdot min^{-0.5}$) the pseudo-first order, pseudo-second order and intra-particle diffusion rate constants, respectively. C represents the external convective mass transfer from the bulk liquid to the surface of the solid as it has same unit with q_t, which gives an idea about the thickness of the boundary layer. The larger the value of C the greater is the boundary layer effect [43]. C_S and C_L are the solid and solution phase solute concentrations ($mg \cdot g^{-1}$), respectively; δ is film thick-