Desalination 259 (2010) 140–146

Contents lists available at ScienceDirect

Desalination

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

Adsorption kinetics and isotherm of Cd(II) ion on *Nannochloropsis* sp biomass imprinted ionic polymer

Buhani [a,*], Suharso [a,*], Sumadi [b]

[a] Department of Chemistry, Faculty of Mathematic and Natural Sciences, University of Lampung, Lampung, Indonesia
[b] Department of Electrical Engineering, Faculty of Engineering, University of Lampung, Indonesia

ARTICLE INFO

Article history:
Received 7 October 2009
Received in revised form 30 March 2010
Accepted 10 April 2010
Available online 15 May 2010

Keywords:
Imprinted ionic
Nannochloropsis sp
Adsorption
Cadmium

ABSTRACT

Adsorption kinetics and isotherm of Cd(II) ion on Cd(II) ion imprinted adsorbent — *Nannochloropsis* sp (Cd (II)–IIP) biomass have been studied at pH of 5 and temperature of 27 °C. Two kinetic models, i.e pseudo-first order and pseudo-second order are applied to fit the experimental kinetic data. The results indicate the best fit obtained with pseudo-first order model, with the value of k_1 in the range of 0.0417–0.1097 min^{-1}. Equilibrium data showed that adsorption of Cd(II) ion on the Cd(II)–IIP following Langmuir adsorption isotherm model with adsorption capacities of 32.114–40.725 mg/g adsorbent which is higher than adsorption capacity of non imprinted ionic polymer (NIP) namely 16.902 mg/g adsorbent. Cd(II)–IIP adsorbent can be used effectively for treatment of cadmium containing wastewaters as an alternative.

1. Introduction

Many heavy metals are toxic and cause environmental damage. One of the heavy metals is cadmium which is toxic and carcinogenic. The sources of these metals are food, drinking water and air. Roughly 15,000 t of Cadmium are produced worldwide each year for nickel–cadmium batteries, pigments, chemical stabilizers, metal coatings and alloy [1]. Yet, because of its low excretion rate (biological half-life = 10–30 years), cadmium accumulates in the body [2]. Therefore, preconcentration, selective separation of trace cadmium from natural water, and waste water industry are very important and need much more attention [3–6].

Several methods have been developed to reduce heavy metal concentration from waste water such as; chemical precipitation, coagulation, complexation, solvent extraction, membrane separation, ion exchange, and adsorption. From these techniques, adsorption is always used because its process is relatively simple and cheap [7,8].

Recently, specific adsorbent is much developed; it contains ligands which interact specifically with metal ion derived from supporting solid modification from inorganic material (like silica) or polymer. Adsorption surface modification is carried out by immobilizing organic functional group derived from natural product (like algae biomass and fungi) or synthesis organic material containing active groups which are able to play a role as heavy metal complexes [9–13].

Algae biomass from several algae species is effective to bind metal ions from aqueous environment [14–16] because algae biomass contains several functional groups which can role as ligands upon metal ions [7,17,18]. But, it has some problems because it has low density and it is easy to be degraded chemically or biologically [14,19]. Therefore, it is not effective to be used as column filling material to adsorb continuously. *Nannochloropsis* sp is one of the algae species which has a potency as an adsorbent to adsorb heavy metals and is in abundance in an aqueous environment as well as it is easy to be cultivated. Based on the research result of Buhani and Suharso [12], immobilization of *Nannochloropsis* sp biomass with sol–gel technique increased adsorption capacity upon metal ions but it was not selective.

Increasing of adsorption capacity and selectivity can be performed by immobilizing algae biomass using silica gel supporting matrix through imprinted ionic technique. Imprinted ionic polymer technique (IIP) can raise adsorption selectivity because metal ion can play a role as a template to form polymer *via imprinted* [20–25]. Imprinted ionic technique is based on copolymerization from isolated monomer or non isolated monomer and complex ion with *crosslinking* agent [26,27]. With this technique, appropriate ligand group will interact with metal ion to form complex which is covered by polymer *via crosslinking*. Then, metal ion will be released (template) if there is an interaction with the same metal ion (target). In addition, it will raise stronger interaction and also selectivity through metal ion target.

In this research, it used biology material from *Nannochloropsis* sp biomass as metal ion Cd(II) complex agent with silica gel supporting matrix. *Nannochloropsis* sp biomass imprinted ionic adsorbent was used to study kinetic model and Cd(II) ion adsorption isotherm in solution. Adsorption isotherms were determined, compared to Langmuir and Freundlich equation, and maximum capacities were calculated for both non imprinted ionic polymer (NIP) and imprinted

* Corresponding authors. Tel.: +62 721 770422; fax: +62 721 770422.
E-mail addresses: buhani_s@yahoo.co.id (Buhani), suharso@unila.ac.id (Suharso).

0011-9164/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.desal.2010.04.019

ionic Cd(II) polymer (Cd(II)–IIP) *Nannochloropsis* sp biomass. The kinetic study of the Cd(II) uptake of (Cd(II)–IIP) *Nannochloropsis* sp biomass allowed the calculation of parameters according to two different kinetic models.

2. Experimental

2.1. Materials

The tetraethoxysilane (TEOS) and ethanol, $CdCl_2 \cdot H_2O$, Na_2EDTA, KNO_3, $HONH_2HCl$, and CH_3COOH used are commercial products of Merck, Germany. NaOH, NH_4OH and HCl (37%) were purchased from Alba Chemical. Algae biomass was collected from Lampung Sea Cultivation Bureau/Balai Budidaya Laut Lampung, Indonesia. It was washed with distilled water to remove dirt and was kept on a filter paper to reduce the water content. Then, the biomass was sun dried for 3 days followed by drying in an oven at 60 °C for 12 h and then ground on an agate stone pistol mortar. The biomass was then sieved to select the particles between 100 and 200 mesh sizes for use.

The sorbent was characterized using infrared (IR) spectroscopy (Prestige-21 Shimadzu, Made in Japan). A scanning electron microscopy and energy dispersive x-ray (SEM-EDX) (JSM 6360 LA, Made in Japan) were used for identification of the element composition. The metal solution was analyzed using an atomic absorption spectrophotometer (AAS) (Model Perkins Elmer 3110, Made in USA) at conditions of wavelength of 228.8 nm, slit of 0.7 nm, lamp current of 8 mA, flow rate of flame gases (air; 9.5 L/min and acetylene; 2.2 L/min).

2.2. Preparation of Cd(II)-imprinted polymer (Cd(II)–IIP)

At synthesis of imprinted ionic Cd(II) with *Nannochloropsis* sp biomass, interacted solution was divided into two parts consisting of solution a filling 5 mL TEOS and 2.5 mL water filled in plastic glass and added 2 drops of HCl solution 1 M up to pH 2, then they were stirred with magnetic stirrer for 30 min until homogeneous. Solution b: an amount of $CdCl_2 \cdot H_2O$ and ethanol was added into plastic glass (Table 1), heated and stirred by a magnetic stirrer until it was dissolved. Then, it was added with biomass and stirred for 1 h. Solutions a and b were mixed and stirred again for 30 min until the homogeneous gels were formed. Formed gel was left for a night and rinsed by water/ethanol 60/40% followed with soaking the gel for 24 h in Na_2EDTA solution 0.1 M and HCl 0.1 M. Further, the adsorbent was dried in an oven for 2 h at temperature of 70 °C. The Cd concentration in the gel before and after released was analyzed by atomic adsorption spectrophotometer (AAS). Obtained adsorbent was grounded and sieved by 200 mesh size.

2.3. Sorption experiments

Adsorption kinetic**:** an amount of 0.3 g adsorbent was interacted with 120 mL of metal ion Cd(II) 100 mg/L at pH 5 with interaction times of 5–120 minutes. Then, the solution was centrifuged and filtrate was taken to identify the metal concentration left in solution using AAS.

Adsorption isotherm**:** an amount of 100 mg adsorbent was interacted with 20 mL of metal ion solution with various concentrations of 0.0–250.0 mg/L. The adsorption was performed in a batch system using a shaker with pH 5 and optimum interaction time (b). Then, the solution was centrifuged and filtrate was taken to analyze the metal concentration left by AAS.

Interaction type**:** in order to determine the interaction type metal ion, it was started with the adsorption process using 500 mg Cd(II) ion solution. Determination of adsorption mechanism was done using sequential desorption method. Desorption was carried out by washing adsorbent adsorbing metal ion using solution which is its different adsorption strengths namely; water, KNO_3 0.50 M, $HONH_2HCl$ 0.30 M in 25% (v/v) CH_3COOH and Na_2EDTA 0.10 M. The metal ion concentration in filtrate was measured by AAS.

Table 1
Solution composition in imprinted ionic Cd(II)–algae biomass polymer synthetic at various concentrations of Cd(II).

Formula	Solution a			Solution b	
	TEOS (mL)	Watr (mL)	Ethanol (mL)	Algae biomass (g)	$CdCl_2$ H_2O (g)
NIP	5.0	2.5	2.5	0.4	–
Cd(II)–IIP-a	5.0	2.5	5.0	0.4	0.0483
Cd(II)–IIP-b	5.0	2.5	5.0	0.4	0.0966
Cd(II)–IIP-c	5.0	2.5	5.0	0.4	0.1932

3. Results and discussion

3.1. Adsorption kinetics

The efficiency of NIP and Cd(II)–IIP biomass *Nannochloropsis* sp adsorbent was evaluated by studying adsorption kinetics of metal concentration Cd(II) in solution and was determined at different times with 100 mg/L starting solution and a sorbent concentration 2.50 g/L. The shape of the curve representing metal uptake versus time (Fig. 1) suggests that two step mechanisms occurs. The first portion indicates that a rapid adsorption occurs during the first 30 min after which an equilibrium is slowly achieved. Almost 90% removal for Cd(II) occurred within 1 h. The different models described in Fig. 1 are applied to experimental data.

Pseudo-first and second order models**,** the kinetic of total Cd(II) adsorption by NIP and Cd(II)–IIP biomass *Nannochloropsis* sp (Fig. 1) was tested with respect to first order model of Lagergren (Eqs. (1) and (2)) and second order model (Eqs. (3) and (4)) [7,28]:

$$q_t = q_e\left(1-e^{-k_1 t}\right) \tag{1}$$

$$\log\left(q_e - q_t\right) = \log q_e - \frac{k_1}{2.303}t \tag{2}$$

$$q_t = \frac{q_e^2 k_2 t}{1 + q_e k_2 t} \tag{3}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{4}$$

where qt and qe (mg/g) are total Cd(II) ion adsorption capacity at time t and at equilibrium, respectively, k_1 and k_2 are the first order and

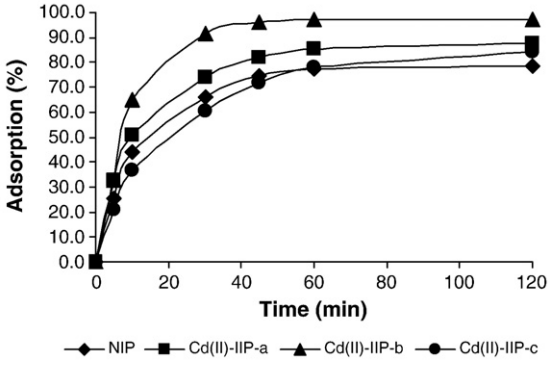

Fig. 1. Cd(II) adsorption kinetics onto NIP, Cd(II)–IIP-a, Cd(II)–IIP-b, and Cd(II)–IIP-c at 27 °C.