Kinetics, equilibrium and thermodynamic study on removal of Cr (VI) from aqueous solutions using low-cost adsorbent Alligator weed

Xue Song Wang *, Ye Ping Tang, Sheng Rong Tao

Department of Chemical Engineering, Huaihai Institute of Technology, Changwu Road, 59 Lianyungang, Jiangsu 222005, China

ABSTRACT

The removal of Cr (VI) from aqueous solutions using Alligator weed, a freshwater macrophyte, was investigated as a function of initial pH, contact time, reaction temperature and adsorbent concentration in batch studies. An initial solution pH of 1.0 was most favorable for Cr (VI) removal. The kinetic experimental data fitted the pseudo-second-order equation, Elovich equation and Langmuir–Hinshelwood equation very well. The adsorption of Cr (VI) onto Alligator weed conformed to the linear forms of the Langmuir, Freundlich and Temkin equations. The removal efficiencies increased with the increased adsorbent dose from 1 to 8 g/L and were 86.6, 97.6 and 99.7% at the adsorbent dose of 8 g/L, solution pH 1.0 and temperatures of 30, 40 and 50 °C, respectively. Thermodynamic parameters (activation enthalpy change, activation entropy change and activation free energy change) revealed that the adsorption of Cr (VI) onto Alligator weed is endothermic, non-spontaneous, with a decreased randomness in nature.

© 2008 Elsevier B.V. All rights reserved.

1. Introduction

Environmental contamination by heavy metals is of growing concern because of health risks on humans and animals. Cr (VI) is a cancer-causing agent and can pose health risks such as liver damage, dermatitis, and gastrointestinal ulcers [1]. Several wastewaters, such as those produced during dyes and pigments production, film and photography, galvanometry, metal cleaning, plating and electroplating, leather and mining, may contain undesirable amounts of chromium (VI) anions [2,3]. The conventional treatment method applied in these industries is based on the precipitation of the hydroxide form of Cr (III). In this method, Cr (VI) is removed by reduction to Cr (III) with reducing agents followed by precipitation with hydroxide compounds. However, this method has high costs associated with the chemical reduction. Biosorption, a technically feasible and economical process, has gained increased creditability during recent years [3]. Although most current research of biosorption is oriented towards the removal of heavy metal cations, the uptake of toxic metal anionic forms by biomass has become a growing concern in this field [3]. The removal of Cr (VI) using various low-cost biosorbents including wool, olive cake, sawdust, pine needle, cactus leaves [4], waste tea [5], defatted rice bran, rice hulls, soybean hulls, cotton seed hulls and Bengal gram husk [6], *Ecklonia* sp. biomass [7], *Aeromonas caviae* biomass [3], brown marine algae *Laminaria japonica*, red marine algae *P. yezoensis Ueda*, agricultural by-products rice bran and wheat bran [8], has been previously studied with promising results.

Alligator weed (a freshwater macrophyte) is an invasive plant that originates from South America and is currently invading many countries throughout the world. The plant invades agricultural areas and blocks drainage and irrigation channels causing problems on agricultural land. Other concerns of Alligator weed include water pollution from plant decomposition. In previous studies, the living biomass of Alligator weed showed a high potential for removing different metals including Co (II), Ni (II), Ag (I), Cd (II), Hg (II) and Pb (II) from the aquatic environment in laboratory experiences [9]. However, it has been demonstrated that the incorporation of heavy metals produces phytotoxic effects on plants resulting in inhibition of chlorophyll synthesis and biomass production that leads to death. Moreover, the use of phytotechnologies as secondary wastewater treatments implies the disposal of high volumes of contaminated plants [10]. The use of dead, dried aquatic plants, for metal removal as a simple biosorbent material has advantages in its high efficiency in detoxifying dilute effluents, minimization of the volume of chemical and/or biological sludge to be disposed of, no nutrient requirements, low cost, conservation, transport, handling. Also, the biomass loaded with heavy metals can be regenerated with acid and/or hydroxide solution that discharge small volumes of concentrated heavy metal [10]. In our laboratory, the non-living biomass of Alligator weed has been successfully used to remove Ni (II) and Zn (II) [11].

* Corresponding author. Tel.: +86 518 85895408; fax: +86 518 85895409.
E-mail address: snowpine1969@yahoo.com.cn (X.S. Wang).

The objectives of this work were to characterize the potential of Alligator weed to remove Cr (VI) from single aqueous solutions. The effects of agitation time, solution pH, and solution temperature, adsorbent dose on its adsorption were investigated.

2. Materials and methods

Alligator weed was obtained from wild specimen growing in Lianyungang, China. The plant tissues were washed with tap water to remove the impurities and then soaked overnight in a 1:10 acetone solution. Afterwards, the material was rinsed with deionized water and dried at 60 °C and finally ground with a mill to pass through a 100-mesh sieve for following biosorption experiments.

FT-IR analysis of the biosorbent used in this study was performed using a Fourier transform infrared spectrometer (FT/IR-5300). The biosorbent powders were blended with IR-grade KBr in an agate mortar and pressed into tablet. The spectra of the biosorbent were recorded.

The surface area of the biomass was determined by the Brunauer–Emmett–Teller (BET). Nitrogen adsorption technique using a Quantasorb surface area analyzer (Model-05). The porosity and particle density were determined by mercury intrusion porosimeter (Micrometrics model-9310) and specific gravity bottle, respectively. The pore volume was obtained as the inverse relation of particle density. The moisture content of the biomass sample was obtained using thermal drying method. These results are listed in Table 1.

The stock solution (1000 mg/L) was prepared by dissolving 2.829 g of potassium dichromate ($K_2Cr_2O_7$) (AR grade) in 1000 mL of deionized water. The stock solution was finally diluted to obtain standard solutions. Solutions of 0.1 mol/L NaOH and/or HCl were used for pH adjustment using a PHS-3C pH meter using a combined glass electrode calibrated with buffers of pH 2, 4, and 7.

Kinetic studies were carried out at constant pH 1.0 with an initial concentration of 100 mg/L and adsorbent dose of 4 g/L at various temperatures (30, 40, and 50 °C). In addition, to investigate the effects of adsorbent dose and initial concentration on kinetic performance, experiments were also carried out at constant pH 1.0 with two different initial concentrations (160 and 320 mg/L) and adsorbent doses from 2 to 10 g/L at 30 °C, respectively. After shaking, the solution samples were withdrawn at suitable time intervals. For the isotherm studies, 0.2 g of biosorbent was put into 50 mL solutions of various concentrations of Cr (VI). The flasks were shaken to reach equilibrium. A known volume of the solution was removed and centrifuged for Cr (VI) analysis. Effect of pH on the adsorption of Cr (VI) was studied by varying the pH from 1.0 to 6.0 at various initial concentrations (40, 80, and 120 mg/L). The effect of temperature on adsorption equilibrium was studied by varying temperatures from 30 to 50 °C. Temperature control was provided by the constant-temperature water bath shaker unit (THZ-82, China Jiangsu Jingtan Guosheng Instrumental Factory). Effects of various biosorbent doses on adsorption of Cr (VI) were investigated by varying the range of biosorbent dose with an initial Cr (VI) concentration 320 mg/L and agitation speed of 200 rpm at various temperatures.
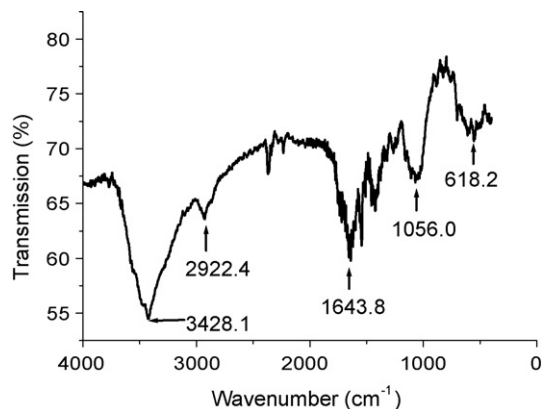
Fig. 1. Infrared spectra of the biomass.

The resulting solutions were centrifuged and the supernatant liquid analyzed. The concentrations of Cr (VI) were determined using diphenylcarbazide method. Diphenylcarbazide forms a purple-violet complex selectively with Cr (VI), and the intensity of this complex was read at 542 nm using a model 722 UV-visible spectrophotometer (China Shanghai Third Component factory). The detection limit of this method was 0.03 mg/L. Analyses were done triplicate samples. Controls comprised of adsorbent in deionized water blank and adsorbent-free Cr (VI) solutions.

The amount of Cr (VI) sorbed by sorbent (q) in the sorption system was calculated using the mass balance:

$$q = \frac{V(C_i - C_e)}{m},\tag{1}$$

and the Cr (VI) percent removal (%) was calculated using the following equation:

$$\text{Removal } (\%) = \frac{C_i - C_e}{C_i} \times 100,\tag{2}$$

where V is the solution volume (L), m is the amount of sorbent (g), and C_i and C_e (mg/L) are the initial and equilibrium metal concentrations, respectively.

3. Results and discussion

3.1. Infrared spectra analysis

In order to determine the functional groups responsible for Cr (VI) uptake, FT-IR technique was used. The infrared spectra are shown in Fig. 1. The adsorption bands identified in the spectra and their assignment to the corresponding functional groups in the sorbent are listed in Table 2. Wave number of 3428.1 cm^{-1} indicates the possible presence of –OH, –NH groups on the sorbent surface. The bands that are observed at 2922.4 and 618.2 cm^{-1} suggest the presence of C–H group. The strong peak at 1643.8 cm^{-1} band is caused by the C=O stretching band of the carboxyl group. The band appears at approximately 1056.0 cm^{-1} is due to C–O stretching vibrations of primer alcohol. These results indicate that the possible presence of

Table 1
The properties of the biomass sample

Parameters	Values
Density (g/cm^3)	0.85
Specific surface area (m^2/g)	36.5
Porosity (%)	42.3
Pore volume (cm^3/g)	0.54
Moisture (%)	24.5

Table 2
IR adsorption bands and corresponding possible functional groups

Wave numbers (cm^{-1})	Functional groups
3428.1	–OH, –NH
2922.4	–CH
1643.8	–COO$^-$, –C=O
1056.0	–C–O
618.2	–CH