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ORIGINAL ARTICLE

Removal of toxic chromium from aqueous solution, wastewater and saline water by marine red alga *Pterocladia capillacea* and its activated carbon

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Abstract *Pterocladia capillacea*, a red marine macroalgae, was tested for its ability to remove toxic hexavalent chromium from aqueous solution. A new activated carbon obtained from *P. capillacea* via acid dehydration was also investigated as an adsorbent for toxic chromium. The experiments were conducted to study the effect of important parameters such as pH, chromium concentration and adsorbent weight. Batch equilibrium tests at different pH conditions showed that at pH 1.0, a maximum chromium uptake was observed for both inactivated dried red alga *P. capillacea* and its activated carbon. The maximum sorption capacities for dried red alga and its activated carbon were about 12 and 66 mg g^{-1}, respectively, as calculated by Langmuir model. The ability of inactivated red alga *P. capillacea* and developed activated carbon to remove chromium from synthetic sea water, natural sea water and wastewater was investigated as well. Different isotherm models were used to analyze the experimental data and the models parameters were evaluated. This study showed that the activated carbon developed from red alga *P. capillacea* is a promising activated carbon for removal of toxic chromium.

1. Introduction

Heavy metal pollution represents an important environmental problem due to toxic effects and accumulation throughout the food chain. These pollutants are toxic and non-biodegradable and probably have health effect (Pellerin and Booker, 2000). Several industries like paint and pigment manufacturing, stainless steel production, corrosion control, textile, leather tanning, chrome electroplating, metal finishing industries, wood preservation, photography, etc. discharge effluent containing hexavalent chromium, Cr^{6+}, to surface water. Hexavalent chromium is toxic and a suspected carcinogen material and it is quite soluble in the aqueous phase almost over the entire pH range and mobile in the natural environment (Gode and Pehlivan, 2005). A very high positive redox potential is demonstrated for acidic solution of hexava-

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lent chromium which is strongly oxidizing and unstable in the presence of electron donors. Several species can be obtained from hexavalent chromium depending on pH and its total concentration. The $HCrO_4^{2-}$ form exists in the solution if the solution pH > 7, while in the pH between 1 and 6, CrO_4^{2-} is predominant. Therefore, within the normal pH range in natural waters, the CrO_4^{2-}, CrO_4^{2-} and $Cr_2O_7^{2-}$ ions are forms expected and they constituted a lot of hexavalent chromium compounds, which are quite soluble and mobile in water streams (Gode and Pehlivan, 2005; Ko et al., 2002). The maximum permissible levels for Cr^{3+} and Cr^{6+} ions in wastewater are 5 and 0.05 mg L^{-1}, respectively. They exist as low levels in the environment. While Cr^{3+} apparently plays an essential role in plant and animal metabolism, the Cr^{6+} is directly toxic to bacteria, plants and animals (Richard and Bourg, 1991). The most severe chromium compounds are chromium oxide and chromium sulfate as trivalent and chromium trioxide, chromic acid and dichromates as hexavalent chromium (Ramos et al., 1994).

Sorption process has been extensively used to remove toxic metals from aquatic medium using low cost adsorbents such as agriculture wastes and activated carbon developed from agriculture wastes (Babel and Kurniawan, 2003; Demirbas et al., 2004; Ahalya et al., 2005; El Nemr et al., 2006, 2007, 2010; Abdelwahab et al., 2007; Wang et al., 2009). Among the most promising biomaterials studied is algal biomass (Vijayaraghavan et al., 2005; Kalyani et al., 2004; Gupta et al., 2001; Zeroual et al., 2003; Abdelwahab et al., 2006a,b; El-Sikaily et al., 2006; Han et al., 2008; Gupta and Rastogi, 2009; Ncibi et al., 2009; Deng et al., 2009; Zakhama et al., 2011). The presence of carboxylic (–COOH), sulfonic (–SO_3H) and hydroxyl (–OH) groups in the marine algae polysaccharides are believed to be responsible for impressive metal uptake by marine algae (McKay et al., 1999; Davis et al., 2003). Moreover, the macroscopic structures for marine algae present a convenient basis for the production of biosorbent particles suitable for sorption process applications (Vieira and Volesky, 2000).

As the most toxic species of chromium cannot be removed directly by precipitation, the main objective of this study was to evaluate the possibility of using dried red alga *Pterocladia capillacea* (DRA) and activated carbon developed from *P. capillacea* (CRA) as sorbents for the elimination of Cr^{6+} from polluted waters by systematic evaluation of the parameters involved, such as pH, sorbents mass, initial chromium concentration and time. The interference of the real wastewater and saline water on the Cr^{6+} sorption was additionally investigated.

2. Materials and methods

2.1. Biomass

Fresh red algal biomass of *P. capillacea* species was collected from Abo-Quir Bay, Alexandria, Egypt. Before being dried, it was washed with sea water and then with tap water followed by washing with distilled water. After this, the clean algal biomass was sun dried for two days followed by air oven drying at 105 °C for 72 h, and the dried red alga (DRA) was milled and sieved to select particles ⩽0.063 mm for use (Deng et al., 2009; Gupta and Rastogi, 2009).

2.2. Activated carbon from red alga (CRA)

The dried red algal (DRA) biomass of *P. capillacea* (1.0 kg) was added in small portion to 600 ml of 98% H_2SO_4 and the resulting reaction mixture was kept for 1 h at room temperature followed by refluxing for 5 h in an efficient fume hood. After cooling to room temperature, the reaction mixture was poured onto cold water (4 L) and filtered. The resulting material was washed repeatedly with water and then soaked in 1% $NaHCO_3$ solution to remove any remaining acid. The obtained carbon was then washed with distilled water until pH of the activated carbon reached 6, dried in an oven at 250 °C for 1 h in the absence of oxygen and sieved to the particle size ⩽0.063 mm and kept in a glass bottle until used.

2.3. Preparation of synthetic solution

A stock solution of 1.0 g L^{-1} was prepared by dissolving the 2.831 g of potassium dichromate ($K_2Cr_2O_7$) in 100 ml and completed to 1000 ml with distilled water. Concentrations ranged between 5 and 100 mg L^{-1} were prepared from the stock solution to have the standard curve. All the chemicals used throughout this study were of analytical-grade reagents. Double-distilled water was used for preparing all of the solutions and reagents. The initial pH is adjusted with 0.1 M HCl or 0.1 M NaOH. All the sorption experiments were carried out at room temperature (25 ± 2 °C).

The concentration of Cr^{6+} ions in solution was measured by using an indirect UV–visible spectrophotometric method based on the reaction of Cr^{6+} and 1,5-diphenylcarbazide, which forms a red-violet colored complex (Gilcreas et al., 1965). The absorbance of the colored complex was measured using UV–VIS spectrophotometer (Milton Roy, Spectronic 21D) using silica cells of path length 1 cm at wavelength λ 540 nm, and Cr^{6+} concentration was determined by comparing absorbance to a calibration curve mentioned above. All the experiments are duplicated and only the mean values are reported. The maximum deviation observed was less than ±5% (Ncibi et al., 2009).

2.4. Red alga characterization

The functional groups present in the red alga and its activated carbon were characterized by a Fourier transform infrared (FT-IR), using KBr disks to prepare the alga samples.

The X-ray diffraction spectrum was obtained by passing the sample through 44 μ copper target. Samples were exposed to X-ray (λ = 1.5418 Å) with the 2θ angle, scan range varying between 4°–9° and scan speed 2 deg/min. The applied voltage and current were 30 kV and 30 mA, respectively.

The morphological characteristics of red alga and its activated carbon were evaluated by using a JEOL JSM-6360 scanning electron microscope with an electron acceleration voltage of 20 kV.

2.5. Simulation studies

Synthetic sea water was prepared by dissolving 35 g of NaCl in 1000 ml distilled water and used instead of distilled water. Different weights of chromium were dissolved in the synthetic sea water to obtain different concentrations of Cr^{6+}.