Ecotoxicology and Environmental Safety 121 (2015) 149–153

Contents lists available at ScienceDirect

Ecotoxicology and Environmental Safety

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

Synthesis of magnetic biocomposite for efficient adsorption of azo dye from aqueous solution

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ARTICLE INFO

Article history:
Received 24 October 2014
Received in revised form
20 April 2015
Accepted 27 April 2015
Available online 7 May 2015

Keywords:
Magnetic biocomposites
Magnetic separation
Adsorption
Azo dyes

ABSTRACT

A novel magnetic biocomposite was synthesized using metal chlorides and aquatic macrophytes by co-precipitation method. The resulting product, magnetic biocomposite was characterized by Fourier transform infrared spectra (FTIR), X-ray diffraction (XRD), Energy-dispersive X-ray spectroscopy (EDX) and Scanning electron microscope (SEM). The adsorption performance of the magnetic biocomposite was tested with removal of Metanil Yellow dye from aqueous solution. The effect of influencing parameters such as initial dye concentration, solution pH and agitation were investigated. The equilibrium isotherm was well described by the Langmuir model with the with maximum adsorption capacity of 90.91 mg/g. Adsorption kinetics experiments were carried out and the data were well fitted by a pseudo-second-order equation. The results revealed that the magnetic biocomposite could efficiently adsorb the azo dyes from aqueous solution, and the spent adsorbents could be recovered completely by magnetic separation process. Therefore, the prepared magnetic biocomposite could thus be used as promising adsorbent for the removal of azo dyes from polluted water.

1. Introduction

Water pollution has become a universal crisis with progression of modern industries (Bhatnagar and Sillanpaa, 2010). Among the contaminants, color effluents are considered to be more harmful substances due to their perilous outcome to the plants, aquatic organisms, animals and human beings. Significantly, azo (–N=N–) group of dyes are widely used in industries such as textile, paper, plastic and leather industries. It would be extremely worthy to remove synthetic dye like azo dyes from industrial wastewaters prior to their release due to their toxic and mutagenic property. Several conventional techniques such as solvent extraction, photocatalytic degradation, chemical coagulation and biodegradation are expensive and not eco-friendly (Chen et al., 2014; Chunhua et al., 2014). Adsorption may be an alternative potential technique for removing dyes from wastewater for its comparatively low cost, high capability, easy regeneration and flexibility in design and performance, etc. Activated carbon (Valix et al., 2006) alumina (Kannan et al., 2008) clay (Liu and Zhang, 2007) waste materials (Gupta et al., 2009; Karthikeyan and Sivakumar, 2012) and many other materials have been recognized as good sorbent for elimination of dyes. However, the high costs of manufacturing and regeneration makes these adsorbents an expensive material (San et al., 2001). For these reasons, many approaches have been attempted in recent years to produce low-cost alternatives. During the last decade, the development of magnetic composite materials has been a stunning new phenomenon with potential application in sequestration of color effluents and caused huge interest due to the amalgamation of exclusive property of organic and inorganic component in solitary material. Magnetic coated biosorbent can be used to adsorb pollutants from aqueous and gaseous effluents and after the adsorption processes, the composite adsorbent can be separated from the medium by using a simple external magnetic field (Yan et al., 2012; Nair et al., 2014). This method of adsorption-separation processes is advantageous in its ease and quickness. To our knowledge, there has been no report regarding the preparation of magnetic composite using aquatic macrophyte and metal chlorides.

In this report, a novel magnetic biocomposites (MBCs) is prepared by fabrication of aquatic macrophytes constituents onto magnetic particles and the structure of MBCs is characterized by FTIR, XRD, EDX and SEM. The prepared MBCs are utilized as adsorbent for sequestration of azo dye (Metanil Yellow) from aqueous solution. The influencing parameters, adsorption kinetics and isotherm are also investigated.

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http://dx.doi.org/10.1016/j.ecoenv.2015.04.037
0147-6513/

2. Materials and methods

2.1. Chemicals

Commercial grade Metanil Yellow (MY) consisting of 70% dye content was used as adsorbate (dye stuff) in this study procured from Sigma Aldrich. All chemicals were of analytical grade and used without further purification. All solutions were prepared with deionized water.

2.2. Adsorbent preparation

2.2.1. Processing of raw aquatic macrophyte

The collected raw aquatic macrophyte were sliced, dehydrated in sunlight and pulverized. The finely powdered micro particles of mesh size of 170 (88 μm) was used as preliminary adsorbent for experimental study from the previous work reported (Sivashankar et al., 2014). The finely powdered aquatic macrophyte was treated with concentrated HNO_3 and successively washed several with water to remove traces of chlorophyll pigment.

2.2.2. Preparation of magnetic biocomposites (MBCs)

The composite adsorbent (sm-$MnFe_2O_4$) used in this study was synthesized by co-precipitation method with a slight modified procedure that was reported in literature (Rongcheng et al., 2005; Han et al., 2011). 0.1 mol of $MnCl_2 \cdot 4H_2O$ and 0.3 mol of $FeCl_3 \cdot 6H_2O$ were prepared in 100 ml deionized water under continuous stirring. 1.0 g of aquatic weed was added to the mixture followed by 10% NaOH and the solution pH was adjusted to 10. Stirring was then continued for 30 min with gradual increase in temperature. The suspension was heated to 95–100 °C for 2 h. After cooling, the suspension was washed several times with distilled water. Solids are separated using centrifugation at a temperature of 20 °C at 5000 rpm. The separated solid particles were first dried at 50 °C for 2 h and then at 110 °C for 3 h. The dried particles were crushed to mesh size of 170 for experimental study.

2.2.3. Immobilization of MBCs

The dried particles of MBCs were immobilized by standard procedure of entrapment method using sodium alginate polymer. Sodium alginate solution of 2.4% (w/v) was prepared and heated until a clear solution is obtained. 1.0 g of MBCs was added into the solution. The suspension was stirred continuously at 70 °C to obtain a homogenous mixture. The suspension was dropped into 3% (w/v) $CaCl_2$ solution to form calcium alginate beads. The beads formed were kept undisturbed for 4 h to acquire saturation. The immobilized MBCs were ready for adsorption experiment after saturation.

2.3. Characterization

The crystalline structure of MBCs was determined using XRD. The surface morphology and composite adsorbent structure was observed using SEM. FTIR analysis was performed in the wavenumber range 450–4000 cm^{-1} to study the inter-atomic nature of bonds and to analyze the functional group present in the obtained MBCs. EDX analysis was used for identifying the elemental composition of prepared MBCs.

2.4. Adsorption of MY dye experiments

The prepared MBCs were used as recyclable adsorbents to remove MY dye from aqueous solution and the adsorption experiments were conducted for both Immobilized and non-immobilized MBCs in batch system. The immobilized MBCs and non-immobilized MBCs are designated as i-MBCs and n-MBCs, respectively. The influence of initial concentration of dye (10–100 mg/L), equilibrium time, solution pH (2–12) and agitation (50–300 rpm) were investigated. MBCs were added to the aqueous solution of MY dye at a known concentration. The suspension was agitated for equilibrium time at room temperature (RT). After the adsorption processes, MBCs were conveniently separated by magnetic separation and the supernatant was immediately analyzed by a UV–vis spectrophotometer (Partha et al., 2013) at maximum wave length (λ_{max}) of 450 nm to measure the concentration of MY dye in the residual solution. The adsorbed amount of MY per unit weight of MBCs at time t, q_t (mg/g), is calculated by following mass balance relationship:

$$q_t = \frac{(c_0 - c_t)V}{m} \quad (1)$$

And dye removal efficiency i.e. % of adsorption is calculated as

$$\%Decolourization = \frac{C_0 - C_t}{C_0} \times 100 \quad (2)$$

where C_0 is the initial dye concentration (mg/L), C_t is the concentration of dye at any time t, V is the volume of solution (L) and m is the mass of MBCs (g).

3. Result and discussion

3.1. Morphology analysis

The surface morphology of the MBCs was examined using SEM. The samples were initially dried in air at 25 °C for 7 days before being analyzed. The MBCs was mounted on SEM and the surface of the sample was then scanned at the desired magnification of 10,000 ×. It was observed that the specimen exhibit floccules, colonized form, hierarchically irregular and porous structured particles. Microscopy observations (Fig. 1) showed that the surface of MBCs is fairly rough, providing a large exposed surface area for better adsorption of MY dye. The porous nature of the magnetic structure reduces diffusional resistance and facilitates mass transfer.

3.2. XRD analysis

Fig. 2 illustrates the XRD pattern of MBCs. It was observed that, the two spectrums corresponding to the structure of magnetic composites (a) magnetic particle ($MnFe_2O_4$) and (b) magnetic biocomposite (sm-$MnFe_2O_4$). Under the reaction conditions employed, there are four types of iron oxides commonly formed

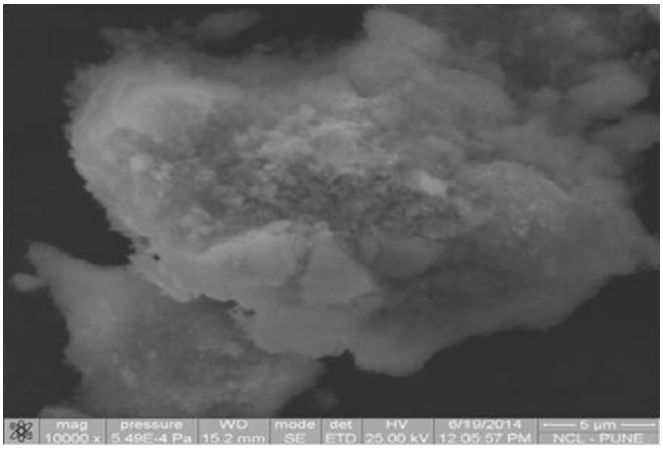

Fig. 1. SEM image of magnetic biocomposite (sm-$MnFe_2O_4$).