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Adsorptive removal of heavy metals and anionic dye from aqueous solution using novel Xanthan gum-Glutathione/ Zeolite bionanocomposite

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ABSTRACT

The present work explored the removal of Ni (II) (85%), Pb (II) (93%) and Congo red (80%) from aqueous solution by ecofriendly novel bionanocomposite. Various characterization techniques including SEM with EDX, TEM, XRD, FTIR, TGA and DTG show successful synthesis of bionanocomposite. The experimental results showed that the maximum adsorption was achieved at pH- 2.1, 4, 5 and contact time- 240, 120, 120 min for Congo red, Ni (II) and Pb (II) respectively. The point of zero charge of bionanocomposite is 8.2 revealing basic nature of adsorbent. The pseudo second order and Freundlich isotherm model were the best obeyed models for describing the adsorption process. The thermodynamic studies revealed that the uptake was endothermic and spontaneous. The desorption with regeneration upto fifth cycle was best achieved by H_2O for Pb (II) and Ni (II), and NaOH for Congo red. The results exhibit that ion exchange, physical and chemical forces were involved in the adsorption process. Therefore, the present bionanocomposite has been proved to be a promising adsorbent that could be explored for the removal of organic and inorganic pollutants from industrial wastewater.

1. Introduction

The toxic and carcinogenic heavy metals such as Pb(II) and Ni(II), and coloured compounds like dyes such as Congo red which are difficult to biodegrade are aesthetically affecting the aquatic ecosystem and humans. Depending on the concentration and exposure time, these pollutants have acute and/or chronic effects on exposed organisms. Pb (II) is being released from several industrial activities such as battery manufacture, oil refining, mining and tanneries. It can damage central nervous system, kidney, liver and reproductive system. Ni(II) has been proved to cause dermatitis, chronic asthma and cancer. It is encountered in wastewater streams from industries such as mining, electroplating, metallurgy, pigment and ceramic industries. The permissible limit of Pb (II) and Ni (II) in drinking water is 0.01 mg L^{-1} (Pandey et al., 2007; Ahmad and Haseeb, 2013). The congo red is a benzedene based anionic dye and has high pollution degree in water due to complicated aromatic structure and poor biodegradability (Yuan et al., 2016; Zheng et al., 2015). It has higher solubility in water about 1 g/30 mL (Salman et al., 2015). In order to control the harmful effect of these pollutants, adsorption is considered to be the most effective, simple, low-cost, versatile and ecofriendly pathway used for the removal of these pollutants (Hernandez-Montoya et al., 2013). Considering water pollution, elaborate studies are reported in the literature for the removal of these pollutants such as Zeolite/Fe_3O_4 nanocomposite (Jahangirian et al., 2013), Diatomite/chitosan-Fe(III) composite (Zheng et al., 2015), Nano crystallite hydroxyapatite (Mobasherpour et al., 2012) and Exopolysaccharide from *Arthrobacter* ps-5 (Shuhong et al., 2014).

Concerning environmental pollution, adsorbents based on natural biopolymers are greatly favoured in view of 'green chemistry'. Xanthan gum has gained much attention that can be used as an organic moiety in the synthesis of bionanocomposite. It is abundantly available, biodegradable, hydrophilic, low-cost and have carboxyl and hydroxyl functional groups. The adsorbability of biopolymer can be further increased by functionalizing it by ecofriendly amino acid namely glutathione using EDC as a cross-linker. Glutathione molecule contain thiol, amine, carboxylate groups that provide coupling possibilities for cross linking. Zeolites have been used as an inorganic nanofiller because of its abundance, easy availability, low-cost, high ion exchange capacity, porous and crystalline nature (Chong et al., 2014). Zeolites are aluminosilicates having a negatively charged lattice that could be balanced by cations present in the solution (Hernandez-Montoya et al., 2013). The modification and cross linking provides large surface area and abundance of adsorption sites for sequestering pollutants.

The present work focuses on toxic and carcinogenic pollutants- Pb (II), Ni(II) and Congo red dye. The purpose of this study is to investigate

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the removal of Pb (II), Ni (II) and Congo red using ecofriendly synthesized bionanocomposite (Xanthan Gum-Glutathione/Zeolite). To the best of our knowledge, this is the first time that such type of combination including xanthan gum, glutathione and zeolite were used to synthesize potential bionanocomposite as an adsorbent that has been employed for the removal of toxic Pb(II), Ni(II) and congo red from aqueous solution. The modification of xanthan gum with glutathione using cross-linker provides ample of adsorption sites and then, further with zeolite provides better thermal stability and large surface area. The bionanocomposite obtained show excellent removal efficiencies for Pb(II), Ni(II) and congo red dye from aqueous solution. The bionanocomposite was then characterized by various characterization techniques. The adsorption studies were carried out by batch adsorption process. The kinetic, adsorption isotherms and thermodynamic parameters were evaluated to determine the adsorption mechanism. All experimental data were analyzed by using Origin Pro 8.1. The desorption with regeneration were studied using various desorbing eluents.

2. Experimental

2.1. Materials

All analytical grade reagents were purchased from commercial sources. Prior to use all glasswares were nicely washed and cleaned. Xanthan Gum (XG) was provided by Sigma- Aldrich (USA). Zeolite (Zeo, $Na_2O{\cdot}Al_2O_3XSiO_2{\cdot}$ YH_2O), Glutathione (Glu reduced 99%) and N-(3-Dimethyl aminopropyl)-N-Ethyl Carbodiimide hydrochloride (EDC, $C_8H_{17}N_3$. HCl) were purchased from Otto-Chemika-Biochemika Reagents. Metal nitrate salts [$Pb(NO_3)_2$, $Ni(NO_3)_2{\cdot}6H_2O$] were provided by Merck. Congo Red ($C_{32}H_{22}N_6Na_2O_6S_2$) was supplied by CDH, New Delhi. Sodium Chloride (NaCl), Sodium hydroxide (NaOH) and Hydrochloric acid (HCl) were of analytical grade. The double distilled water was used throughout the study.

2.2. Synthesis of bionanocomposite

The synthesis was done by melt intercalation technique reported previously (Pavlidou and Papaspyrides, 2008). Firstly, 10 g of zeolite was left for dispersion in double distilled water for 48 h with moderate stirring at room temperature. Secondly, 5 g of xanthan gum in 200 mL of water was dissolved at 60 °C till a clear solution was prepared. To this solution, add slowly 0.1 M solution of glutathione (25 mL) keeping the solution flask on moderate stirring at 60 °C then 0.05 M solution of EDC was added to it. This solution was left on ultrasound sonication for 2 h at 60 °C. Finally, both the solutions were mixed and left for mild sonication for 6 h at 60 °C. The precipitation was done using 200 mL acetone. After filtering, the precipitate was washed with double distilled water then dried in hot air oven at 80 °C for 3 h. Powdered in mortar for subsequent studies.

2.3. Instrumental techniques

The Scanning electron microscopy (SEM) images and Surface composition measured using Energy dispersive X-ray spectroscopy (EDX) were obtained using model JSM, 6510LV, JEOL, Japan. The Transmission electron microscopy (TEM) (TEM, JEM 2100, JEOL, Japan) was used for observing particle size. The FTIR analysis of samples were performed in an FTIR spectrometer (Perkin-Elmer 1600 infrared spectrometer) with KBr disc technique in the region of 400–4000 cm^{-1}. The Thermogravimetric and derivative thermogravimetric analysis (TGA-DTG) was conducted with thermogravimetric analyzer (Model Perkin Elmer, STA 6000) under inert atmosphere from 15 to 900 °C at a heating speed of 0.01–100 °C/min. The X-ray diffraction (XRD) measurements were performed on a Model- Bruker AXSD8 Advance X-Ray Diffractrometer with CuKα radiation (λ = 1.5406A°), 2θ angle was stepped from 3° to 135°. pH was measured using pH meter (Perkin Elmer, USA). The concentration readings of heavy metal ions and Congo red were analyzed using atomic absorption spectrometer (GBC 902, Australia) and UV–Visible spectrophotometer (T70 UV/VIS Spectrometer PG Instruments Ltd, U.K.) (λmax = 497 nm).

2.4. Adsorption studies

The adsorption studies were carried out using batch adsorption mode. The effects of various experimental parameters such as concentration (20–100 mg L^{-1}), pH (1 − 7), contact time (5–360 min), temperature (303–323 K) on the adsorptive removal of adsorbate ion were studied. Typically, 0.02 g of adsorbent was dispersed in a conical flask with 20 mL of adsorbate solution of known concentration with subsequent shaking for optimum contact time and pH. pH was adjusted using 0.5 M NaOH and 0.5 M HCl. The adsorbate was filtered using Whatman Filter paper 1. The % removal of adsorbate was calculated from the following Eq. (1):

$$removal(\%) = \frac{(C_0 - C_e)}{C_0} \times 100 \quad (1)$$

The amount of adsorbate adsorbed on adsorbent per unit mass of adsorbent (q_e, mg g^{-1}) was calculated by Eq. (2):

$$q_e = \frac{(C_0 - C_e)}{m} \times V \quad (2)$$

where, C_0 (mg L^{-1}) is initial adsorbate concentration, C_e (mg L^{-1}) is adsorbate concentration at equilibrium, V (L) is the volume of the solution and m (g) is the mass of the adsorbent used (Mahida and Patel, 2016).

2.5. Study of point of zero charge (Ppzc)

In order to know the surface charge of adsorbent, point of zero charge (Ppzc) study was carried out by solid addition method reported elsewhere (Rao et al., 2015). 20 mL of 0.1 M NaCl was taken in conical flasks in series with pH ranging from 1 to 12. The pH was adjusted using 0.1 M HCl and 0.5 M NaOH and initial pH was measured (pHi) then 0.02 g of adsorbent was added in each flask. The mixture was then left for 24 h to attain equilibrium. Finally, the mixture was filtered and final pH (pHf) was measured using pH meter. The point of zero charge was obtained by plotting ΔpH values against pHi.

2.6. Desorption studies

The desorption and regeneration studies for Pb (II), Ni (II) and Congo red were carried out by batch adsorption mode using various desorbing agents such as H_2O, 0.1 M HCl and 0.1 M NaOH (50 mg L^{-1}, 20 mL and 0.02 g adsorbent).

3. Results and discussion

3.1. Characterization

SEM with EDX is depicted in Fig. 1 (Magnification: 5000 ×). The SEM with EDX of bionanocomposite (a) shows high crosslinking and presence of functional groups on the surface of adsorbent which provides binding sites for the adsorbate molecules. The weight% of various atoms present in the bionanocomposite (a') are in the order as follows- O(45.7) > C(27.68) > Na(10.5) > Si(6.49) > Al(5.64) > N(2.93) > S (1.07) which is in accordance of the precursors present from which bionanocomposite is synthesized. The SEM (b) with EDX of Pb(II) loaded bionanocomposite depicts the maximum loading of Pb(II) onto the surface of adsorbent as spherical beads showing the adherence of Pb (II) on the available binding sites of functional groups. The EDX of Pb (II) loaded bionanocomposite (b′) shows the weight% and presence of