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Gum xanthan-psyllium-cl-poly(acrylic acid-co-itaconic acid) based adsorbent for effective removal of cationic and anionic dyes: Adsorption isotherms, kinetics and thermodynamic studies

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ABSTRACT

The present work highlights the synthesis of the adsorbent based on Gum xanthan-psyllium hybrid backbone graft co-polymerized with polyacrylic acid-*co*-polyitaconic acid chains for the rapid sequestration of auramine-O (Aur-O) and eriochrome black-T (EBT) dyes from the aqueous fluid. The excellent dye removal efficiency of 90.53% for EBT and 95.63% for Aur-O was found at initial dye concentration of 30 mg L^{-1} (EBT) and 15 mgL^{-1} (Aur-O) 40 mL^{-1} with an adsorbent dose of 600 mg within time duration of 5 h and 323 K temp. The adsorption isotherm data fitted well with Langmuir isotherm and Freundlich isotherm for Aur-O and EBT dyes ($R^2 \geq 0.90$), respectively. The adsorption kinetics depicted that pseudo-second order kinetics was followed simultaneously with intra-particle diffusion for both the dyes. Thermodynamic parameters such as ΔG°, ΔH° and ΔS° were also calculated and confirmed the spontaneity, randomness and endothermic nature of the adsorption process. Further, the adsorbent exhibited good recyclability efficiency for the capture of Aur-O and EBT from aqueous solution with minimal activity decline after six and three cycles, respectively. So, the synthesized adsorbent could be used successfully by the textile industries for the treatment of dye contaminated water with excellent competency.

1. Introduction

With the advent of industrialization the human beings due to their profitable interests are rapidly exploiting the natural sources especially the water resources by supplementing them with toxic industrial wastes without pre-treatment. Major water pollutants include heavy metals, dyes, biodegradable waste, sediments, fluorides, toxic chemicals containing nitrates, phosphates and radioactive pollutants (Reddy and Lee, 2013). Of these, dyes remain the most potential water pollutants with the commercial availability of almost 100,000 dyes which are used extensively in the field of textile, paper, leather, printing, concrete and pharmaceutical industries (Gong et al., 2008). The excessive usage of water during the dyeing process is one of the main the concen. About 100 L of water is consumed to process about 1 kg of fabric in traditional textile finishing industries (Couto, 2009). The binding ability of dyes with the fabric varies with the class of the dyes used. The dye loss in waste water varies from 2% to 50% for basic dyes and reactive dyes,-respectively owing to extreme contamination of water sources (O'Neill et al., 1999). It is estimated that 280,000 t of textile dyes are discharged in textile industrial effluent every year worldwide (Jin et al., 2007). Dyes make the water unfit for drinking purpose and also imparts unsightly appearance which is major public concern. The dyes are the organic molecules with very high water solubility and its degradation products are mostly carcinogenic in nature. It is also observed that it reduces the penetration of sunlight into the water bodies thereby affecting the photosynthesis process and increasing the biological oxygen demand (BOD) of contaminated water (Ahmad et al., 2015; Yagub et al., 2014; Ahmad et al., 2012; Zahrim et al., 2011; Asfarama et al., 2015). There are several government policies and private organizations available to reduce the dumping of dye effluent into water bodies and cleaning of contaminated water by suitable treatment methods. The various physico-chemical parameters studied for textile effluent with their permissible limits includes: colour (25 Pt-Co scale), pH at 30 °C (5.5–9), Total Hardness (500 mg L^{-1}), BOD (100 mg L^{-1}), COD (250 mg L^{-1}), Total Dissolved Solids (2100 mg L^{-1}), Total suspended solids (100 mg L^{-1}), Turbidity (10 NTU), chlorides (600 mg L^{-1}),

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sulphides (2 mg L^{-1}), silica, (250 mg L^{-1}), calcium (200 mg L^{-1}), iron (3 mg L^{-1}), oil and grease (10 mg L^{-1}) (Elango et al., 2017).

The physico-chemical technologies which are used extensively for the removal of dyes from industrial effluent include adsorption, chemical oxidation, precipitation, coagulation, filtration, electrolysis, photodegradation, and biological, and microbiological methods. (Rafatullaha et al., 2010; Khankrua et al., 2013; Jancar et al., 2010; Allegre et al., 2004; Sanghi et al., 2007). Out of all the above mentioned methods, adsorption process is found to be most effective and economical without any secondary harmful products (Fu and Viraraghavan, 2001). The usage of non-convential low cost adsorbents based on palm kernel seed coat, ginger waste, rice husk, magnetic alginate beads, gum xanthan, psyllium, gum ghatti and chitosan is highly recommended as adsorbents for removal of toxic dyes from past few decades (Tang et al., 2007; Sharma et al., 2015; Kaith et al., 2016a; Ahmad et al., 2015; Vakilia et al., 2014). The Hydrogels based on biopolymers is a rapidly emerging field of adsorbent for the removal of toxic dyes due to its cumulative characteristics like dye adsorption, biodegradability and reusability (Kaith et al., 2016b; Das, 2013; Cook et al., 2012).

Auramine-O (4,4'-dimethylaminobenzophenonimide) is a cationic dye used extensively in the paper, textiles and leather industries as a coloring material (Mall et al., 2007). Eriochrome black-T (Sodium 1-[1-Hydroxynaphthylazo]-6-nitro-2-naphthol-4-sulfonate) is an anionic dye generally used in complexometric titrations. The carcinogenic activity of both these dyes has been reported in literature (Dong et al., 2013).

Present work is concerned with the synthesis of eco-friendly adsorbent based Gum xanthan-psyllium hybrid backbone under the influence of microwave radiations for the removal of toxic auramine-O (cationic) and eriochrome black-T (anionic) dyes from the aqueous fluid. The dye adsorption efficiency was improved for both the dyes by the stepwise optimization of various process parameters such as adsorbent dose, initial dye concentration, contact time and temperature. Adsorption isotherm, adsorption kinetics and adsorption thermodynamics of the synthesized adsorbent was studied. Also, the adsorption-desorption of dyes was carried out for number of cycles to establish the reusability potential of the synthesized adsorbent. Also with the comparison with adsorbent already reported in literature directly signified that the candidate polymer possessed excellent dye removal efficacy and can be used effectively for treatment of dye laden toxic effluent with good economy.

2. Experimental

2.1. Materials and methods

Gum xanthan and psyllium as a backbone were procured from Sigma Aldrich and Sidhpur Isabgol Factory Gujarat, India, respectively. Acrylic acid, itaconic acid and ammonium persulphate were obtained from S D fine chemicals Ltd. Cross linker glutaraldehyde and Initiator ammonium persulphate were purchased from Merck, India Ltd.

The characteristic functional groups present in the hybrid polymeric backbone and the synthesized matrix were studied using Agilent Technologies Carry 630 FTIR Spectrophotometer possessing diamond crystal, in the range of 400 cm^{-1} to 4000 cm^{-1}. Scanning Electron Microscopy-Energy Dispersive X-Ray Spectroscopy (SEM-EDX) was used for the determination of the changes in the surface morphology and the qualitative elemental constitution upon grafting onto hybrid backbone were obtained using JEOL JSM-6490LV electron microscope at 10 kV with platinum coating. XRD (Broker AXS, X-ray diffractometer, India) with Cu-Kα (λ = 1.54 Å) radiation operated at 40 kV and 40 mA for Bragg's angle 2θ ($10 < \theta < 60$) at the scanning rate of 2°/min was used to record the enhanced crystallinity of polymeric backbone on graft co-polymerization and introduction of crosslinks. The absorbance spectra for dye removal studies were obtained using Agilent Technologies Carry 631 UV–Vis Spectrophotometer. The weighing was performed on CPA225D Sartorius analytical balance.

2.2. Synthesis of the GP-cl-P(AA-co-IT) hydrogel

The synthesis of cross-linked binary graft co-polymer of gum xanthan-psyllium hybrid backbone with the co-polymer mixture of poly (acrylic acid-*co*-itaconic acid) was carried out using free radical polymerization technique in presence of microwave radiations (MW). For each experiment, 1.0 g of Gum xanthan–psyllium (1:1, w/w) hybrid backbone was added to about 6.0 mL of solvent in the reaction flask and mixed thoroughly with continuous stirring till the homogenous thick slurry was obtained. It was followed by dropwise addition of monomer mixture of acrylic acid (11.960 mol L^{-1}) and itaconic acid (0.896 mol L^{-1}) to the reaction vessel with thorough mixing. To the resulting mixture 0.058 mol L^{-1} glutaraldehyde as a crosslinker and 0.029 mol L^{-1} ammonimum persulphate as free radical initiator were added followed by MW irradiation for 65 s (Sharma et al., 2017). After the completion of reaction, the graft co-polymer obtained was cooled to room temperature and homopolymer adhering to its surface was removed through solvent extraction. The final product was dried in a hot air oven at 60 °C till constant weight was obtained.

The superabsorbent capability of the synthesized sample was estimated in terms of liquid uptake capacity. Liquid uptake behavior of synthesized material was studied after every 4 h for the duration of 24 h. 100 mg sample was immersed in 30 mL distilled water and the increase in weight was noted after every 4 h. The traces of water adhered to the sample surface were wiped-out using filter paper. The process was repeated until equilibrium was achieved. The percentage swelling (P_s) which corresponds to liquid uptake capacity was calculated as per Eq. (1) (Sukriti et al., 2017a):

$$P_S = \frac{W_S - W_d}{W_d} \times 100 \quad (1)$$

Where, P_s = percentage swelling; W_s = weight of swollen sample; W_d = weight of dry sample.

Optimization of the all the reaction parameters were done stepwise with respect to percentage swelling to fabricate the sample with maximum liquid uptake capacity. All the reactions were performed in triplicate and in three independent batches for the reproducibility of the percentage swelling capacity values. The analysis for the data obtained was performed using Microsoft Excel 2010.

2.3. Dye adsorption studies

The adsorption experiments were carried out using batch mode using GP-cl-poly(AA-co-IT) as adsorbent for the removal of eriochrome black-T (EBT) and auramine-O (Aur-O) dyes. Each batch consist of three independent experiments and for each process parameter optimized three batches were conducted. The various process parameters such as contact time of adsorbent with dye solutions, dose of the adsorbent, temperature of the dye solutions and initial concentration of the dye solutions were optimized in order to obtain maximum removal of both the dyes from the aqueous solution. The changes in the concentartion of the residual dye solution upon adsorption by the sample were noted after every 30 min for the time duration of 5 h after which equilibrium was achieved. The changes in dye concentartion was analyzed using UV–VIS spectrophotometer at 531 nm λ_{max} of EBT and 434.8 nm λ_{max} of Aur-O dyes. The percentage removal of the dye was calculated as per the Eq. (2) (Sukriti et al., 2017b):

$$\%DyeRemoval = \frac{C_o - C_e}{C_o} \times 100 \quad (2)$$

Where C_o is the initial dye concentration (mg L^{-1}) and C_e (mg L^{-1}) is concentration of unadsorbed dye remaining in the solution.

Optimization of adsorbent dose was done by varying the amount from 300 to 700 mg /40 mL of 30 mg L^{-1} and 15 mg L^{-1} EBT and Aur-