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Synthesis of nano-sized chitosan blended polyvinyl alcohol for the removal of Eosin Yellow dye from aqueous solution

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ABSTRACT

The current investigation aimed at synthesizing the nano-sized chitosan particles and blending it with the polyvinyl alcohol (PVA). This composite proved to be a good adsorbent for the removal of Eosin Yellow (EY) dye from the aqueous solution. The characterisation studies like TEM, SEM, XRD and FT-IR were carried out for the chitosan/PVA blend. The removal of EY dye by the chitosan/PVA composite was optimized by varying the certain operating parameters such as initial dye concentration, adsorbent dose, solution pH, contact time and temperature. The adsorption isotherms for the adopted system were studied in association with Langmuir, Freundlich and Temkin adsorption models. The adsorption isotherm data was best adopted with the Langmuir model. The Langmuir monolayer adsorption capacity of the chitosan/PVA blend for EY dye molecules was calculated as 52.91 mg/g. Adsorption kinetic data were applied to the pseudo-first order, pseudo-second order, Weber and Morris intraparticle diffusion and Boyd kinetic models. The adsorption kinetic was best obeyed with the pseudo-second order kinetics. The thermodynamic parameters were evaluated for the present system and it was found that the present system was spontaneous and exothermic in nature. The adsorbed EY dye molecules were desorbed from the spent chitosan/PVA using HCl solution. The desorption results indicates that the recovered adsorbent can be effectively reused for further adsorption cycles. The prepared material possesses excellent adsorption potential to treat the industrial dye wastewater.

1. Introduction

Dyes are complex aromatic structures, toxic, non-biodegradable, carcinogenic which are being used as a colorants in many industries like textile, paper, printing, leather, food and plastic [17]. These industrial wastewater discharges the large amount of coloured substances into the nearby water sources which in turn to pollute the whole aquatic systems [25,18,15]. Also, it is difficult to treat the dye effluents for the removal of colorants due to its inert properties and high capital investment in spite of its lower concentration of dye [21]. The industrial effluents containing these dyes in high concentration create severe health issues in humans as they may lead to cancer, tumours, jaundice, allergies, skin irritation, heart defects and mutations [5,27].

Eosin Yellow [EY is called as 2-(2,4,5,7-tetrabromo-6-oxido-3-oxo-3H-xanthen-9-yl) benzoate] is a pink coloured hydrophilic, anionic dye, which also exhibits yellow-green fluorescence. EY dye is widely applied in the Gram straining of the bacterial species because of its red colour and strong adsorption of red blood cells [8]. It is also a heterocyclic dye contains bromine atoms and it is being used in the various industrial fields such as dyeing, printing, leather, paints and fluorescent pigments [11]. It was mainly found due to its vivid colour. The outcome of EY dye from such industries was found to provide the harmful effects to the living environment. EY dye molecules were severely affects the human beings in terms of severe eye and skin irritation with redness and pain, damage to kidneys, liver and lungs. It is also permanently damage the cornea by destroying the retinal ganglion of the eye [8]. Among the various methods available for the treatment of dye containing effluents like oxidation-ozonation, biological treatment, coagulation-flocculation and membrane process, adsorption was found to be more effective due to its easiness and cheaper cost of adsorbent [28,20,13,26,19].

Chitosan is a low molecular weight polysaccharide composed of β (1,4) linked 2-deoxy-2-amino-D-glucopyranose and partially of β (1,4) linked 2-deoxy-2-acetamido-D-glucopyranose. Chitosan is a linear, heterogeneous, biocompatible, biodegradable, low cost adsorbent, renewable, non toxic, hydrophilic, high chemical stabil-

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ity and high selectivity [33,31,34,4,7,38]. Nano sized chitosan pose better advantageous properties such as high specific surface area, absence of internal diffusion resistance, smaller size and quantum size effect which will lead to exhibit higher sorption capacities. The common mode of preparing chitosan nanoparticles was done by the addition of tri sodium polyphosphate (TPP) into the chitosan solution. Since TPP is a nontoxic, multivalent and capable of forming gels through the ionic interactions. The chitosan nanoparticles were prepared by using TPP can be used as of eco friendly in nature. The chitosan shows a cationic behaviour in acidic media; the protonation of amine groups leads to adsorption of anionic dyes by electrostatic attraction [1].

Polyvinyl alcohol (PVA) is an odourless, tasteless, translucent and white or cream coloured granular powder. It is soluble in water, slightly soluble in ethanol but insoluble in other organic solvents. PVA possess many excellent properties such as biocompatible, biodegradable, nontoxic, good mechanical properties, tensile strength, good fibre and film forming ability and flexibility [2,29,24,10,9]. Blending of synthetic polymers onto chitosan can introduce the desired properties and enlarge the field of applications by choosing the various types of side chains. Chitosan cross linked with glutaraldehyde has been blended with the copolymers and which was used as a chelating agent for metal ions and dyes. Chitosan blended with PVA provides improved tensile strength, mechanical and physical properties [16,35–37].

In the present research, the chitosan/PVA blend was prepared for the removal of EY dye from the aqueous solution. The adsorption influencing parameters such as initial EY dye concentration, adsorbent dose, pH, temperature and contact time were optimized for the highest removal of EY dye from the aqueous solution. The prepared chitosan/PVA blend was characterized by the scanning electron microscopic (SEM), x-ray diffraction (XRD) and Fourier transform infrared (FT-IR) spectroscopic analyses. The adsorption isotherms such as Langmuir, Freundlich and Temkin models were used to fit with the adsorption equilibrium data. The adsorption kinetic data was applied to the different adsorption kinetic models such as pseudo-first order, pseudo-second order and intraparticle diffusion models. The desorption studies were also carried out for the regeneration of chitosan/PVA blend using HCl as an eluting agent.

2. Experimental

2.1. Chemicals

All the chemicals used for the present research was of analytical grade. These chemicals were supplied by Sigma Aldrich, India.

2.2. Preparation of chitosan nanoparticles

The 2% of chitosan solution of 100 mL was prepared in 2% acetic acid, added drop wise with 0.6% w/v of Tri sodium polyphosphate in the ratio 5:2, which leads to the formation of chitosan nanoparticles upon continuous stirring for an hour through ionic interactions [1]. The obtained solution was centrifuged at 10,000 rpm for half an hour and left undisturbed at 4 °C for 24 h. The settled nanoparticles were separated out and dried at room temperature. The characterization of the chitosan nanoparticles was carried out by using TEM analysis.

2.3. Characterization studies

Transmission electron microscopic (TEM) image of chitosan nanoparticles was done using computer aided transmission electron microscopy of Philips make. Scanning Electron Microscopic (SEM) characterization was carried out using Quanta FEG-SEM type instrument in vacuum environment. The samples were coated with *Au* to make it electrically conductive and supported on metallic disks to picturize images at different magnifications.

2.4. Chitosan/PVA blend preparation

The nano-sized chitosan suspended in 2% acetic acid solution was mixed with PVA in the ratio of 1:3. The blending of these 2 polymers were done using 3% glutaraldehyde, which acts as a cross linking agent. The solution was stirred well at room temperature (30 °C) for about 30 min to obtain the uniform blend of chitosan/PVA composite. The formed gel like membrane was crushed and dried at 45 °C for about 48 h. Finally, the prepared materials were used as an adsorbent for the removal of EY dye.

2.5. Preparation of EY dye solution

A stock solution of 1000 mg/L was prepared by dissolving the required quantity of EY dye powder [molecular formula: $C_{20}H_6Br_4Na_2O_5$; molar mass 691.85 g/mol [3] in a double distilled water. The standard solutions of 10 mg/L, 20 mg/L, 30 mg/L, 40 mg/L and 50 mg/L were prepared from stock solution using double distilled water. The concentration of EY dye solution was measured at 520 nm using UV–vis spectrophotometer (JASCO, USA). The pH of the wastewater sample was measured using the pH meter (HI 98107, Hanna equipments private limited, Mumbai, India). The pH of the wastewater sample was maintained to the required value by pouring 0.1 M NaOH or 0.1 M HCl solutions.

2.6. Batch adsorption experiments

The adsorption of EY dye onto chitosan/PVA blend was optimized for the maximum removal of EY dye from the aqueous solution by varying the operating parameters such as adsorbent dose, initial EY dye concentration, pH, temperature and contact time. 100 mL of 10 mg/L of initial EY dye concentration was taken in the series of conical flasks to optimise the varying adsorbent dose ranging from 0.1 g to 0.5 g at constant pH. This adsorption system was kept at constant stirring speed of160 rpm in a temperature controlled incubation shaker for known time. The initial EY dye concentration was varied from 10 mg/L to 50 mg/L with the optimized adsorbent dose, constant pH and the maximum removal of EY dye was calculated. Similarly, the pH was varied from 2 to 9 (increments of 1), contact time from 10 min to 60 min (increments of 10), temperature from 30 °C to 60 °C (increments of 10) was also carried out. The residual EY dye concentration was estimated by taking the supernatant alone into account and it was analyzed using UV–vis spectrophotometer at 520 nm. All the experiments were done for 3 trials and the average values were taken for calculations. The % removal of EY dye in each case was determined using the following formula:

$$\%R = \frac{C_o - C_e}{C_o} \times 100 \qquad (1)$$

Where C_o is the initial EY dye concentration (mg/L) and C_e is the final or equilibrium concentration of EY dye in the solution (mg/L).

Adsorption isotherm data could be modelled by taking the equilibrium data from the equilibrium studies of 10–50 mg/L of EY dye concentrations with 0.2 g/100 mL of chitosan-PVA. This adsorption system was operated under equilibrium conditions. Once the system attains the equilibrium, the adsorption mixtures were separated and the supernatant was analyzed for the residual EY dye concentration by using UV–vis spectrophotometer. The