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Preparation of Dicarboxylic Acid Containing Sulfonamide Based Resin and Removal of Basic Dyes

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Polymer and dye interaction leading to polymer-dye complex formation exhibits many interesting and important practical features. For this purpose, dicarboxylic acid containing resin was prepared in two steps starting from poly (styrene-divinyl benzene) (PS-DVB) (10% crosslinking) based beads with a particle size of 400-590 μm, according to the synthetic protocol; chlorosulfonation, sulfamidation with iminodiacetic acid. Dye extraction experiments were carried out by contacting wetted resin samples with aqueous dye solutions at room temperature. Capacities were determined by colorimetric analysis of the residual dye content. Dye sorption capacity of the resin was found to be (0.67-0.63 $g\,g^{-1}$ resin). This material is also able to remove the cationic dyes completely even from highly diluted aqueous dye solutions.

Keywords acid functional resin; basic dye removal; polymeric sorbent; sulfonamide

INTRODUCTION

Dyes are aromatic compounds which can be used to impart color to other materials. The complex aromatic molecular structures of dyes usually come from hydrocarbons such as benzene, naphthalene, anthracene, toluene and xylene. Today there are more than 10,000 dyes with different chemical structures available commercially and over 7×10^5 tons of these dyes are produced worldwide annually (1,2).

However, dyes are important water pollutants which are generally present in the effluents of the textile, leather, paper, rubber, plastics, cosmetics, pharmaceuticals, and foodstuff industries. Dye wastewater discharge into environmental water bodies deteriorates the water quality, and may cause a significant impact on human health due to mutagenic, carcinogenic effects of some dyes or their metabolites (3,4).

Though many dyes are inert and non-toxic at the waste concentrations discharged into surface waters, some are harmful to aquatic life in rivers where they have been discharged. Moreover the color they impart is very undesirable to the water user. Therefore, color removal from waste-water is a major environmental problem.

The conventional methods of color removal from industrial effluents include ion exchange, activated carbon adsorption, membrane technology, and coagulation (5). Amongst all, the sorption process by activated carbon has been shown to be one of the most efficient methods to remove dyes from effluents (6). However, relatively high operating costs and problems with regeneration of the spent carbon hamper its large-scale application (7). This subsequently led to search for a more economical alternative sorbent. A number of investigations have shown that agricultural by-products such as date pith, sawdust, corn corb, barley husk, rice hull, and bagasse pith have the potential of being used as alternative sorbent for the removal of dyes in textile wastewater (8–13).

Some biological and physical/chemical methods have been employed for dye wastewater treatment (14–20). In all these methods, the sorption has been found to be economical and effective in dye wastewater treatment technology as it can remove various dyes with lower treatment cost.

The interaction between polymer and dye leading to polymer-dye complex formation exhibits many interesting and important practical features. Coulombic, hydrophobic, and steric interactions are major factors governing the thermochemical and dynamic aspects of complex formation. Taking the environmental requirements into account, the development of water-based colored polymer materials is one of the modern targets for the chemical industry.

Adsorption techniques employing solid adsorbents are effective methods for water decontamination. Most commercial systems currently use activated carbons and organic resins as adsorbents to remove dye in wastewater because of their excellent adsorption abilities (21–23).

A large variety of non-conventional adsorbent materials have been also proposed and studied for their ability to remove dyes (24).

Some of the reported adsorbents include clay materials (25), zeolites (26), siliceous materials (27), agricultural wastes (28,29), industrial by-products (30,31) and biomass (32).

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The radiation synthesis of copolymeric hydrogels based on acrylamide/acrylic acid, acrylamide/itaconic acid and acrylamide/maleic acid have been successfully used for the removal of basic dyes from aqueous solutions (33–35). These reports showed that the carboxyl groups added onto chitosan may increase its affinity for basic dyes.

In the previous studies, ethylenediamine modified rice hull, carboxylic groups containing cyclodextrin polymer, and calcium alginate beads were used to remove basic dyes (36–38).

Crosslinked polymers are preferred as support due to their insolubility. Since, isolation of one of the entities is reduced to a simple filtration. If the functional group attached to the crosslinked polymer is selective for a targeted compound, it will be possible to pick it up and separate easily from the mixtures.

Polystyrene-based resins are most widely used as polymeric sorbents. Since, they can be modified by using organic reactions, ie; chloromethylated polystyrene is very important sorbent for modification reactions. Chloromethylated polystyrene-divinylbenzene copolymers were modified by an Arbuzov-type reaction to obtain phosphonate ester/phosphonic acid grafted styrene-divinylbenzene copolymer micro beads (39).

In this study, chlorosulfonated polystyrene-divinyl benzene copolymer beads were modified with iminodiacetic acid to prepare acid containing polymeric sulfonamide based resin. The obtained resin was used for removal of basic dyes.

EXPERIMENTAL

Materials

Iminodiacetic acid (SIGMA -ALDRICH), Divinyl benzene (DVB), 55% of which is a mixture of meta and para isomers), Methylene blue (E. Merck), Crystal violet (E. Merck), Chloroacetic acid (E. Merck), Chlorosulfonic acid (Fluka), Styrene (Fluka), and all the other chemicals used were analytical grade commercial products.

Crosslinked Poly (Styrene-Divinyl Benzene) Beads

Beads were prepared by the suspension polymerization of a mixture of styrene (54 mL, 0.48 mol) and DVB (55% grade, 10 mL, 0.038 mol) in toluene (60 mL), using gum-Arabic as stabilizer, according to a previously described procedure (40). The beads were sieved and the 420–590 μm size fractions were used for further reactions.

Chlorosulfonation of the Beaded Polymer

The beaded polymer was chlorosulfonated using chlorosulfonic acid as described in the literature (40). The degree of chlorosulfonation was determined by analysis of the liberation of chloride ions. For these purpose, a polymer (0.2 g.) sample was added to 10% NaOH (20 mL) and boiled for 4 h. After filtration and neutralization with HNO_3 (5 M), the chlorine content was determined by the mercuric-thiocyanate method. This gave a final chlorosulfonation degree of $4\,\text{mmol} \cdot \text{g}^{-1}$.

Preparation of Dicarboxylic Acid Containing Sulfonamide Based Resin

The chlorosulfonated polymer (8 g) was added portion wise to a stirred solution of iminodiacetic acid (6 g, 0.045 mol) in 2-methyl-1- pyrrolidone (25 mL) at 0°C. The mixture was shaken with a continuous shaker for 12 h at room temperature. The reaction content was poured into water (500 mL), filtered, and washed with excess water. The product was dried under vacuum at 40°C for 24 h. The yield was 10.8 g.

Determination of the Carboxylic Acid Content of the Resin

To 15 mL of 1 M NaOH solution 0.21 g of the resin II was added and left to stand overnight. The mixture was filtered and titrated with 1 M HCl the resulting 1.5 mL of the titrant indicates $7.3\,\text{mmol} \cdot \text{g}^{-1}$ carboxyl content.

Extraction of the Basic Dye by the Resin

For this purpose, carboxylic acid containing polystyrene resin (0.23 g) was used and the sorption experiments were performed by using methylene blue (0.4 g/ 50 mL).The capacity of the resin was determined by using colorimetric methods and was calculated as 0.63 g dye/g resin for methylene blue.

Regeneration of the Resin

The dye loaded samples (0.1 g) were interacted with 10 mL of $H_2SO_4(5\,\text{mol}\,\text{L}^{-1})$ and stirred at room temperature for 24 h. After cooling, the mixtures were filtered, and 2 mL of the filtrate was removed for colorimetric analysis of the dyes. The regeneration capacity of the hydrogel was found as 0.50 g/g resin for methylene blue.

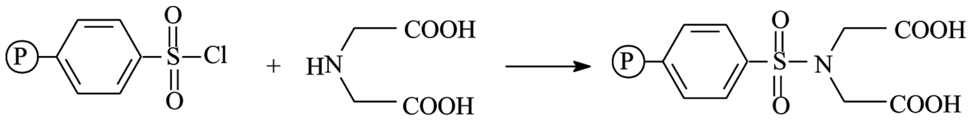
Kinetics of the Dye Sorption

A batch kinetic experiment was performed by using highly diluted dye solution (8×10^{-3} g dye /L water). For this purpose, resin (0.2 g.) was wetted with distilled water (1.5 mL) and added to a solution of dye (90 mL). The mixtures were stirred with a magnetic stirring bar and aliquots of the solution (5 mL) were taken at appropriate time intervals for the analysis of the residual dye contents by the method as described above.

RESULTS AND DISCUSSION

Preparation of the Resin

Dicarboxylic acid containing resin was prepared by the reaction of crosslinked chlorosulfonated polystyrene resin and iminodiacetic acid (Scheme 1).



SCH. 1. Preparation of the resin.

This resin was characterized by determining the carboxylic acid content by FT-IR spectrophotometer. Carboxylic acid content was calculated as $7.3\,\text{mmol}\cdot\text{g}^{-1}$.

The resin was characterized by FT-IR spectrophotometer (Fig. 1). In the sulfonamide resin, S=O stretching vibration occurs at $1362\,\text{cm}^{-1}$ and $1156\,\text{cm}^{-1}$. The C=O stretching vibrations are observed in the range of $1730–1600\,\text{cm}^{-1}$.

Extraction of Dyes

Dye extraction experiments were carried out simply by contacting wetted bead samples with aqueous dye solutions at room temperature. Capacities were assigned by colorimetrical analysis of residual dye contents. Dye sorptions capacities are given in Table 1.

The resin shows reasonably high dye sorptions. It is important to note that the resin can be used in a wide pH range (Table 2).

At low pH, the carboxyl groups on the surface of resin that are responsible for binding with basic dye are predominantly protonated (–COOH), hence incapable of binding the basic dye. As the pH increased, the sorption became favorable due to the deprotonation of the carboxyl groups ($-\text{COO}^-$), resulting in sorption sites that were available for binding with the basic dye. With the increasing pH, the number of positively-charged sites decreased and the number of negatively charged sites increased. This phenomenon favors the sorption of positively-charged dye due to electrostatic attraction (41).

Dye Sorption Kinetics of the Resin

This material is able to remove the anionic dyes completely even from highly diluted aqueous dye solutions which are highly important. We performed batch kinetic sorption experiments with highly diluted dye solutions (0.004 g dye-0.008 g dye/L water) to investigate the efficiency of the resin in the presence of trace quantities

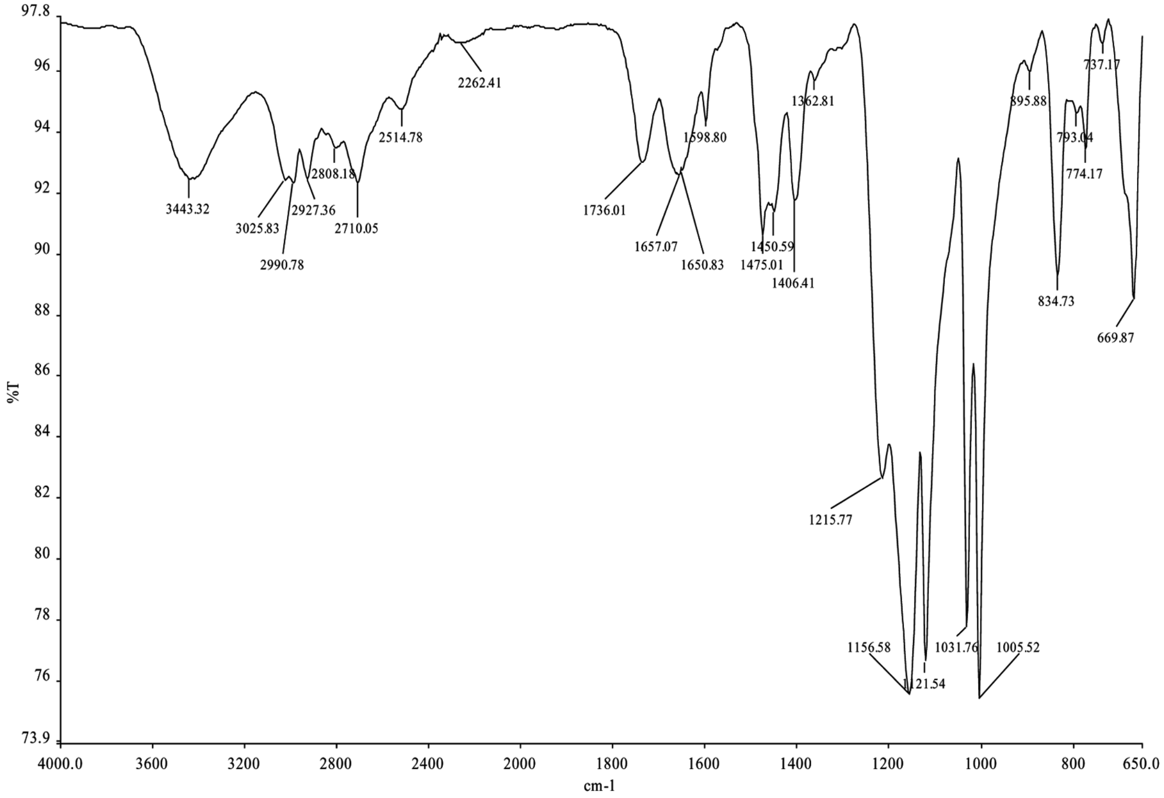


FIG. 1. FT-IR Spectrum of the resin.

TABLE 1
Sorption capacities of the resin

Dye	Capacity (g dye/g resin)	λ_{max} (nm)
Crystal violet	0.67	591
Methylene blue	0.63	664

TABLE 2
Maximum dye sorption capacity of the resins depending on pH

Dye	pH	Capacity(g dye/g resin)
Crystal violet	2.0	–
	4.0	0.64
	5.0	0.63
	8.0	0.68
Methylene blue	2.0	0.50
	4.0	0.52
	5.0	0.64
	8.0	–

This property is important in utilization of the resin in industrial applications.

of dyes. The concentration–time plot in Fig. 2 shows that within about 20 min of contact time, the dye concentration falls to zero for methylene blue.

Regeneration of the Resin

Alkaline regeneration works well for strong and weak basic sorbents and acid regeneration works for most of the dyes (42).

For the regeneration of dyes from the loaded resin, 5 mol L^{-1} H_2SO_4 was used. When the loaded samples were contacted with 5 mol L^{-1} H_2SO_4 for 24 h, the amount of recovered dyes is around 0.50 g dye/g polymer for methylene blue, which is 79% of the capacity of fresh polymer.

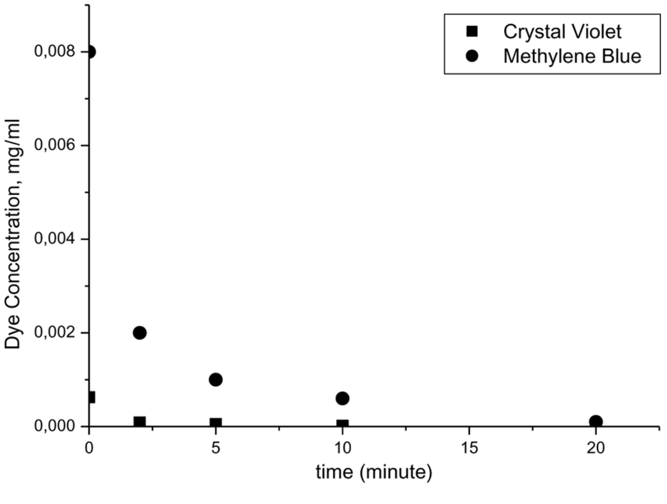


FIG. 2. Sorption kinetic of the resin.

CONCLUSION

Crosslinked dicarboxylic acid containing sulfonamide based resin was prepared starting from chlorosulfonated polystyrene and iminodiacetic acid. The resulting beads are highly effective in the removal of dyes and the resin format renders it a potential material for technological use. Under non-buffered conditions, the dye uptake capacity is around 0.67 g crystal violet/g polymer and 0.63 g methylene blue/g polymer respectively.

Additionally, the resin does not hydrolyze in acid and base solutions, due to the high stability of the sulfonamide linkage to acid and base hydrolysis which is a very important property for the regeneration.

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