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Removal of Azo Dye Molecules from Aqueous Solution Using Novolac Resin Based Network Polymer

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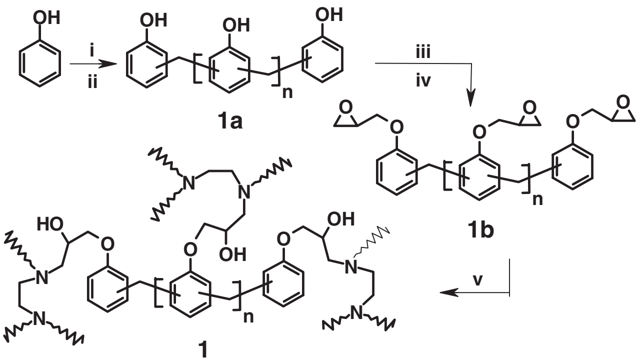
Synthesis of novolac resin based novel network polymer **1** based on the reaction between novolac epoxy resin and ethylenediamine has been achieved for the first time and its sorption characteristics toward methyl orange as azo dye source have been investigated.

Toxic azo dyes can exist in the environment, mainly via wastewater. Some of the azo dyes or their metabolites are harmful to the human body.[1] Thus, development of effective sorbents for the removal of dye colorants from wastewater is of great interest.[2,3] The construction of polymeric sorbents which can effectively extract azo dye molecules is receiving considerable attention in the area of separation science and analytical chemistry.[2c,4,5] Phenolic resins are a class of synthetic materials that have found increasing applications in recent years. However, to the best of our knowledge, the use of phenolic resin has been explored very little in this field.[6] In continuation of our interests in this field,[5a] we report herein the synthesis of a new novolac-based network polymer as potential sorbent for azo dye sources like methyl orange (MO). The chemical resistance, dimensional stability, low-cost, branched structure and multifunctional nature of novolac type phenolic resin enable it to be an ideal precursor for network design.

Thus, crosslinkable novolac-based epoxy resin is a very attractive and extremely useful economic precursor for the preparation of unique polymeric network structures. The synthesis of titled polymeric network **1** is illustrated in Scheme 1. It is hoped that the multiple functional groups (amino, hydroxy, and ether) within the network polymer **1** will impart hydrophilicity on the entire network, which can be advantageously utilized in manipulating the extraction of dye molecules.

The molecular structures of **1a** and **1b** were confirmed by FT-IR and ^{1}H NMR data. The molecular weight of **1b** was estimated from GPC analysis. Just like **1a** and **1b**, **1** could not dissolve in water and in common organic solvents, so **1** has been successfully characterized by FT-IR spectroscopy. The FT-IR spectrum of **1** shows the broad absorption band centered at 3393 cm^{-1} that is the characteristic of the O–H and N–H stretching frequencies. The band observed at 1507 cm^{-1} can be attributed to N–H plane bending vibrations. Figure 1 shows a SEM image of the network polymer **1** revealing the presence of discrete micropores on the surface.



Scheme 1. (i) Aqueous formaldehyde (37%), oxalic acid, reflux, 30 min; (ii) oxalic acid, reflux, 1 h; (iii) 1-chloro-2,3-epoxypropane, NaOH, heat; (iv) NaOH, heat; (v) ethylenediamine, 1,4-dioxane/methanol, heat.

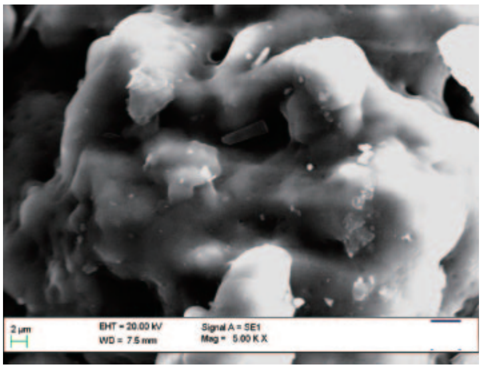


Figure 1. Scanning electron micrograph of **1**.

The swelling behavior of **1** in water as determined from swelling ratio–time plot revealed the dramatic increase in swelling ratio at the initial stage of the contact period of 10 h, and thereafter, it reached equilibrium within 48 h. This is indicative of the fact that the network structure contains amino, hydroxy, and ether functional groups that have good affinity for the formation of hydrogen bonding with water molecules.

The adsorption ability of **1** toward MO as azo dye source was evaluated as a function of contact time at fixed pH values of 2.30, 7.20, and 10.96 as were adjusted upon addition of dil HCl and NaOH solution. For this purpose, the network **1** was suspended in solutions containing MO at different pH values, and shaken occasionally. After different intervals, the polymer was filtered off.

The residual concentrations of the MO solutions at fixed pH values of 2.30, 7.20, and 10.96 were determined using UV–vis spectrophotometry at $\lambda_{\max} = 504$, 461, and 457 nm, respectively (Figure 2). However, upon successive increase in adsorption time, the adsorption capacity[6] for methyl orange dye was increased and reached the adsorption equilibrium within 48 h as evidenced from Figure 3. Moreover, from Figure 3, it can be observed that the pH value of the solution strongly affects the adsorption performance of this adsorbent.

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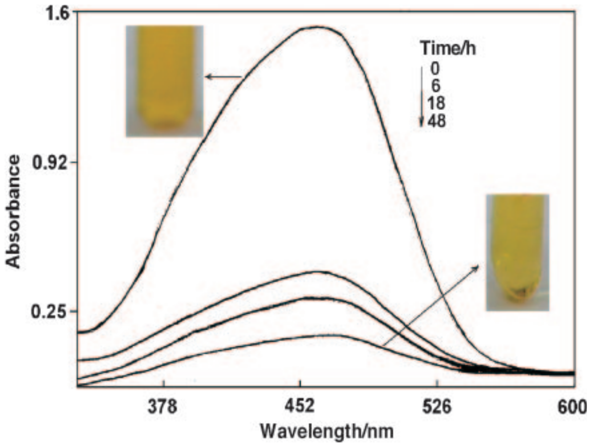

Figure 2. UV–vis spectral change of the solution of MO (7.28×10^{-5} M) at 461 nm as a function of adsorption time for **1** (pH 7.20, 25 °C).

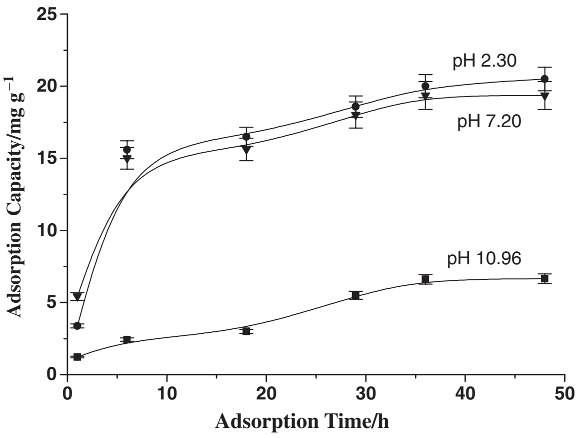

Figure 3. The effect of adsorption time on the MO adsorption capacity of **1** at pH 2.30 (●), 7.20 (▼), and 10.96 (■) at 25 °C.

The adsorption isotherm was determined by using the Freundlich model.[7,8] The plot with $\log q_e$ vs. $\log C_e$, where q_e is the amount of dye adsorbed onto **1** and C_e is the equilibrium concentration of dye in solution, showed linear relationship demonstrating that the adsorption follows Freundlich isotherm (Figure 4).

The parameters of Freundlich isotherm at different pH values are given in Table 1. The Freundlich constants K_f and n, related to the adsorption capacity and adsorption intensity, were determined to be in the range of 8.1116–10.6998 and 1.0576–1.1939, respectively at pH 2.30 and 7.20 indicating beneficial adsorption ($10 > n > 1$). Furthermore, the regression coefficient R^2 was found to be 0.8771–0.9445 demonstrating the applicability of Freundlich adsorption isotherm law in the adsorption of MO onto **1** at the pH ranges as given in Table 1. Therefore, the manipulation of adsorption capacity of **1** with pH-adjustment showed its potentiality in the removal of dye colorant from aqueous solution. FTIR spectroscopy was used to achieve qualitative information on the chemical interactions in the isolated dye-adsorbed network (dry). The shifting of resonance at 1173 cm^{-1} corresponds to SO_3^- group to lower wavenumber ($\Delta\nu = 9$ cm^{-1}) manifests the chemical interaction.

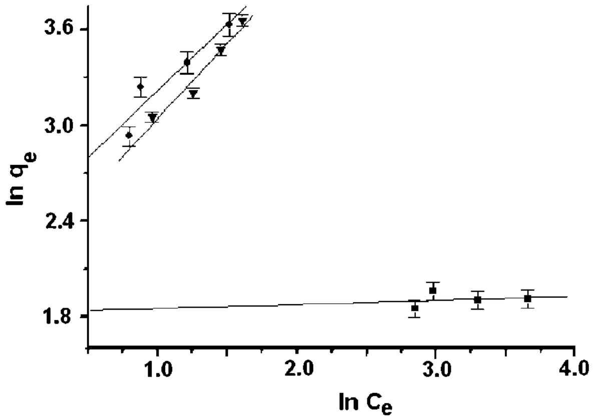

Figure 4. Freundlich isotherms for the adsorption of MO onto **1** at pH 2.30 (●), 7.20 (▼), and 10.96 (■) at 25 °C.

Table 1. Freundlich Constants of the Adsorption Isotherms for MO onto **1** at Different pH Values

pH	K_f	n	R^2
2.30	10.699	1.193	0.8771
7.20	8.111	1.057	0.9445
10.96	6.143	38.759	0.0411

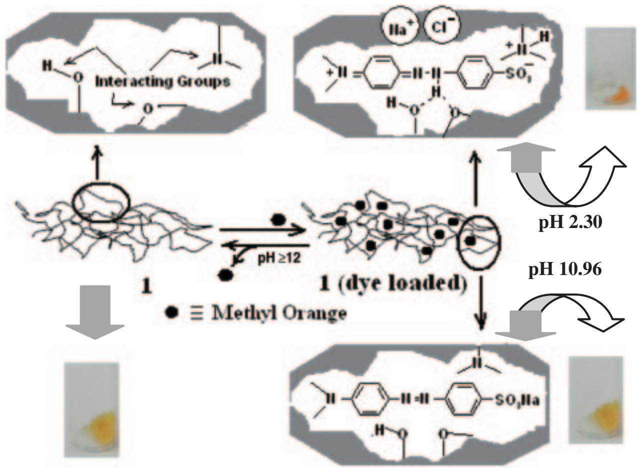

Figure 5. A proposed mechanism of adsorption: chemical interactions occurring within the polymer matrix associated with visual color change.

Figure 5 represents the anticipated mechanism of the pH-induced adsorption of MO onto **1**. The presence of a varying number of interacting groups (amino, hydroxy, and ether functionalities) into the domains of **1** could be attributed to facilitate the binding of hydrophilic azo dye, for instance, MO. In acidic aqueous solution (pH 2.30), the amino groups of **1** get protonated by HCl and $-SO_3Na$ group of MO becomes ionized into its anionic form, leading to efficient ionic interaction between $-N^+$ and $-SO_3^-$ moieties. In addition, effective hydrogen-bonding interactions ($^+N-H\cdots{}^-O_3S-$ and $-O-H\cdots{}^-O_3S-$) are supposed to occur in adsorbing MO within the matrix. At the same time, Na^+ prefers to reside with Cl^-. The well-known protonation event of azo N-atom of MO at this pH region is also expected to be very fruitful in assisting the adsorption of MO through hydrogen bonding with the interacting groups as illustrated in Figure 5. When the medium is close to neutrality (pH 7.20), the SO_3Na group of MO becomes partially ionized, and moderately effective ionic as well as hydrogen-bonded interactions turns out to be equally important in the adsorption process. In the basic region (pH 10.96) the protonation of amino groups of **1** and the ionization of the SO_3Na group of MO are practically forbidden. Consequently, the interaction between MO and **1** may involve only weak hydrogen-bonding forces, resulting in the abrupt drop in adsorbability. The pH-dependent known behaviors of structurally related molecules[2c,9] support the protonation/ionization of amino and sulfonate groups. It is important to note that the equilibrium adsorption capacity of MO under the pHs studied was hardly affected in the presence of salting-out agents like sodium chloride (0.1 M), indicating that strong interactions (ionic and hydrogen bonding) between network and MO are essentially independent of salting-out effect. A color change could be observed easily on keeping **1** in contact with dye solution as shown in Figures 2 and 5. In order to find out the economic success of the adsorption process, the regeneration of the dye-loaded sorbent was also investigated. Desorption occurs from the dye-loaded sorbent on adjusting the pH of the medium toward very basic region (pH $\geq$12), indicating the removal of about 90% of adsorbed dye molecules and thus **1** can be reused.

In summary, the new and low-cost crosslinkable novolac-based epoxy resin has been used in the design of network polymer **1**. Because of the simplicity in synthesis, pH-induced adsorption of azo dye molecules and pH-driven regeneration, this sorbent should have potential application in the field of separation and environmental sciences aiming to the treatment of azo dye-containing effluents, and analytical chemistry. Further studies toward the development of a variety of novolac-based network materials by using various amines, which can substantially manipulate the adsorption properties and broaden the application potential are under progress.

Experimental

Novolac Oligomer 1a. The synthesis was performed utilizing phenol and formaldehyde in the ratio of 1.2:1. In the reaction, a stoichiometric amount of formaldehyde and phenol were taken in water and refluxed for 30 min in the presence of oxalic acid catalyst (1.2 mmol). Then another 1.2 mmol oxalic acid was added and refluxing was continued for 1 h. An oily layer appeared, was separated and dried over anh. Na_2SO_4 to yield the product. FT-IR (KBr): $\nu_{max} = 3442$, 2919, 2846, 1604, 1501, 1379, 1256, 1095, 1005 (w) cm^{-1}; ^1H NMR (DMSO-d_6, 400 MHz): δ 9.31–9.11 (bm, Ar-O*H*, H-bonded), 7.16 (t, $J = 12$ Hz, ArH), 6.98–6.88 (m, ArH), 6.76 (m, ArH), 6.66 (m, ArH), 3.79–3.64 (m, Ar–CH_2–).

Novolac Epoxy Resin 1b. A mixture of **1a** (3.5 g), 1-chloro-2,3-epoxypropane (47.2 g, 0.51 mol), NaOH (0.8 g) in 5 mL water was stirred in a water bath for 30 min. Then another 0.7g NaOH was added and heating was continued for 40 min. The light violet color gradually turned to yellow. The organic layer was separated and excess 1-chloro-2,3-epoxypropane was removed in vacuo. Then the organic phase was washed with water repeatedly. The residual water in organic phase was removed under reduced pressure to yield the product. FT-IR (KBr): $\nu_{max} = 3431$, 2936, 1640, 1387, 1008, 904 cm^{-1}; ^1H NMR (DMSO-d_6, 400 MHz): δ 7.29 (t, $J = 10$ Hz, ArH), 7.12–7.09 (m, ArH), 6.96 (d, $J = 8$ Hz, ArH), 6.86 (bm, ArH), 3.98–3.63 (bm, $ArOCH_2$–, Ar–CH_2–, epoxide proton), 3.57–3.51 (m, Ar–CH_2–, epoxide protons), 3.24 (bm, epoxide protons), 2.86–2.83 (m, epoxide protons), 2.70 (s, epoxide protons). GPC (using polystyrene and THF): $M_w = 3300$, MWD 1.10.

Network Polymer 1. A mixture of novolac epoxy resin **1b** (0.45 g), ethylenediamine (0.224 g, 3.74 mmol), 1,4-dioxane (0.8 mL), and methanol (0.4 mL) was stirred at 95–100 °C for 3 h. The network polymer precipitated as yellowish solid. Product was purified by thoroughly washing with deionized water. FT-IR (KBr): $\nu_{max} = 3393$, 2926, 2848, 1604, 1507, 1450, 1243, 1115, 1024, 805, 734 cm^{-1}.

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6 The sorbed amount (mg g^{-1}) at equilibrium was calculated by the mass balance relationship: $q_e = [(C_0 - C_e)V]/W$; where C_0 and C_e are the initial and equilibrium concentrations (mg L^{-1}) respectively. V is the volume of solution (L), W is the weight of the sample (g).

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