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EFFECT OF SOLVENTS ON ADSORPTION OF ANIONIC DYE ON ALUM DOPED POLYANILINE

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ABSTRACT

Polyaniline was synthesized by oxidative polymerization method by using ammonium persulphate as oxidant and doped with potash alum in aqueous medium. Adsorption of dye on doped polyaniline was performed in different range of solvent and was studied by UV-VisSpectroscopy. The effects of solvent on adsorption of the dye were investigated.The adsorption was much more facile in water than in other solvents on the alum doped PANI surface.

KEY WORDS
Polyaniline
Adsorption
Anionic dyes
Potash alum, solvents

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INTRODUCTION

Water pollution is an important environmental issue, and receives major worldwide concern. According to a recent study, approximately 7000000 tons of different dyes are produced annually in the world, and more than 60 percent of the world dye production is consumed by textile industries (Blackburn, 2004).The waste effluent from the textile, paper, leather tanning, food processing, plastics, cosmetics, rubber, printing and dye manufacturing industries contain synthetic dyes which are recalcitrant organic molecules, resistant to aerobic digestion and are stable to light, heat and oxidizing agents (Chatterjee *et al*., 2009). Thus removal of dye pollutants from wastewater is a scientific challenge. Various treatment methods have been developed, for instance coagulation, chemical oxidation, membrane separation, electrochemical processes, and adsorption techniques. Among these techniques, adsorption has been considered as a promising and a cost-effective process for dye removal from wastewater (Gomes *et al*., 2005). Although activated carbon is an appropriate adsorbent for removal of traditional pollutants such as phenols, dyes, organic acids and heavy metals. However, there are some drawbacks associated with activated carbon, which is costly in regeneration and nonselective. To circumvent these drawbacks associated with activated carbon some other materials have been reported for instance natural organic matter, natural and synthetic polymers, inorganic solid which are effective for dye removal.

Polymeric materials have attracted significant attention for diversified applications including pollutant removal/ remediation, because of their high specific surface area, high porosity, adsorption capacity, and excellent thermal/chemical stability (Tomida *et al*., 2001).

Polyaniline (PANI) is exclusive among allpolymeric material as its properties can be reversibly controlled by both protonation and charge-transfer doping (MacDiarmid*et al*., 1987; Yoshikawa*et al*., 1989).Since PANI exhibits relatively high surface area and porosity and is reported to be utilized as adsorbent for adsorption of proteinand DNA (Meada and Armes, 1995 ; Chowdhury *et al*. 2002; Smith and Knowles 1990; Miksa and Slomkowski, 1995; Minehan *et al*.1994; Saoudi *et al*. 1997; Saoudi *et al*. 1997) .

Mahanta*et al*.reported that doped polyaniline can be used as better adsorbent than undopedone. This doping can be achieved by an acid for instance camphorsulphonic acid, p-toluenesulfonic acid or simple protonic acid which have pH less than 4 (Mahanta *et al*., 2009; Chiang and MacDiarmid, 1986).This doping condition presents a severe and destructive environment for industrial applications. Thus there is a need to develop the environment friendly and nontoxic methods.

Recently we have synthesized potash alum doped polyaniline by using potash alum, a cheap environment friendly substance as dopant (Patra *et al*., 2015).We are now interested to explore the alum doped PANI for the removal of dyes.

Solvent plays the crucial role during adsorption, as the process may be considered as a competitive process between the adsorbate and solvent, and certain number of solvent molecules must first be removed when adsorbate molecules approach the adsorbent. This paperpresent the results of adsorption of the anionic dye on alum doped polyaniline in presence of different solvents, starting from less polar solvent to more polar pure water in order to know extreme feasibility of adsorption.

MATERIALS AND METHODS

Ammonium persulfate (APS) $[(NH_4)_2S_2O_8]$ (Merck), Potash alum (Merck), N-methyl-2-pyrrolidone (NMP) (Spectrochem India), Tetrahydrofuran (THF) (Merck India), were used as received. Aniline (Merck India) was distilled under vacuum before use. Methylene Blue (MB) (Nice Chemicals, India), Rhodamine-B (RB) (Lobachemie, India), Methyl Orange (Fisher Scientific)were used as received. Acetone (Merck India), methanol (Spectrochem India), Dimethyl sulphoxide(Spectrochem India) andacetonitrile (Spectrochem India) were used as received.

Adsorption experiment

The adsorption kinetics of the dyes onto doped polyaniline was carried out by varying solvent, temperature of medium. In a typical experiment, 0.1g of doped PANI was added to 50 ml of different dye solutions and stirred for 8 hrs. Samples were collected at different time intervals and the concentration of the dye was determined by UV - Vis spectroscopy in the range from 200nm to 800nm.

Synthesis and characterization of doped polyaniline

Polyaniline (Emeraldine base) was synthesized by chemical oxidative polymerization method using APS as oxidant (Kolla *et al*., 2005). The emeraldine base was doped with Potash alum. In a typical procedure, 200 mg polyaniline base was taken in a flask, to this 15 mL of THF was added and stirred for 1 hour. 35 mL of 0.1 M solution of Potash alum in water was added to the flask and stirred for 24h. Then the doped polyaniline was filtered and washed with 300mL of water. The powder was dried in the vacuum at 50ºC for 24h.

RESULTS AND DISCUSSION

Synthesis of alum doped polyaniline was carried out as per our reported procedure (Patra *et al*., 2015). The structure of the alum doped polyaniline is shown in Fig.1.

At the beginning two types of dyes Cationic (Methylene Blue and Rhodamine - B) and anionic (methyl orange) shown in Fig. 2 were tested for the adsorption in aqueous medium using 0.1 gm of doped polyaniline and 100ppm of dye initial dye concentration.

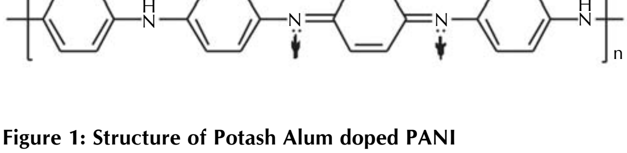

Figure 1: Structure of Potash Alum doped PANI

When the cationic and anionic dyes are compared, it is observed that there is no significant adsorption of cationic dyes such as Methylene Blue and Rhodamine B. This clearly indicates that polymer backbone has positive charge and the interaction is in between negatively charged sulphonated group of dye with the positively charged PANI. Furthermore, the adsorption of anionic dyes is not possible, when undoped polyaniline is used as adsorbent.

Effect of variation of Solvent:

In order to study the effect of solvent the adsorption was carried out in presence of various solvents starting from low polar solvent to high polar solvent, water. The amount of dye adsorbed at time t (q_t) was obtained by using equation (1).

$$q_t = \frac{V(C_o - C_t)}{m} \quad \text{.....(1)}$$

Where C_0 and C_t are the initial and final dye concentration at time t (mgL^{-1}) respectively, V is the volume of dye solution (L) and m is the mass of the adsorbent used (g).

Figure 4 shows the plot of amount of dye (q_t) adsorbed versus time. In case of all the solvent there is a sharp rise in value of q_t with increase of time then reached at plateau after 6 hour. At this value there is dynamic equilibrium between the amount of dye adsorbed and desorbed from adsorbent. Also it is observed that in case of water, the q_t value is more compared to the other solvents at a particular time.

The percentage of removal of dyes was calculated by using equation (2),

$$R(\%) = \frac{100(C_o - C_t)}{C_o} \quad \text{.....(2)}$$

Where C_0 and C_t are the initial and final dye concentration at time t ($mg.L^{-1}$) respectively

The percentage removal of MO was investigated in different solvents and the results are presented in Fig 5.The experiments were carried out with different solvents like acetone, acetonitrile, methanol, DMSO for initial dye concentration of 100ppm and by using 0.1g of doped PANI. It was observed that adsorption of MO is high in case of water than other solvents. Furthermore, with increase in polarity of the solvent, the adsorption increases, this may be attributed to ionic dyes are more soluble in polar solvent than less polar solvent. More is the solubility of the dye, more easily it can approach to the adsorbent and adsorbed by electrostatic force of attraction. The non-polar solvents are not used for adsorption studies as the dye is not soluble in nonpolar solvent.

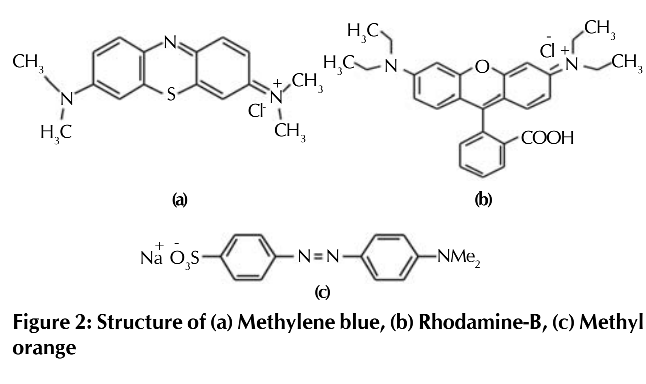

Figure 2: Structure of (a) Methylene blue, (b) Rhodamine-B, (c) Methyl orange

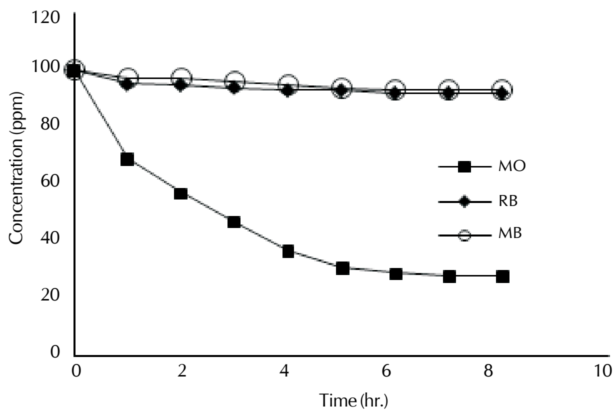

Figure 3: Show the variation of the dye concentration with time in presence of alum doped PANI.

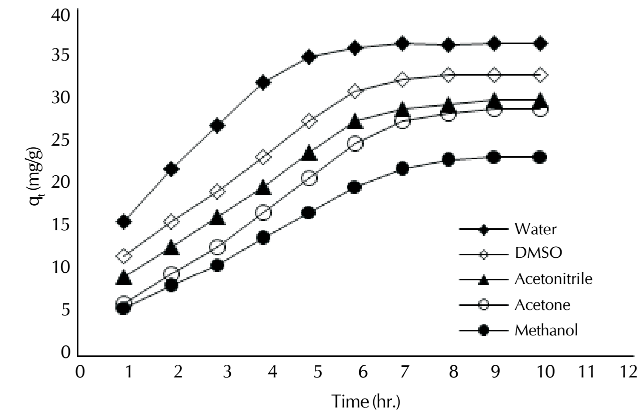

Figure 4: Removal efficiency of MO onto doped PANI in different solvent

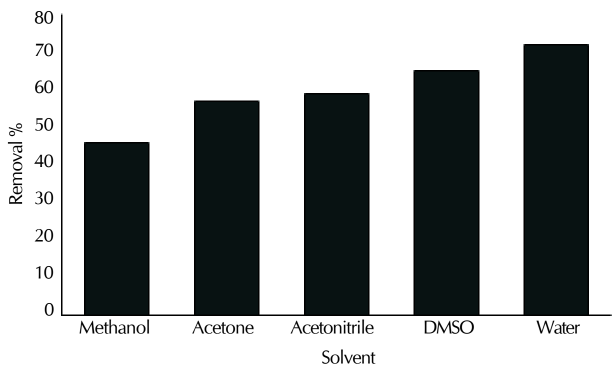

Figure 5: concentration profile of MO onto doped PANI in different solvents

Potash alum doped PANI was efficiently used as an adsorbent for the removal of anionic dye (MO). The effect of solvents, allowing us to predict the changes to the local electrostatic environment and surface coverage of dye on alum doped PANI. Water is the most suitable solvent among all other solvents, in which the removal of the dye is more. The removal efficiency is dependent on nature of solvent of the medium.Alum doped polyaniline can be used to remove the dyes from water in economical way which is useful for environmental protection and wastewater treatment.

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