Polyaniline for Removal of Methyl Orange Dye from Waste Water

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***Abstract* - Conducting polymers have emerged as effective adsorbents in the field of waste water treatment due to their cost effectiveness and higher environmental stability. The present investigation deals with the application of Polyaniline, a potential conducting polymer, for the removal of a toxic textile dye (Methyl Orange), from wastewater. The applied adsorbent, Polyaniline has been synthetically prepared by chemical oxidative polymerization of aniline with doping of an organic acid (oxalic acid). Batch studies were conducted to determine the effect of several influential parameters such as pH, amount of adsorbent, contact time and concentration at different temperatures. Preliminary adsorption studies revealed that maximum decolorization occurred at pH 3 after 5 hours of contact time. Almost 92% Methyl Orange removal was achieved at 50°C with 0.03 g of the adsorbent. Studies revealed the efficiency of polyaniline for the removal of methyl orange from waste water.**

***Keywords*: Adsorption; Azodye; Methyl Orange; Polyaniline; Textile effluent**

I. INTRODUCTION

Water pollution caused due to the dumping of the industrial effluents in the water bodies is a matter of great concern in today's scenario. Untreated disposal of this effluent into receiving body either causes damage to aquatic life or human beings in addition to posing several carcinogenic or mutagenic threats [1].Various techniques like chemical precipitation, membrane filtration, ozonations, coagulation, flocculation, biodegradation, ion exchange and adsorption have been used for the removal of dyes from waste water[2],[3] Adsorption has proven to be an efficient method for the treatment of these effluents and removal of hazardous wastes [4]. Adsorption process employs several substances like rice husk, agricultural waste etc [5], [6] for water purification and dye removal, amongst which activated carbon has been widely used although being an expensive adsorbent [7]. In recent years, the need for safe and economical methods for the elimination of dyestuffs especially azo dyes from contaminated waters has necessitated research interest towards the production of low cost alternatives to commercially accessible activated carbon.

Azo dyes are well known carcinogenic organic substances [8]. One of this class of dyes, Methyl Orange, which is the main focus of the study, inadvertently enters the body through ingestion and metabolizes into aromatic amines by intestinal microorganisms which can even lead to intestinal cancer [9]. Methyl Orange (MO) is a water-soluble azo dye (Fig. 1), widely used in the textile, printing, paper manufacturing, pharmaceutical and food industries, and also in research laboratories [10]. An artificially synthesised adsorbent, Polyaniline doped with oxalic acid has been used for the removal of Methyl orange from aqueous solution in the present research.

Polyaniline (PAni) is a polyaromatic amine which is one of the most potentially useful conducting polymers and has received considerable attention in recent years because of its low cost of synthesis, easy process ability and environmental stability. Polyaniline is generally used in rechargeable batteries, electrochromic devices, chemical sensors, photo voltaic cells, flexible LED, electromagnetic interference (EMI) shielding, solar cells, anticorrosion coatings, sensors etc.[11],[12]. It has also recently been used by some researchers for the removal of heavy metals and dyes [13]-[15].

II. MATERIALS AND METHODS

A. *Adsorbate and Reagents*

Methyl Orange (MO), is a water soluble toxic azo dye having IUPAC name as Sodium *p*-dimethylamino azobenzenesulphonate, and molecular formula and molecular weight $C_{14}H_{14}N_3NaO_3S$ and 327.34 g mol^{-1} respectively.

A stock solution of MO was prepared in distilled water (0.001 M).The working solutions were prepared by diluting the stock solution with distilled water to give appropriate concentration of the working solutions.

All the chemicals used were of analytical grade and prepared in distilled water. Aniline was obtained from Qualigen and distilled before use. MO was supplied by Merck. MO showed an

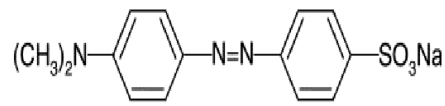

Fig.1 Methyl Orange

Intense absorption peak in the region of 498 nm which corresponds to the maximum absorption of the MO monomer. All experiments were carried out in aqueous solutions using distilled water

B. *Adsorbent*

Polymerization of aniline monomer (Qualigen, A.R. Grade) (Fig. 2) was carried out by oxidative polymerization method using ammonium per sulphate (Loba) as an oxidant and aqueous conducting media containing organic acid oxalic acid (Qualigen). The synthesis was carried out by taking 1.2 mL of the monomer solution and 2 M oxalic acid and stirring continuously at low temperature (0-4 °C) for 30 minutes, in a three necked flask. The oxidizing agent, ammonium per sulphate was then added drop wise after complete addition of which the reaction mixture was kept under constant stirring for 24 hr. A dark green precipitate of the polymer formed which was then isolated by filtration followed by drying in an oven at 60-70 °C for 24 hr.

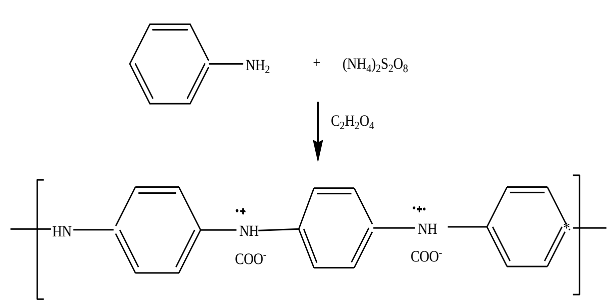

Fig.2 Polymerization of Aniline

C. Instrumentation

The pH measurements were performed using a digital pH meter DPH 500 (Global) Absorbance measurements were carried out on UV/Visible double beam Spectrophotometer model number 2203 (Systronics).

D. Batch Studies

Several factors that affect the adsorption process such as pH, particle size, amount of adsorbent, contact time and initial dye concentration were studied during the adsorption of MO over Polyaniline.

25 ml of dye solution was taken in 100 ml of volumetric flask with the appropriated amount of adsorbent and was shaken periodically for 1 hr at 100 rpm in an orbital shaker. Effect of pH was studied by varying the pH of the solution from 1-10 for the 4×10^{-4} M dye concentration, with 0.03 g of Polyaniline at 30 °C. Similarly the effect on adsorption rate was investigated by varying the particle size and adsorbent dosage for the same dye concentration. Contact time studied were carried out for the 0.03 g Polyaniline 4×10^{-4} M MO 30 to 400 minutes system at different temperatures, to evaluate the equilibrium time for maximum adsorption to take place. In order to find the effect of initial dye concentration over adsorption process, batch experiments were performed in the range of 1×10^{-4} to 10×10^{-4} of the dye solution with fixed amount of Polyaniline at 30, 40 and 50 °C.

III. Results and Discussion

A. Effect of pH

The adsorption process was investigated for the current system in the pH range 1-10, since pH is a key factor. Results indicated that maximum adsorption of MO onto Polyaniline was at pH 3. (Fig.3) clearly reveals that as the pH of the solution increases from 1 to 3 and the adsorption of dye increased from 7.362 to 19.632×10^{-4} g, while it decreased to 0.818×10^{-4} g at pH 10. The higher adsorption of the dye at low pH may be due to the protonation of nitrogen atom in adsorbent. In aqueous solution, dye molecule gets dissociated into anions. As a result the adsorption occurs through electrostatic interaction between the two counterions.However with increase in pH (4-10) protonation reduces leading to the reduction of active sites in polymer [16].

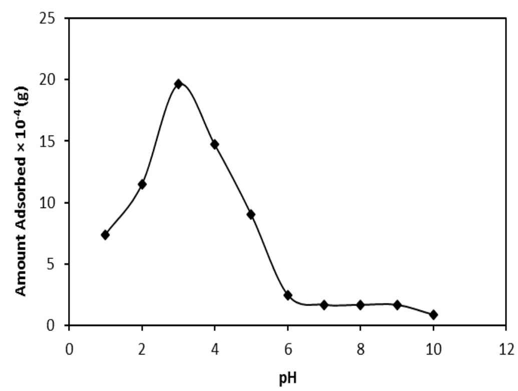

Fig. 3 Effect of pH on adsorption of 4×10^{-4} M MO onto Polyaniline at 30 °C

B. Effect of Amount of Adsorbent

Studies were conducted by varying the amounts of the adsorbent ranging from 0.01 to 0.05 g in a fixed concentration of $4X10^{-4}$ g at 30, 40 and 50°C at pH3. It was observed that the adsorption of dye increased with an increase in amount of adsorbent due to increased adsorbent surface area and availability of more adsorption sites (Table I). But after 0.03g, increase in adsorption was not found to be effective. Therefore 0.03g was optimum dosage chosen for all further studies.

Table I. Effect of amount of adsorbent on adsorption of MO onto Polyaniline at 30, 40 and 50 °C

Amount of adsorbent(g)	Amount adsorbed ×10^{-4}g)		
	30^0C	40^0C	50^0C
0.01	5.73	9.81	11.45
0.02	8.99	11.45	13.90
0.03	11.45	13.90	17.99
0.04	12.27	14.72	18.81
0.05	13.09	15.54	19.63

C. Effect of Particle size

Particle size plays a very important role as it largely deals with the availability of surface area for adsorption to take place. In the present preliminary study, three mesh sizes were analysed viz. 72, 100 and 150 BSS. The results of adsorption for different sizes of mesh were analysed with the batch experiments on 4 ×10^{-4} M MO solution with 0.03 g of Polyaniline(Table II). As the mesh size increased adsorption increased due to availability of larger surface area for adsorption. It was also noted that the rate constants increased with increase in mesh size with decrement in half life.

Table II. Effect of Particle size on adsorption of MO onto Polyaniline at 30 °C

Mesh Size	Amount adsorbed ×10^{-4} (g)	k (h^{-1})	$t^{1/2}$
72	27.81	0.079	8.76
100	29.45	0.096	7.22
150	30.27	0.108	6.42

D. Effect of Contact time

Contact time studies showed that the maximum uptake of the dye took place after 5 hrs of interaction between adsorbent and adsorbent. Fig.4 depicts the increase in adsorption of MO with increase in contact time from 30 to 400 minutes. The amount of dye adsorbed increased from 1.636, 2.454, 3.272 to 18.81, 22.08 and 23.72 × 10^{-4} g at 30, 40 and 50 °C respectively after 5 hr. of contact time. Similar results have been reported by Mittal et al. [17] during decolourization of a hazardous textile dye using low cost materials.

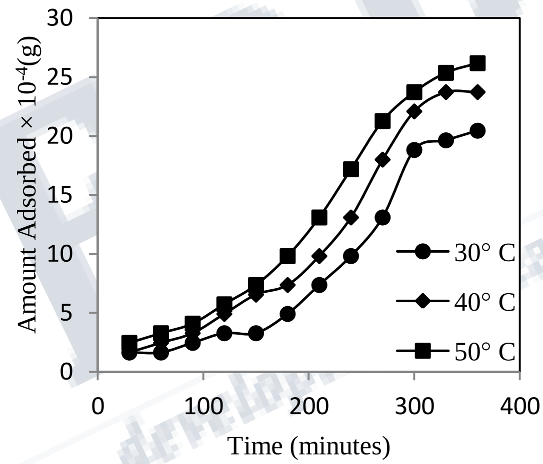

Fig. 4 Effect of contact time on adsorption of MO onto Polyaniline at 30, 40 and 50°C

E. Effect of Initial Dye Concentration

Effect of initial dye concentration on adsorption of MO over Polyaniline was studied for 1×10^{-4} to 10 ×10^{-4} M at different temperatures at optimum pH 3 and adsorbent dosage of 0.03 g. It was observed that adsorption increased rapidly from 6.544 to 42.536 ×10^{-4} g from 30 to 50 °C with increase in concentration from 1×10^{-4} to 10×10^{-4} (Fig. 5). Initially the adsorption rate was rapid till 5 ×10^{-4} M and thereafter remained almost constant. Higher adsorption at lower concentration may be due to the greater degree of interaction between the dye and adsorbate molecules [18].

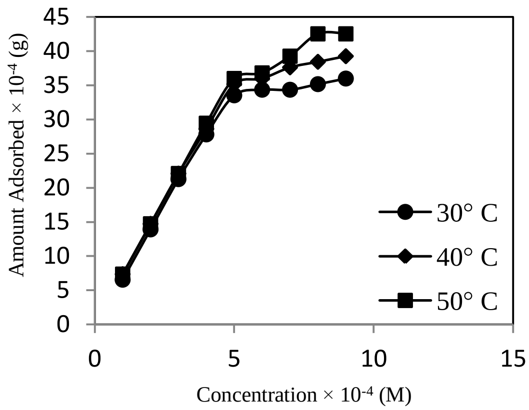

Fig. 5 Effect of initial dye concentration on adsorption of MO onto Polyaniline at 30, 40 and 50 °C

IV. Conclusion

Azo dyes being the largest consumed dye in textiles are threat to water bodies affecting both the aquatic and human life. Batch studies carried out on Polyaniline for adsorption of a toxic textile dye, Methyl Orange resulted in higher percentage of removal proving effective application of Polyaniline in treatment of textile waste water. Maximum removal was obtained after 5 hr with very less amount of adsorbent at low pH. Preliminary investigation revealed the potential of Polyaniline for the removal of dyes from waste water.

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