

Removal of Orange-G and Alizarin Red S from Aqueous Solution by CuCl₂ Doped Polyaniline Composite Assisted by UV light

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This work describes the adsorption of Orange-G and Alizarin Red S, from aqueous solutions onto 8 % PANI-CuCl₂ adsorbent. Adsorption studies were performed by UV light irradiated batch experiments as a function of process parameters such as contact time, initial dye concentration, dosage of adsorbent and initial pH. Temperature was varied to investigate its effect on the adsorption capacity. Equilibrium adsorption isotherms were measured and the experimental data were analyzed by using Langmuir equation. Pseudo-second-order kinetic model was found to correlate with the experimental data well. The experimental data obtained in the present study indicates that CuCl₂ doped with polyaniline can be attractive options for removal of dye from waste water.

Keywords: Adsorption, Orange-G, Alizarin Red S, PANI-CuCl₂.

INTRODUCTION

Dyes are chemicals that can produce bright colours and firmly attached to various materials which have been used extensively in paper, pulp, plastic, hair colouring, paint, carpet, printing and textile industries. Among these various industries, textile ranks first in usage of dyes for colouration of fibre [1]. Dyeing industries are the largest sector in India. It was calculated about 7×10^5 tones of dyes are produced annually worldwide [2]. Approximately 50 % of these are discharged as effluent into nearby water bodies without any prior treatment [3] which increases the turbidity and pollution strength on the aquatic environment due to toxic degradation products formed [4,5]. Removal of dyes from the water sources will be tedious due to complex aromatic molecular structure [6]. For wastewater treatment various methods are performed like coagulation [7], oxidation [8], ozonization [9], photocatalytic degradation [10], ultrafiltration [11] and adsorption [12]. Adsorption method is proved to be most popular and effective technique for the treatment of pollutant removal process [13]. A number of materials have been used as adsorbents to combat the menace of dye pollution. Adsorption using polyaniline (PANI) is one of the most extensively used technique because of excellent adsorption efficiency for degrading the sulfonated azo dyes. Composite materials of PANI with that of organic or inorganic materials have attracted the researchers as a potential class of materials for a wide range of applications [14-18]. In this study we used CuCl₂ doped PANI composite salt which has been

observed as a good adsorbent for removal of dye from waste water. Cu²⁺ enhances the photocatalytic activity [19]. Perusal of literature reveals that little exploration of adsorption study reported using this adsorbent [16-19].

EXPERIMENTAL

Preparation of adsorbent and adsorbate: All chemicals used were of analytical grade. Aniline and HCl were procured from Merck Specialities (P) Ltd., Mumbai. Ammonium persulphate was obtained from Loba Chemie Pvt. Ltd., Mumbai. Copper(II) chloride was obtained from E. Merck (India) Ltd., Mumbai. Orange-G and Alizarin Red S dyes were used in the adsorption studies obtained from Qualigens and Loba Chemie Pvt.Ltd., Mumbai. Dyes were used without further purification. Metal salt doped with PANI prepared according to the method reported in the literature [20]. Stock solution of dye (Orange-G as well as Alizarin Red S) was prepared by dissolving 0.5 g of dye in distilled water making it up to 500 mL in a standard flask. Working concentrations in the range of 30-70 mg/L for Orange-G and 20-100 mg/L for Alizarin Red S were prepared by serial dilution. Orange-G and Alizarin Red S dyes were standardized with the Beer-Lambert law by measuring the optical densities of the various concentrations of the dye solution at λ_{max} 480 and 520 nm, respectively using MAPADA-V-1100 D spectrophotometer.

Adsorption experiment: 100 mL of dye solution of required concentration was taken in a 250 mL beaker which contains

the required amount of PANI-CuCl₂ composite. Dye solution with the adsorbent were agitated at 250 rpm in RIS 24-BL orbital shaker and exposed to 6 ampere UV lamps simultaneously. At appropriate time interval 10 mL of aliquot was withdrawn, centrifuged and filtered. The filtrate was collected separately in a clear dry test tube and then the optical density of the clear supernatant dye solution was measured till the equilibrium was attained. Blank experiment carried out for each dye without adsorbent.

RESULTS AND DISCUSSION

Characterization of adsorbent and adsorbate: FTIR technique was used to examine the surface groups of adsorbent. Infrared spectra of the adsorbent and dye-loaded adsorbent samples, before and after the adsorption process, were recorded in the range 4000–400 cm⁻¹. FTIR spectra of PANI samples doped with CuCl₂ and dye loaded PANI composite are shown in Fig. 1a (before adsorption), Fig. 1b (after adsorption of Orange-G) and Fig. 1c (after adsorption of Alizarin Red S). In 1a spectrum the band at 3434.70 cm⁻¹ is ascribed to N-H stretching vibration after adsorption which is shifted to lower frequency 3241.83 cm⁻¹ (Orange-G) and 3433.94 cm⁻¹ (Alizarin Red S). Two strong vibration peaks at 1568.82 cm⁻¹ and 1417 cm⁻¹ represent the stretching frequencies of quinoid and benzenoid rings of polyaniline, respectively which is shifted to 1571.54 cm⁻¹ and 1423.35 cm⁻¹, 1565.20 cm⁻¹ and 1415 cm⁻¹ after adsorption of Orange-G and Alizarin Red S. The observed peak at 1302.82 cm⁻¹ is related to C-N stretching frequency after interaction with Orange-G and Alizarin Red S is slightly shifted to lower frequency 1299.81 cm⁻¹ and 1301.81 cm⁻¹. The strong wide peak at 1137 cm⁻¹ corresponds to in-plane bending of the C-H band disappeared after dye adsorption. New bands observed at 1012.67 cm⁻¹ in Orange-G and 1020.89 cm⁻¹ in Alizarin Red S may be due to interaction of sulphonic acid group of the dyes with adsorbent material [21]. These results demonstrate physical forces are participated in the adsorption.

SEM analysis: Scanning electron microscopy is widely used to study the morphological features and surface characteristics of adsorbent materials. The PANI-CuCl₂ composite is analyzed by SEM before (Fig. 2a) and after adsorption of Orange-G and Alizarin Red S (Fig. 2b and 2c). The PANI-CuCl₂ has heterogeneous surface, micro-pores and meso-pores as seen from its surface micrographs. In this case the sponge like structure with some bright spots confirms the presence of

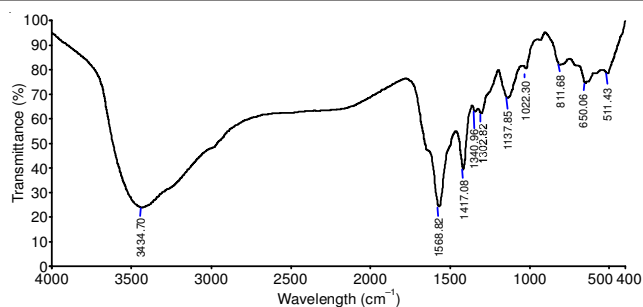


Fig. 1a. Before adsorption

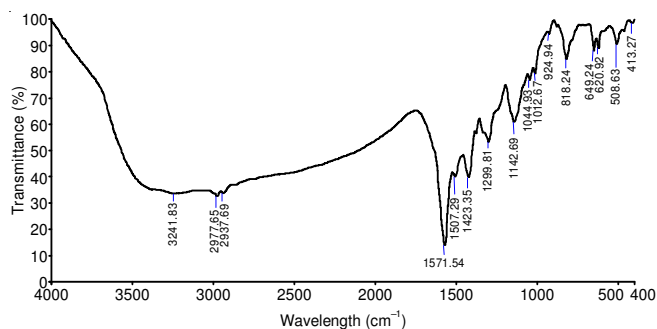


Fig. 1b. After adsorption of Orange-G

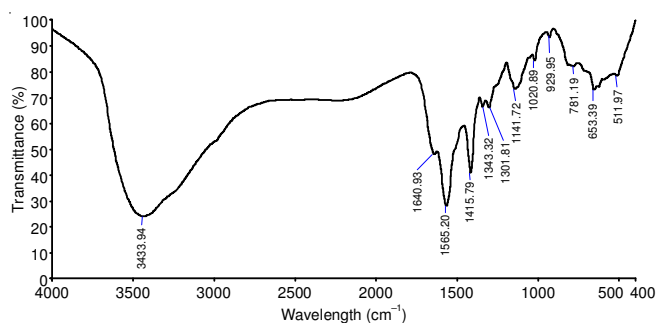
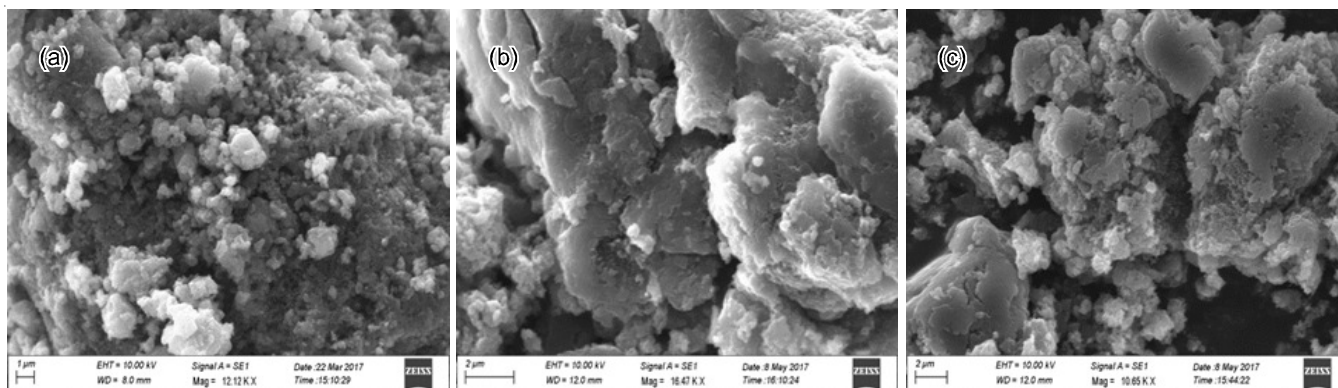


Fig. 1c. after adsorption of Alizarin Red S

polymer. The flake structure after adsorption may be the Orange-G and Alizarin Red S coverage on PANI-CuCl₂ composites.

Effect of contact time: The adsorption data for the uptake of effluent *versus* contact time on 50 and 60 mg/L of Orange-G and Alizarin Red S were carried out. The equilibrium time required for the adsorption of dye is as shown in Fig. 3. At the beginning adsorption rate is faster as the dye ions are adsorbed by the exterior surface of the PANI-CuCl₂ composite. When the adsorption of the exterior surfaces reaches saturation, the ions exerted onto the pores of the adsorbent and are adsorbed

Fig. 2. SEM images of PANI-CuCl₂ composite before (a) and after adsorption of Orange-G (b) and Alizarin Red S (c)

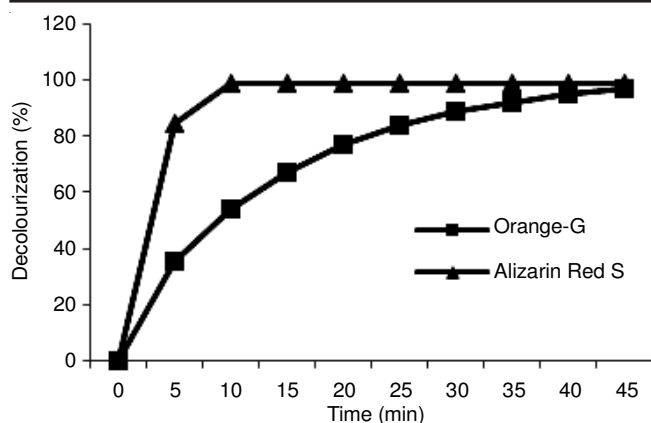


Fig. 3. Effect of contact time of Orange-G and Alizarin Red S on % removal. Adsorbent dose 0.3 g/L, pH for Orange-G is 3.35 and pH for Alizarin Red S is 4.73

by the interior surface of particle and this process takes relatively long contact time.

Effect of adsorbent dosage: The adsorption experiments have been performed to ascertain the effect of variation of amount of adsorbent on the uptake of the dye. Fig. 4 shows the removal of dyes with time for different amount of adsorbent at constant initial concentration of 50 mg/L of Orange-G and 60 mg/L of Alizarin Red S respectively. It was observed that the adsorption of dye increases with increase in the amount of adsorbent initially and further increase in the composite dosage did not show much increase in the removal rate and adsorption equilibrium. The number of binding sites on the adsorbent surfaces increases with the amount of adsorbent materials and thus greater number of dye molecules can bind if the amount of adsorbent is increased. Initially a rapid removal of dyes was attributed to the availability of the reactive sites.

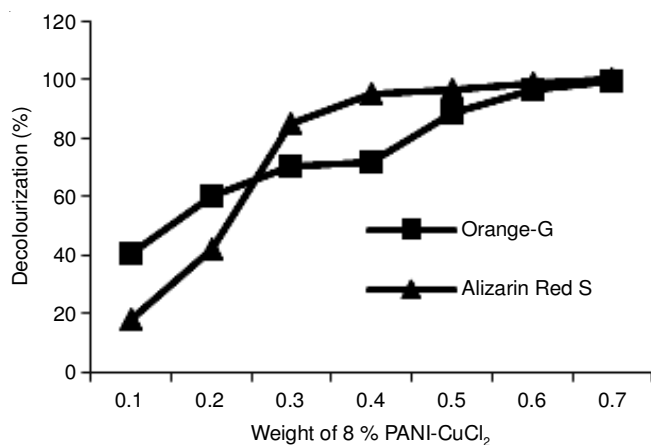


Fig. 4. Effect of adsorbent dosage

Effect of initial concentration of dye using 8 % PANI CuCl₂: To study the adsorption capacity, experiments were conducted with different initial concentrations of Orange-G and Alizarin Red S in the presence of 8 % PANI-CuCl₂ composite with constant weight (0.3 g/L). Table-1 shows the concentration profiles of Orange-G and Alizarin Red S (ranging from 30-70 mg/L and 20-100 mg/L respectively) at different time intervals. It was observed that the time required for equilibrium adsorption of dyes increase with increase in initial dye concentration

Orange-G			Alizarin Red S		
Initial dye conc. (mg/L)	Time (min)	Removal (%)	Initial dye conc. (mg/L)	Time (min)	Removal (%)
30	20	91.8	20	5	97.05
40	30	92.1	40	7	97.56
50	50	94.4	60	8	98.46
60	70	95.3	80	15	98.79
70	90	95.7	100	20	99.06

because the dye molecules needed to diffuse to the adsorbent sites by intra-particle diffusion.

Effect of temperature: The adsorption studied for dyes onto adsorbent at different temperatures is displayed in Fig. 5a and 5b. It was found that the adsorbed amount decreased with increase in temperature suggest the exothermic adsorption process observed in Orange-G (Fig. 5a) whereas adsorbed amount increased with increase in temperature indicate endothermic effect observed in Alizarin Red S (Fig. 5b). Generally, the adsorption of contaminants from aqueous solution is related with the system temperature, where both the adsorption rates as well as the sorption capacity affected.

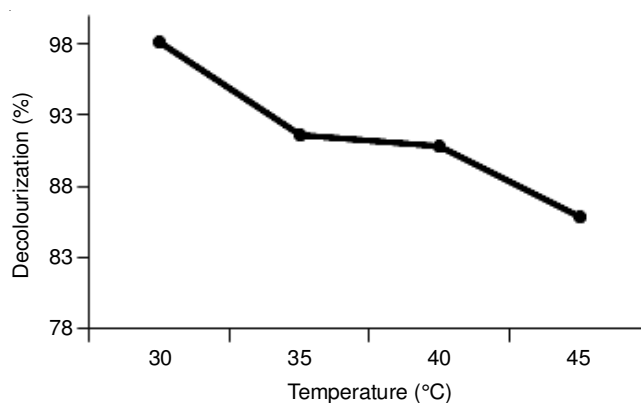


Fig. 5a. Effect of temperature on Orange-G dye

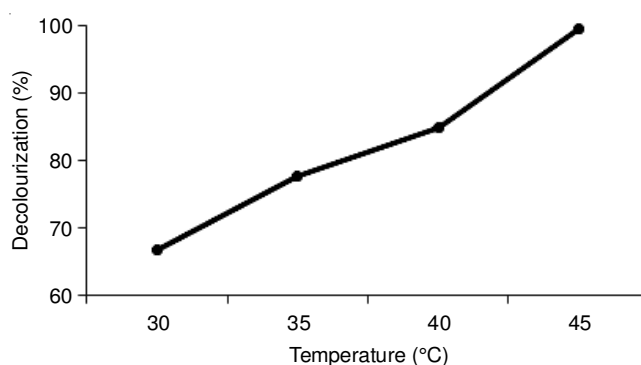


Fig. 5b. Effect of temperature on Alizarin Red S dye

Adsorption isotherms: It is necessary to carryout adsorption isotherm studies to apply the adsorption technique for practical purpose. A relationship can be established between the amount of adsorption (q_e) of the adsorbate per unit weight of the adsorbent (mg/g) and C_e , the equilibrium concentration of the adsorbate (mg/L). Langmuir [22] equation is commonly used for describing the adsorption isotherms (figures not shown). The linear equation of Langmuir is represented as follows:

$$C_e/Q_e = (C_e/Q_0) + (1/Q_0b) \quad (1)$$

Q_0 and b are the Langmuir constants, indicating the adsorption capacity and energy of adsorption respectively. Langmuir plot drawn between, C_e/q_e versus C_e .

Pseudo 2nd order: The adsorption mechanism over a complete range of the contact time is explained by the pseudo-second order kinetic model [23] which is represented by the following equation:

$$t/q_t = 1/k_2q_e^2 + t/q_e \quad (2)$$

where k_2 is rate constant for 2nd order adsorption ($\text{g mg}^{-1} \text{min}^{-1}$), while k_2 and q_e are determined from slope and intercept of plot t/q_t vs. t (figures not shown).

Intra-particle diffusion: Adsorption is a multilayer process, involving transport of solute particle from the aqueous phase to the surface of the solid adsorbent followed by diffusion into the interior of the pores. The possibility of intra-particle diffusion is tested by plotting a graph between the amount of dye adsorbed and time $t^{1/2}$ at different time intervals. Where k_p is intra-particle diffusion rate constant ($\text{mg g}^{-1} \text{min}^{0.5}$). The plot of q_t vs. $t^{1/2}$ is linear indicates occurrence of intra-particle diffusion (Figs. 6 and 7) and the negatively charged anionic group of dyes undergoes chemical interaction with positively charged backbone of PANI.

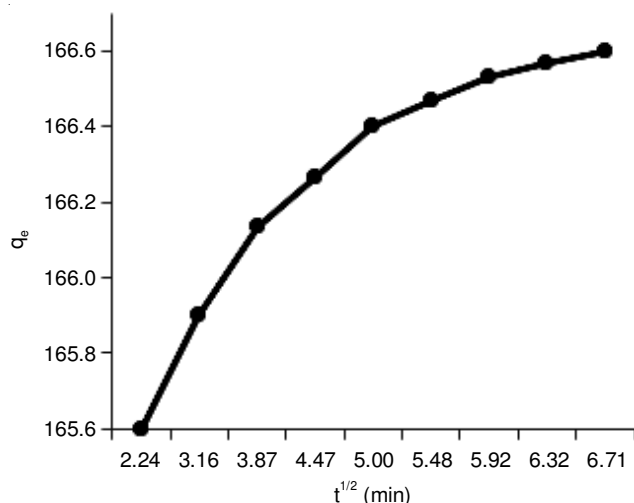


Fig. 6. Intraparticle diffusion curve for Orange-G

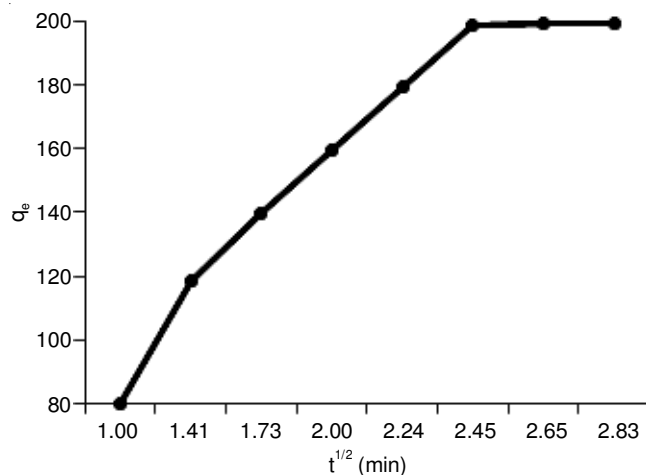


Fig. 7. Intraparticle diffusion curve for Alizarin Red S

Conclusion

It is concluded that CuCl_2 doped polyaniline composite is an efficient adsorbent for the removal of sulphonic acid dyes by UV lamp assisted batch process at acidic pH. Dyes under study show Alizarin Red S adsorbed at faster rate than Orange-G.

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