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Photocatalyzed Anionic Dye Adsorption from Synthetic Wastewater by Using Polyaniline-$CuCl_2$

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The adsorption efficiency of $CuCl_2$ doped polyaniline (PANI) as photocatalyst in bleaching of Eosin yellowish and Congo red have been investigated. The effect of different parameters like contact time, initial dye concentration, dosage of adsorbent, variation of % PANI-$CuCl_2$ composite and pH on the rate of photocatalytic bleaching of dyes has been reported.

Keywords: Eosin yellowish, Congo red, PANI-$CuCl_2$ composite, Adsorption efficiency.

INTRODUCTION

Dyes are extensively used in textile, plastic, paint and paper industries. Effluents from such industries are important sources of water pollution. The effluents discharged from dyeing industries are highly coloured with large amount of suspended organic solid, which affects aquatic life and human beings by mutagenic and carcinogenic effects [1,2]. Acid dyes are organic sulphonic acids and the commercially available forms are usually sodium salts, which exhibit excellent dyeing quality due to their water solubility. Normal methods of dye removal such as flocculation [3], precipitation, anaerobic process [4] and chemical oxidation [5] are generally expensive. The survey of literature reveals that among the physico-chemical treatment process for dye removal, adsorption is highly efficient, inexpensive and easy to adapt [6]. Among these technologies, semiconductor photocatalysis, as a "green" technology, has been widely applied in purifying air and eliminating the organic contamination of water and has become one of the most important applied facets of heterogeneous catalysis [7].

Several workers investigated the feasibility of using conducting polymers as adsorbent because of the low cost of synthesis and easy processability. There are few studies regarding the use of doped polyaniline for the removal of dyes in literature [8-12]. Polyaniline doped with acids has been utilized for removal of anionic dyes while PANI doped with copper chloride has been used for the removal of azo dyes reported by Bingol *et al.* [13]. Cu^{2+} enhances the photo catalytic activity [14,15] and it can be used for the selective removal of anionic dyes from the aqueous solution. The interaction between the negatively charged anion of the dye and the positively charged PANI backbone is responsible for the anionic dye adsorption by PANI emeraldine salt from aqueous dye solution [16-18]. Visible light or UV irradiation has been used for the removal of dyes from wastewater with PANI based nano composite [19-21]. The PANI-$CuCl_2$ composite shows selective adsorption of dyes and highly enhanced photo-degradation of dyes under UV and visible light irradiation. In present study, most frequently used equations applied in solid/liquid systems to describe adsorption isotherms are Langmuir and Freundlich models and the most popular isotherm theory is the Langmuir model which is commonly used for the adsorption of dyes. The main aim of this study is to use PANI-$CuCl_2$ composite adsorbent with photo degradation efficiency for the degradation of Eosin yellowish, Congo red under UV lamp irradiation.

EXPERIMENTAL

In the experimental studies, RIS 24-BL orbital shaking incubator (Remi) was used to stir the dye solution. R-8C laboratory centrifuge, REMI motors used to centrifuge the dye solution. MAPADA-V-1100D spectrophotometer model was used for determination of dye concentrations. Equip-Tronics digital pH meter model EQ-610 was used in pH measurements for adsorption experiments.

Aniline and HCl were obtained from Merck Specialities (P) Ltd., Mumbai. Ammonium persulphate was obtained from Loba Chemie Pvt. Ltd., Mumbai. $CuCl_2$ was obtained from E. Merck (India) Ltd., Mumbai. Eosin yellowish and Congo red dyes was used in the adsorption studies obtained from Loba Chemie Pvt. Ltd., Mumbai. Dyes were used without further purification.

Preparation of PANI-$CuCl_2$: Copper(II) chloride doped polyaniline was synthesized by chemical oxidation coupled with polymerization, where ammonium persulphate was used as an oxidant. Appropriate amount of ammonium persulphate dissolved in water was mixed with the solution of aniline dissolved in 1.5 M HCl and then $CuCl_2$ dissolved in water, where added into the solution mixture and stirred at 400 rpm for 5 h at room temperature. A colour change from golden yellow through blue to dark green was observed. After the polymerization, the solution was filtered, washed and dried leading to $CuCl_2$ doped PANI sample [16].

Preparation of stock dye solution: Stock solution of each dye (Eosin yellowish as well as Congo red) was prepared by dissolving 0.5 g of it in distilled water and making it up to 500 mL in a standard flask.

Standardization of dye solution: Eosin yellowish and Congo red dyes were standardized with the Beer-Lambert law by measuring the optical densities of the various concentrations of the dye solution at λ_{max} 517 and 498 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-$CuCl_2$ composite. Dye solution with the adsorbent were agitated at 250 rpm in RIS 24-BL orbital shaker and exposed to 6 ampere UV lamp 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.

Variation of contact time: Effect of contact time was studied by taking 100 mL of dye solution with appropriate concentrations in a 250 mL beaker containing 0.03 g of 8 % PANI-$CuCl_2$.

Effect of initial dye concentration: Effect of initial dye concentration was observed by varying concentrations of Eosin yellow (4-12 mg/L) and Congo red (25-45 mg/L) with 0.3 g/L of 8 % PANI-$CuCl_2$.

Effect of 8 % PANI-$CuCl_2$ dosage: To evaluate the percentage decolourization dependence on the dosage of adsorbent was studied by varying dosage of 8 % PANI-$CuCl_2$ from 0.1 to 0.7 g/L with suitable concentration of dye.

Effect of temperature: The effect of temperature was studied by carrying out the adsorption studies with the dye at four different temperatures from 30 to 45 °C.

Effect of pH: The effect of pH on decolourization was studied at pH 2 to 9.

Effect of % $CuCl_2$ in PANI-$CuCl_2$: The influence of percentage of $CuCl_2$ dopant in PANI-$CuCl_2$ composite was investigated by varying the percentage of $CuCl_2$ from 2 to 16 % on decolourization.

Desorption studies: The dye adsorbed 8 % PANI-$CuCl_2$ was mixed with 100 mL of aqueous acid or base (0.1, 0.025 N of HCl and 0.1, 0.025 N of NaOH) is subjected to agitation with exposure to UV light. The solution after appropriate time interval was centrifuged. The optical density of the centrifugate was measured.

RESULTS AND DISCUSSION

The adsorption studies of Eosin yellowish and Congo red have been investigated. The percentage of decolourization exhibited an increasing trend as the time of exposure to UV light increased and reached equilibrium (Fig. 1).

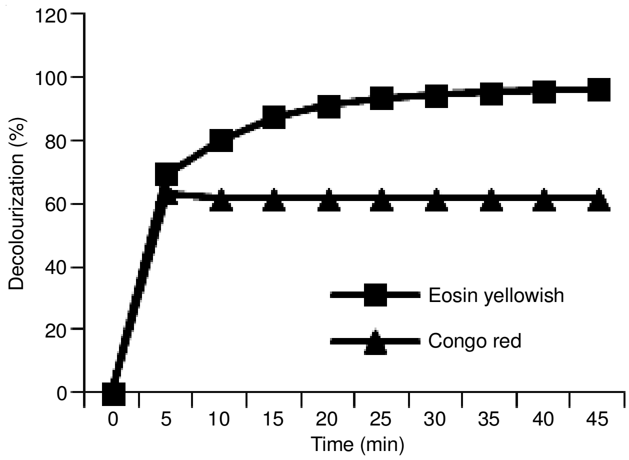

Fig. 1. Effect of contact time of Eosin yellowish and Congo red on % removal. Adsorbent dose 0.3 g/L, pH for Eosin yellowish is 3.17 and pH for Congo red is 4.93

Increase in dye concentration increases the time required to reach equilibrium and it was found that the percentage of removal was not varied considerably with change in initial dye concentration at constant adsorbent weight (0.3 g/L) (Table-1). The effect of variation of 8 % PANI-$CuCl_2$ composite (from 0.1 to 0.7 g/L) for each dye at 30 °C.

TABLE-1
EFFECT OF INITIAL DYE CONCENTRATION

Eosin yellowish			Congo red		
Initial dye conc. (mg/L)	Time (min)	Removal (%)	Initial dye conc. (mg/L)	Time (min)	Removal (%)
4	10	97.7	25	4	60.08
6	20	97.9	30	6	61.57
8	30	97.9	35	8	62.50
10	65	97.9	40	12	64.09
12	75	98.1	45	18	65.60

It was found that the percentage removal increased with increase in PANI-$CuCl_2$ dosage and reached a limiting value. Results of effect of dosage were quite logical on the basis of increase in absorption site (Fig. 2). The influence of temperature on the rate of decolourization is negligible. This result indicates that the reaction is a photocatalyzed reaction (Fig. 3).

The pH of the medium plays a vital role on adsorption of dyes. The percentage of decolourization is decreased with increase of pH. The initial pH may affect the charge on the surface of the adsorbent, altering its capacity to adsorb dye molecule (Fig. 4).

The effect of percentage of $CuCl_2$ in PANI-$CuCl_2$ composite on the rate of decolourization was investigated by varying the percentage of $CuCl_2$ (from 2 to 16 %). The rate of decolourization increased considerably with increase of % of $CuCl_2$ from 2 to 8 (Fig. 5). The impact of percentage of $CuCl_2$ on adsorption capacity was negligible beyond 8 %. The rate of decolourization of dyes by 8 % PANI-$CuCl_2$ was found to be higher than PANI-ES (emeraldine salt). Adsorption isotherm is usually the ratio between the quantity adsorbed and remaining in solution at fixed temperature. In the present study, the experimental data was fitted into Freundlich linearized equation and the plot of ln C_e *versus* ln q_e wasfound to be linear which

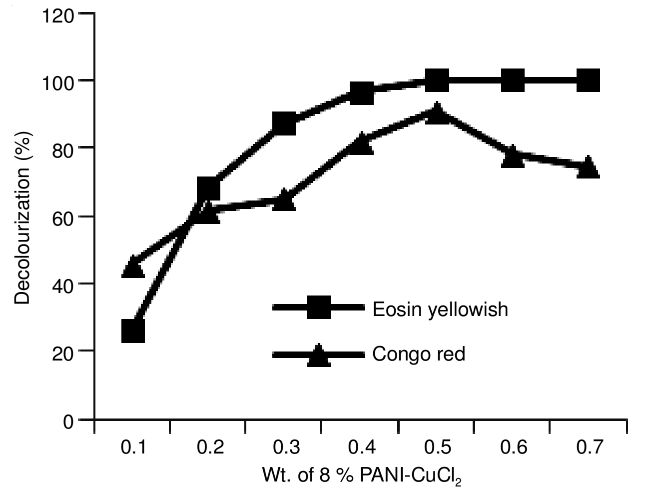

Fig. 2. Effect of adsorbent dosage adsorbent on Eosin yellowish, Congo red

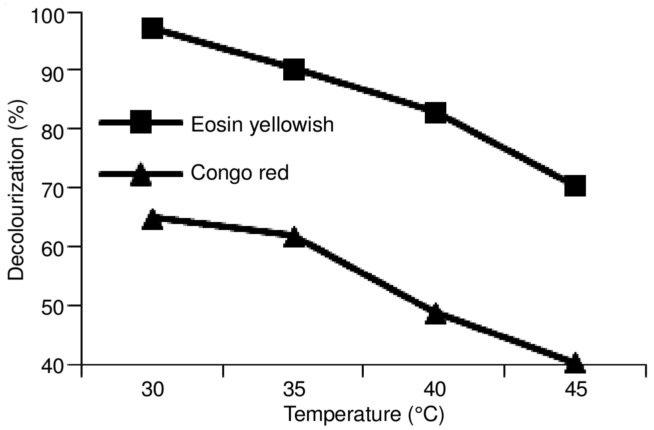

Fig. 3. Effect of temperature on Eosin yellowish and Congo red

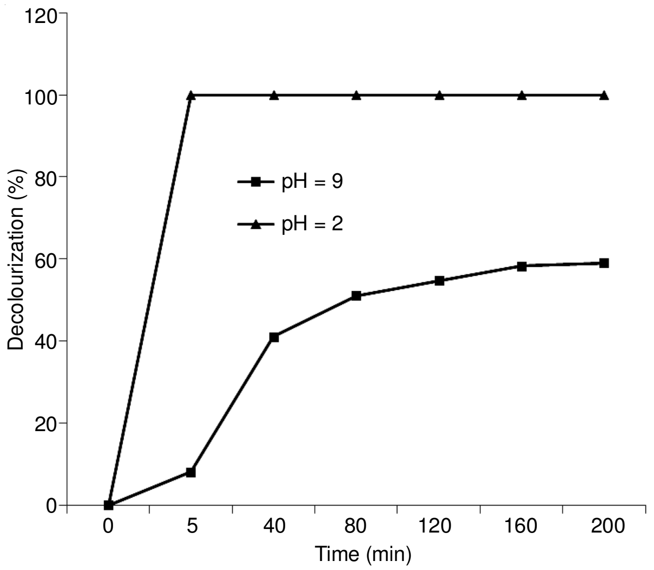

Fig. 4. Effect of pH on Eosin yellowish dye

indicates that the adsorption of above dyes over 8 % PANI-$CuCl_2$ follows Freundlich isotherm (figures not shown).

From Langmuir isotherm study, the adsorption of two dyes on PANI-$CuCl_2$ is a favourable process for the concentration range studied (figures not shown) from the calculated R_L value

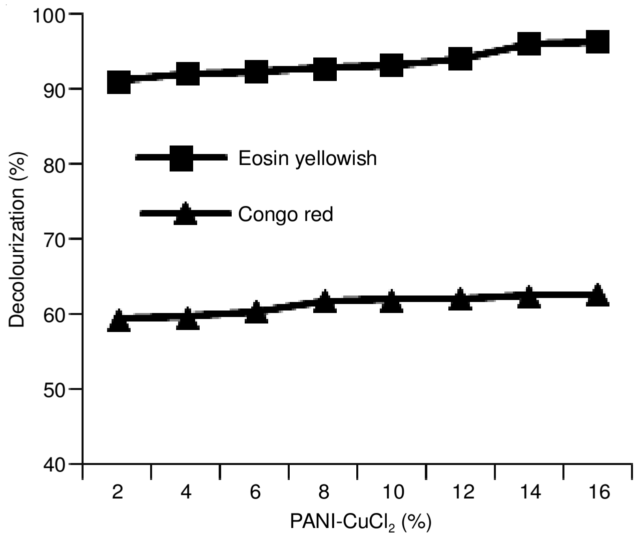

Fig. 5. Effect of %PANI-$CuCl_2$ on Eosin yellowish and Congo red

for Eosin Yellowish is 0.856 and for Congo Red is 0.915. The plots of t/q_t against t were linear, showed that the reaction kinetics follows pseudo-second order rate equation (figures not shown).

FTIR spectra of PANI-$CuCl_2$ composite before and after adsorption has been given in Fig. 6. The characteristic bands at 1568.82 cm^{-1} arises mainly from both C=N and C=C stretching for quinonoid form, while the band near 1417 cm^{-1} is attributed

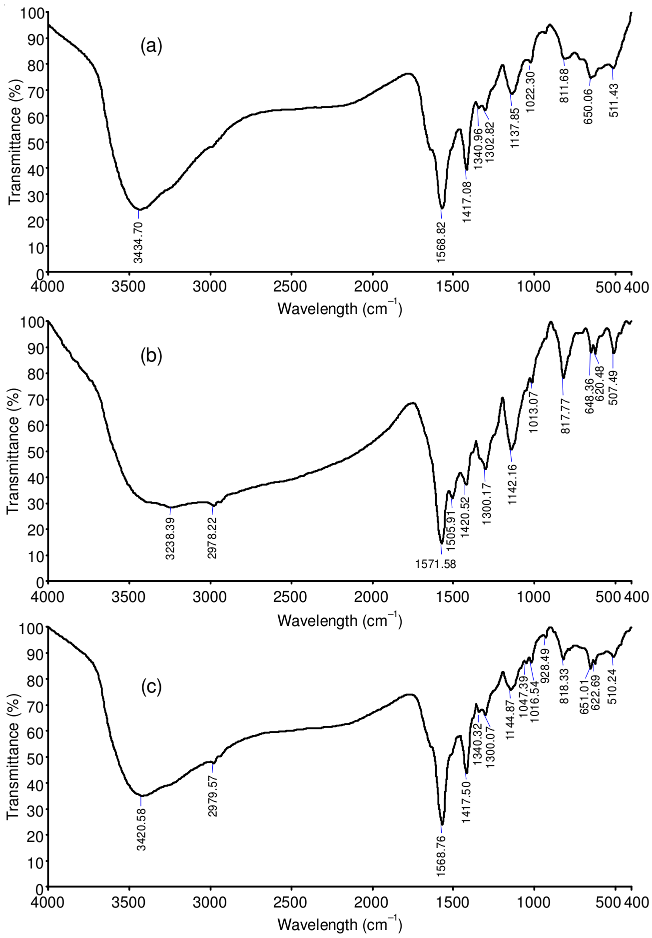

Fig. 6. FTIR spectra of PANI-$CuCl_2$ composite (a), after adsorption of Eosin yellowish (b) and Congo red (c)

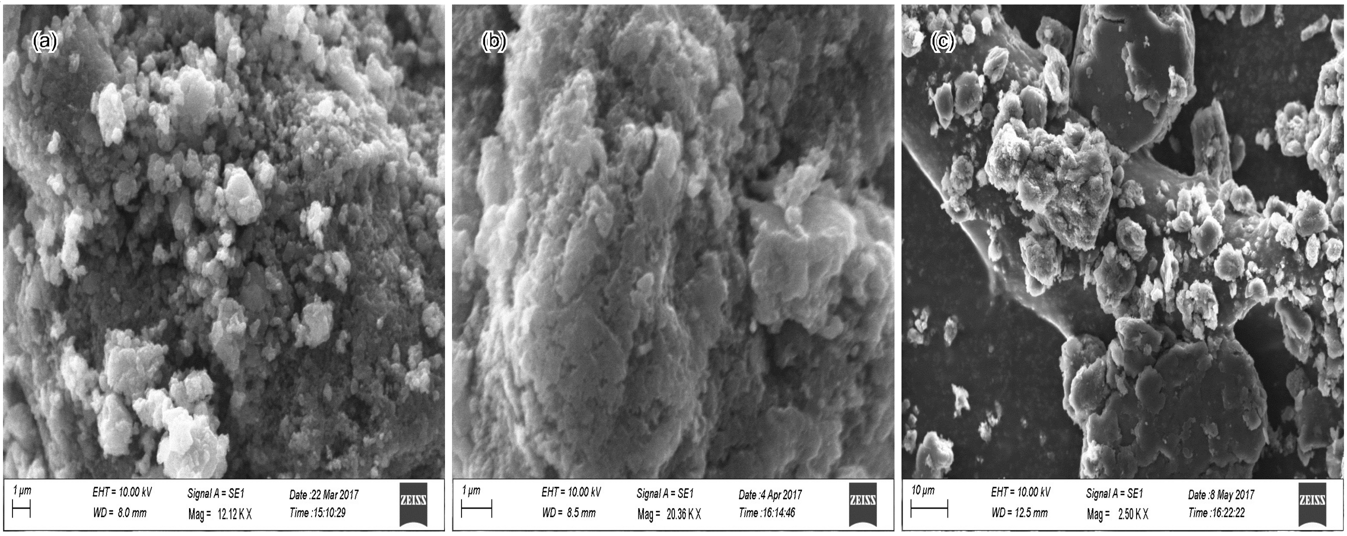

Fig. 7. SEM images of PANI-$CuCl_2$, before adsorption (a), after adsorption of Eosin yellowish (b) and Congo red (c)

to the C-C aromatic ring stretching of benzenoid unit. The peaks at 1302.82 and 811.68 cm^{-1} can be assigned to C-N stretching of the secondary aromatic amine and aromatic C-H out-of-plane bending vibration, respectively [22]. FTIR spectra of the composite after the adsorption of Eosin yellowish and Congo red has showed no significant changes observed indicating that the removal of these two dyes occurred *via* physisorption.

The scanning electron microscopy image of PANI-$CuCl_2$ is shown in the Fig. 7a. It can be seen that the surface is irregular and porous, which provides a good platform for adsorption of dyes. The flake and solid deposited structure after adsorption of Eosin yellow (Fig. 7b) and Congo red (Fig. 7c) support the adsorption of dye on composite.

Conclusion

In this article, the adsorption of Eosin yellow and Congo red on PANI-$CuCl_2$ composite with respect to contact time, dosage of adsorbent, effect of initial dye concentration, pH and temperature is discussed. Equilibrium adsorption of Eosin yellow is found to be in greater percentage than Congo red.

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