SORPTION STUDIES FOR COLOUR REMOVAL OF SPENT ORANGE DYE EFFLUENT USING POWDERED ACTIVATED CARBON

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ABSTRACT

Textile effluents pose considerable impact on soil and water due to indiscriminate discharge of partially/untreated effluent. Development of effective treatment technology for colour removal is difficult, since dyes are continually being upgraded to suit market demands. This investigation aims at feasibility of sorption for colour removal of spent orange dye effluent using powdered activated carbon (PAC). Experimental results show that the colour removal efficiency is maximum (93%) at pH 2 for a dose of 1.5 g/L of PAC.

INTRODUCTION

Dyeing of cotton yarn uses large volumes of water in scouring, bleaching, dyeing and finishing operations. On an average about 150 to 200 litres of wastewater is generated per kg of yarn dyed. The effluent contains high organic and inorganic solids. Most of the inorganic solids are highly dissolved and are in the ionic state, whereas organic solids are both soluble and in the colloidal form. Dissolved organic matter is contributed by detergents, soaping substances and other wetting agents used as auxiliary chemicals in the dyeing process. Reactive dyes are coloured compounds that contain liable functional groups capable of forming covalent bond with active sites of hydroxyl ions in cotton yarn or fibre. This bond formation between the functional group and the yarn results in high wet fastness properties. These dye stuffs are generally employed to yarn along with auxiliary chemicals under normal conditions.

Indiscriminate discharge of effluents from dyeing units into the environment possesses potential damage to natural water and land environment. Impact of colour restriction of photosynthesis and reaeration process are the pertinent problems associated with the receiving water bodies (Mittal and Gupta 1994). Discharge of textile dye effluents on land, causes physical and engineering properties of soils to be considerably changed (Mallikarjuna Rao & Chinnappa Reddy 1996). As such dyeing wastes need to be treated before discharge into the environment.

Adsorption onto activated carbon is a well recognized technology in water and waste water purification. The efficiency of carbon adsorption has been well documented in treating a broad spectrum of pollutants including organic, inorganic and gaseous pollutants. Adsorption process is a sludge free operation and produces high quality treated effluents. The treatment yields effluent suitable for recycling, and dyes could be recovered from adsorbent regeneration effluent (Thakur et al. 1997). Activated carbon prepared from various materials like coal, charcoal, wood charcoal or coke, etc. has been used as sorbent and found to be highly efficient. Activated carbon has demonstrated its potential in removing colour from textile dye effluents (McKay and Allen 1980, Gupta et al. 1986, Ramprasad 1983, Barton 1987, Lin 1993, Venkata Mohan & Karthikeyan 1995, Thakur et al. 1997, Kumar & Ravi 1998). They also reported that colour uptake decreases with an increase in size of the adsorbent.

The adsorptive capacity of porous adsorbents is generally proportional to the specific surface area. That is, the adsorption increases with the increase of the surface area. In fact, that most consistent thing about dyeing effluents is the fact that they will consistently change. Moreover, a dye responding to the particular treatment may not be effectively treated by other methods. Adsorption using activated carbon and locally available low cost adsorbents such as saw dust, fly ash and clay minerals etc., have been extensively used for the removal of colour from industrial dye waste water (Patnaik et al. 1995, Deo & Ali 1996). In the present investigation an attempt has been made to treat the spent orange dye effluent by sorption using powdered activated carbon (PAC). Standard batch adsorption experiments were conducted using the established procedures. Yarn dye effluent was used in the experimental work.

MATERIALS AND METHODS

Glassware: All the glassware used in the present investigation was of "Corning". After sorption experiments, all the glassware used were soaked overnight in chromic acid bath and rinsed thoroughly with tap water followed by distilled water before next use.

Water: Water used in all the batch sorption experiments was distilled water. The colour and turbidity of distilled water was nil with pH, 6.5 to 7.5.

Dyes: Reactive dyes used to make spent orange dye effluent in this study were acquired directly from the manufacturers. The details of the selected dyes and their other related properties are given in Table. 1.

Sorbent: Powdered activated carbon was used in the present study. Typical analysis of activated carbon as quoted by the manufacturer (Lakshmi Carbon Pvt. Ltd., Nizamabad) is presented in Table 2.

Effluent (Simulated Dye Bath): The effluents used in present investigation were prepared in the laboratory, which are similar to the effluents of local textile industries. Details of preparation of 1 litre simulated dye bath are presented in the Table 3.

Spent Orange dye effluent, pH = 10.5 and $\lambda_{max} =$ 545 nm

Colour Measurement: Concentration of dye colour was determined calorimetrically using C-160-MKII spectrophotometer (Photoelectric Instruments Pvt. Ltd., Jodhpur), consisting of a single beam grating with a wavelength ranging from 340 to 950 nm. First, optimum wavelength (the wavelength that is absorbed to a greater extant) was determined by scanning (measuring %T/OD) at every 10 nm intervals) and then at every 5 nm interval within the short range of ± 25 nm and a calibration curve was prepared with a known concentration of dye solution (%T/OD) verses dye concentration by measuring percentage of T/OD at optimum wave length (λ_{max}). Colour concentration wave is then determined by measuring %T/OD at optimum wavelength and readily for colour (dye) concentration from the calibration curve.

Agitated non-flow batch sorption studies: Agitated non-flow batch sorption studies were conducted at room temperature (29 ± 2°C) by bottle point method. For equilibrium time studies, 100 mL of 50 mg/L concentration of sorbate solution was transferred into a 250 mL capacity of stoppered glass bottle. Sorbent was weighed accurately and then added to five bottles. 1.5 g/L of sorbent was added to 100 mL spent orange dye effluent. This quantity of sorbent was arrived by number of trials. The bottles, sealed with glass stoppers, were placed in horizontal oscillating shaker and with 100 rpm

Table. 1 Characteristics of dyes chosen for present investigation.

Sl.No	Commercial Name	C.I. Generic Name	Application Class	Chemical Class	Colour
1	Procin Brilliant Yellow M4G	C.I. Reactive Yellow 22	Reactive	Monoazo	Yellow
2	Procion Red Brown H4R	C.I. Reactive Brown 9	Reactive	Monoazo	Brown
3	Procion Brilliant BlueMR	C.I. Reactive Blue 4	Reacitve	Anthraquinone	Blue

Table 2: Typical analysis of activated carbon.

S.No	Parameter	Powdered Activated Carbon
1	Surface Area, m^2/g	950
2	Pore (micropore), cm^3/g	0.48
3	Volume (mesopore), cm^3/g	0.09
4	Distribution (macropore), cm^3/g	0.04
5	Density, g/cm^3	1.002

Table 3: Typical composition of spent orange dye effluent from a local textile industry (Srimurali 2001).

S.No	Description of the Item	Quantity Present in g/L of Dye bath
1	Procion Brilliant Yellow M4G	0.033
2	Procion Red Brown H4R	0.012
3	Procion Brilliant Blue MR	0.042
4	Caustic Soda (NaOH)	0.300
5	Hydrogen peroxide (H_2O_2)	0.100
6	Soda ash (Na_2CO_3)	2.900
7	Salt (NaCl)	16.000
8	Hydrochloric acid (HCl)	0.400
9	Lisspol paste	0.800

Table 4: Linearised, Langmuir adsorption isotherm constants.

Name of Dye	Langmuir Constants		
	Q^0 (mg/g)	b (L/mg)	R_L
Spent Orange Dye	22.77	1.4707	0.0134

and shaken for varying intervals of time (5, 10, 20, 30, 60, 90, 120 minutes). At the end of desired time intervals bottles were removed from the shaker and filtered through 41 Whatman filter paper with pore size 0.45μm and analysed for residual colour concentration. Sorption kinetics studies were conducted to determine the equilibrium time required for dye solution.

For the sorption intensity and sorption capacity studies, 100 mL of 50 mg/L concentration of sorbate solution were transferred into a 250 mL capacity of glass bottles and accurately weighed amount of sorbent was added to five glass bottles. Different weights of sorbents (0.5 g/L, 0.7 g/L, 0.9 g/L, 1.2 g/L, and 1.5 g/L) were considered. The stoppered glass bottles were placed in horizontal oscillating shaker and shaken for equilibrium time i.e., 90 minutes. This period of time is more than

adequate to ensure equilibrium between sorbent and solute for the studied concentration of dye. After equilibrium period, samples are withdrawn and filtered through 41 Whatman filter paper and analysed for residual colour concentration. Batch isothermal studies were conducted to find out the sorption intensity and sorption capacity by varying the doses of sorbents, the concentration of dye remaining constant.

RESULTS AND DISCUSSION

Effect of initial concentration and contact time: The effect of initial concentration and contact time on removal of spent orange dye is shown in Fig. 1. Rapid uptake of dye was observed during the initial stage of contact time and maximum removal was observed within 30 minutes and equilibrium time was around 90 minutes.

Sorption equilibrium studies: Adsorption process of any given system proceeds until the concentration of the solute remaining in solution is in the state of dynamic equilibrium with the concentration of the solute sorbed onto the adsorbent surface. At the equilibrium condition, there exists a well defined distribution of the sorbate between aqueous and solid phases and this distribution ratio at any contact time during the process is a measure of the equilibrium position already reached. Several mathematical relationships have been developed to describe the equilibrium distribution of solute between the solid and liquid phases. These relationships, called adsorption isotherms, are functional expression for the variation of adsorption with the concentration of the adsorbate in the bulk solution at a constant temperature. Several types of isothermal sorption models were proposed and the most commonly used relationships are between the amount sorbed at equilibrium and the concentration of sorbate remaining in solution after equilibrium has reached.

Langmuir (1918) developed a quantitative modal that has been widely applied to describe experimental adsorption data. The langmuir isotherm is based on the assumption that maximum adsorption corresponds to a saturated monolayer of solute molecule on the adsorbent surface, that the energy of adsorption is constant, and that there is no transmigration of adsorption, sites have equal affinity for the sorbate molecules and that the presence of sorbed molecules at one site will not affect the sorption of molecules at any other adjacent site. The Langmuir equation was originally derived from kinetic consideration and later, it was derived on the basis of statistical mechanics, thermodynamics, the law of mass action, theory of absolute reaction rates and the Maxwell-Boltzman distribution law. Langmuir adsorption model, called idealized localized monolayer modal, predicated that under equilibrium condition and constant temperature, the sorption should obey function of the form:

$$\frac{X}{m} = \frac{Q^\circ b C_e}{1 + b C_e} \qquad \qquad ... (1)$$

Where 'X' is the amount of material adsorbed (mg), 'm' is weight of adsorbent (mg), 'C_e' is concentration of the solute remaining in the solution (mg/L), 'Q°' is the maximum surface coverage (formation of monolayer) of sorbent (mg/g) and 'b' is the adsorption energy constant of Langmuir isotherm (L/mg).

Equation 1 can be rearranged into a linear form as:

$$\frac{1}{(X/m)} = \frac{1}{Q^\circ} + \frac{1}{b C_e} \qquad \qquad ... (2)$$

A plot between $1/(X/m)$ and $1/C_e$ yields a straight line having a slope of $(mC_e)/X$ and an intercept

of $1/(X/m)$. The monolayer capacity ($Q°$), determined from the plot, defines the total capacity of the adsorbent for a specific adsorbate. Agitated non-flow batch isothermal equilibrium sorption studies were conducted for spent orange dye by varying the mass of the sorbent and keeping the sorbate concentration constant. Batch isothermal equilibrium sorption data were further processed employing the modified Langmuir adsorption isotherm model (Equation 2).

The plot between (m/X) and $1/C_e$ for spent orange dye is given in Fig. 2. It may be observed that the plot is linear and this suggests the homogeneous nature of the sorbent surface and depicts the formation of monolayer coverage of sorbate (dye) molecule over the sorbent surface.

For a Langmuir type sorption process, the shape of the isotherm indicates the nature of sorption as favorable or unfavorable and may be classified by a term separation factor (R_L), a dimensionless constant (Hall et al. 1966) given as:

$$RL = \frac{1}{1 + bC_o}$$

The separation factor (R_L) indicates the isotherm shape as:

$R_L < 1$ Unfavorable

$R_L > 1$ Unfavorable

$R_L = 1$ Linear

$0 < R_L < 1$ Favourable

$R_L = 0$ Irreversible

The values of R_L have been computed for spent orange dye effluent and are presented in a Table 4. The values of spent orange dye effluent indicate that the PAC dye sorption interaction is a favourable type of sorption since the value is in the range $0 < R_L < 1$. Similar observations were reported by Weber & Chakravorty (1974) and Ramprasad (1983). The present investigation indicates that the adsorption process is favourable and adsorbent has good potential.

Effect of solution pH on dye colour uptake: The pH of the solution may exert a profound influence on the sorptive uptake of dye colour. It would seem due to its influence on the surface of the sorbent and ionization/dissociation of the sorbent molecule. The dissociation of OH^- and H^+ ions, which have tendency to be adsorbed quite strongly on the adsorbate, may further influence the sorption reaction. The distribution of OH^- and H^+ ions on the surface of the adsorbent imparts ion exchange property to the sorbent and the sorbate ions present in the solution displace OH^- and H^+ ions held at the surface in order to achieve a state of equilibrium. The ionization of the sorbate in aqueous medium also affects the extant and nature of the sorption uptake. Distribution of residual forces onto surface of the sorbent exerts both electronegative and electropositive ions as well as uncharged ions.

In order to investigate the effect of solution pH on the sorption of dye molecules by sorbent and to identify the range of pH where high uptake of colour takes place, agitated non-flow batch sorption experiments were conducted at different solution pH values ranging from 2 to 10.5. The influence of solution pH on sorption of spent orange dye effluent onto PAC is shown in Fig. 3. It may be observed from Fig. 3 that spent orange dye exhibited high uptake at a lower solution pH range of 2 to 5. However, PAC showed 93% uptake of spent orange dye at pH 2, which is characteristic of anion sorption. This suggests that the dye in aqueous phase dissociates in the lower pH range. At low pH ranges there is a possibility of oxidation of the surface oxygen complexes present on the surface
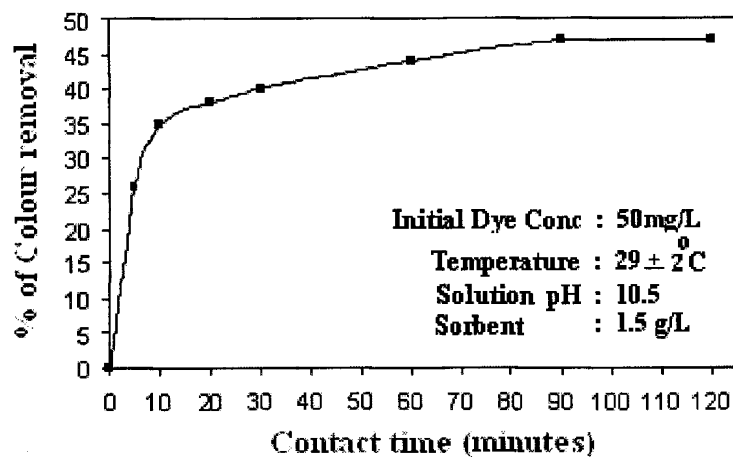
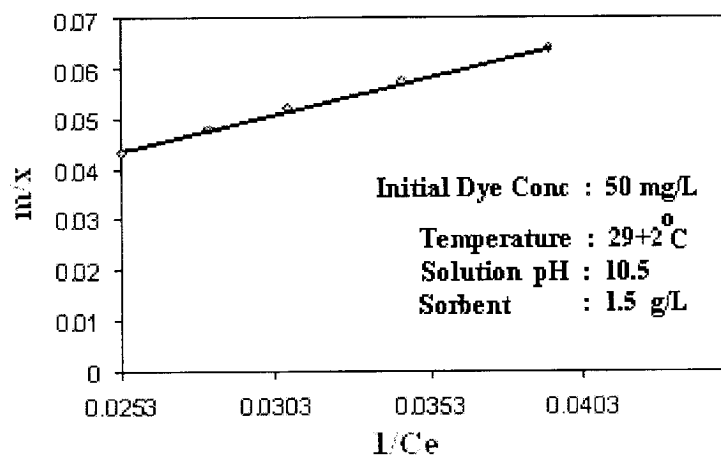Fig. 1: Effect of contact time on removal of spent orange dye.

Fig. 2: Langmuir sorption isotherm for spent orange dye waste.
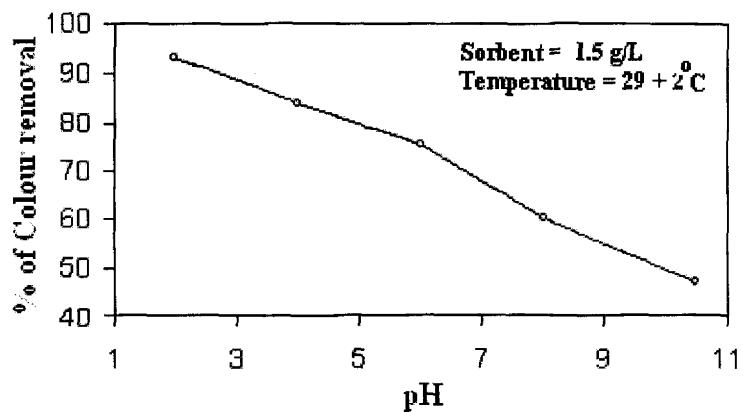
Fig. 3: Influence of pH on sorptive uptake of dye colour .

which may impart positive charge to the PAC surface. The dissociated (cation) dye molecule, which is negatively charged, will presumably be attracted towards the PAC surface and this may result in high sorption uptake. Inhibition of dye sorption onto PAC surface at higher solution pH ranges may be attributed to the increase of hydroxyl ion and formation of aqua complexes and the surface attaining negative charge, and the competition between OH⁻ ions and colour anions. These observations agree well with the observations of Ramprasad (1983) and Venkata Mohan (1997).

CONCLUSIONS

The experimental results show that powdered activated carbon is more suitable adsorbent for removal of spent orange dye colour. Removal of 93 percent of colour is possible if the adsorbent dose is 1.5g/L at solution pH 2. The initial sorption rates are rapid. About 81 percent of total adsorption takes place within 20 minutes of contact time and reaches equilibrium in 90 minutes. The equilibrium adsorption of the present study followed Langmuir adsorption equations.

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