Decolourization of C.I. Direct blue 78 aqueous solution in presence of exfoliated graphite under ultrasound irradiation

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This paper reports an efficient and convenient removal of C.I. Direct blue 78 dye from aqueous solution by the combination of ultrasound and exfoliated graphite. The effects of various factors such as pH, temperature, dosage of exfoliated graphite and initial concentration of dye were studied. The results show that ultrasound irradiation significantly improves removal of C.I. Direct blue 78 from aqueous solution in presence of exfoliated graphite. A removal of 98% was achieved within 20 min using 1.0 g/L exfoliated graphite at pH 1 and 25°C for 50 mg/L Direct blue 78 aqueous solution. Direct blue 78, solution was discoloured nearly 100% at 45°C. The maximum adsorption capacity of exfoliated graphite towards the dye was found to be 152.9 mg/g. Langmuir isotherm equation fits better than Freundlich isotherm equation for describing the isotherm data for the present system. The adsorption of Direct blue 78 over exfoliated graphite follows first-order kinetics.

Keywords: Adsorption, Decolourization, C.I. Direct blue 78, Ultrasound, Exfoliated graphite

Adsorption as an efficient method has been reported for the removal of colours and organic compounds from industrial process or waste effluents[1] due to its easy methodology and operations[2]. Different adsorbents have been used for the removal of various pollutants from aqueous solutions[3]. In recent years, there has been some significant contribution in this field. Some researchers revealed that hen feathers can absorb dyes efficiently[4]. Some waste materials such as de-oiled soya and bottom ash have proved to be potential adsorbents for the removal of dyes from aqueous solutions[5].

Exfoliated graphite is an excellent inorganic material extensively used in chemical, mechanical, and atomic energy fields because of its excellent properties. Due to its large pores structure, exfoliated graphite has been tried as an absorbent with a high sorption capacity especially for macromolecular organic materials. It has many characteristics including low density, no pollution of the environment and easy disopal[6]. Toyoda and Inagaki[7] reported that exfoliated graphite is very effective in providing protection from heavy oil pollution, and the heavy oil sorption capacity of the exfoliated graphite reached more than 80 g per gram of exfoliated graphite. The possibility of simultaneous removal of oil and dyes dispersed in wastewater by exfoliated graphite has also been explored[8].

The recent increase in the applications of ultrasound for environmental remediation has attracted many researchers to investigate the effects of ultrasound on sorption and desorption processes[9]. The effect of ultrasonic irradiation on removal of organic contaminants from aqueous solutions can be explained physically or chemically. Physically, the ultrasonic waves can clean surface of solid absorbent particles, reduce the particle size and increase mass transfer. Chemically, when ultrasonic waves are irradiated into aqueous solution, cavitation occurs. The violent collapse of the cavitation bubbles generates localized "hot spots" with a transient high temperature and pressures which provides an unusual mechanism for generating high-energy chemistry[10], and cause reaction to take place rapidly.

Recently, the removal of some dyes such as direct scarlet 4BS[11], disperse blue 2BLN[12], acid black 210[13] and acid brown 348[14] from their aqueous solutions, has been carried out using exfoliated graphite under ultrasound irradiation. Direct blue 78 is a highly water soluble trisazo dye. It is widely used in dyeing

textile cotton, viscose fiber, nylon, wool, paper and leather. Though the dye is resistant to direct aerobic bacterial degradation but it can form potentially carcinogenic aromatic amines in anaerobic conditions[15]. Herein, the removal of Direct blue 78 from aqueous solution by the combination of ultrasound irradiation and exfoliated graphite has been reported.

Experiment Procedure

Materials

C. I. Direct blue 78 (Tetrasodium 2-[[4-[[4-[[1-hydroxy-6-(phenylamino) -3-sulfo-2-naphthalenyl] azo]-1-naphthalenyl]azo]-6-sulfo-1-naphthalenyl]azo] -1,4-benzenedisulfonic acid; $C_{42}H_{25}N_7Na_4O_{13}S_4$; mol. wt. 1055.9; C. I. No.: 34200) (Fig. 1) was supplied by Hebei Dingzhou Arpino LCD Material Co. Ltd. and used without any further purification. An aqueous solution of the dye was prepared by dissolving calculated amount of dye in distilled water. The exfoliated graphite was prepared according to the method reported elsewhere[11,16] with exfoliation volume of 300 mL/g (20-40 mesh, bulk density: 3.33×10^{-3} g/cm^3). All the other reagents were of A. R. grade.

Apparatus and analysis

Ultrasonic irradiation was accomplished using a BUG 25-06 ultrasonic cleaner (Shanghai Branson), with a frequency of 25 kHz, and a nominal power of 250 W. The total acoustic power injected into the sample solution was found to be 0.63 W by calorimetry[17]. A TU-1901 double beam UV-Vis spectrophotometer (Beijing Purkinje General Instrument Co., Ltd.) was used to determine the dye concentrations. A pH meter (PHS-3C, Shanghai Hongyi Instrument Equipment Co., Ltd.) was employed for measuring pH values in the aqueous solutions. The colour removal ratio was calculated as follows: removal ratio = $(1-C_t/C_0) \times 100\%$, where C_0 is the initial dye concentration, C_t is the dye concentration after time t of ultrasound or combined ultrasound/sorbent treatment.

Procedure

A 100 mL glass vessel was filled with 50 mL of aqueous solution of Direct blue 78, the initial pH of the solution was adjusted to the required value by adding either NaOH or HCl and then the ultrasound irradiation started. The sorbent was added to the solution with starting the ultrasound irradiation simultaneously. In order to compare the decolourization efficiency with and without ultrasound, a thermostat stirring was employed to agitate the Direct blue 78 solution containing sorbent. At selected intervals, samples were withdrawn, filtered, and analyzed. The dye concentration was measured using the UV-Vis spectrophotometer at 605 nm, which corresponds to the maximum absorbance of Direct blue 78 solution. The calibration curve was linear in the range studied.

Results and Discussion

Effect of different absorbents under ultrasound irradiation

Figure 2 shows removal of Direct blue 78 using ultrasound and different absorbent. When the initial concentration of dye was 50 mg/L, the dosage of adsorbent was 1.0 g/L, the removal ratio were 29.5, 55.2, 57.8 and 98.0% corresponding to diatomaceous, kaolinite, activated carbon and exfoliated graphite, respectively. The amount of dye adsorbed onto each of the absorbent was 14.7, 27.6, 28.9 and 49.0 mg/g, respectively. Among them the dye removal capacity of exfoliated graphite is the biggest. From these results, it can be inferred that the adsorption of the dye greatly depends on the pore size of adsorbent.
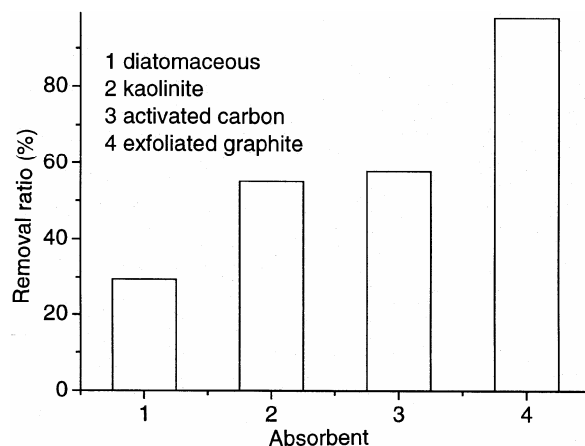

Fig.2— Effect of different absorbents on the removal of Direct blue 78. Initial concentration: 50 mg/L, Irradiation time: 20 min, temperature: 25°C, dosage of absorbent: 1.0 g/L, pH=1

Fig.1— Chemical structure of Direct blue 78

The adsorption of Direct blue 78 on diatomaceous, kaolinite and activated carbon is very low due to their microporous structures while exfoliated graphite is higher due to its macrospores structure, so exfoliated graphite was chosen as adsorbent for further experiments.

Effect of ultrasound irradiation

Figure 3 shows the removal of Direct blue 78 under ultrasound irradiation, exfoliated graphite and exfoliated graphite combining ultrasound. The removal ratio were 5.0, 36.4 and 65.1%, respectively. The results showed that the combined use of ultrasound irradiation and exfoliated graphite gives better removal of Direct blue 78 from aqueous solution.

The most pertinent effects of ultrasound on liquid-solid systems are mechanical and are attributed to symmetric and asymmetric cavitation. When cavitation occurs in a liquid near a solid surface, the dynamics of cavity collapse changes dramatically. Close to a solid boundary, cavity collapse is very asymmetric and generates high-speed jets of liquid, which leads to the formation of microjets of substrate dissolved in solvent that impinge on the exfoliated graphite surface resulting in the promotion of adsorption. The potential energy of the expanded bubble is converted into kinetic energy of a liquid jet that moves through the bubble's interior and penetrates the opposite bubble wall. These jets hit the surface with tremendous force. These phenomena increase the rate of mass transfer near the surface and interior site of exfoliated graphite, and induce the adsorption to occur rapidly[18].

Effect of contact time and temperature

The colour removal ratios of Direct blue 78 at different adsorption times and temperatures were investigated in the presence of ultrasound and exfoliated graphite. Figure 4 shows the time-dependent variations of the removal ratio of Direct blue 78 at different temperatures. It is observed that the colour removal in the presence of exfoliated graphite increased gradually with time and was almost contant after 20 min. The removal ratio was 65.1, 65.6 and 66.2% at 25, 35 and 45°C, respectively. This indicated that the sorbent performance may be slightly improved with increasing temperature and the adsorption is endothermic. It also implied that the adsorption process could be carried out at ambient temperature, which is preferred for industrial applications.

Effect of exfoliated graphite dosage

The colour removal at different exfoliated graphite dosages in the presence and absence of ultrasound are shown in Fig. 5. By the simultaneous

Fig. 4— Effect of temperature. Initial concentration: 50 mg/L, dosage of absorbent: 0.3 g/L, *p*H=1

Fig. 5— Effect of exfoliated graphite dosage. Initial concentration of dye: 50 mg/L, contact time: 20 min, temperature: 25°C, *p*H=1
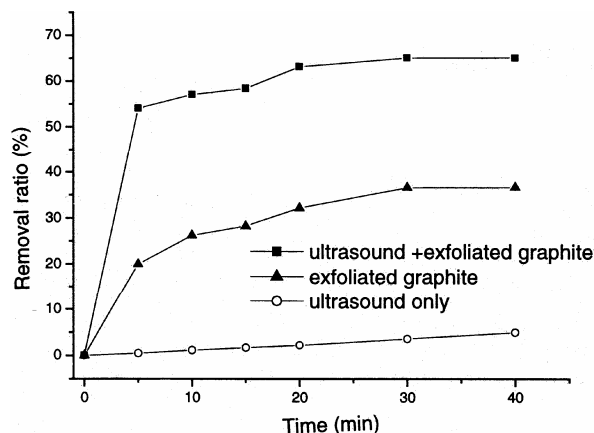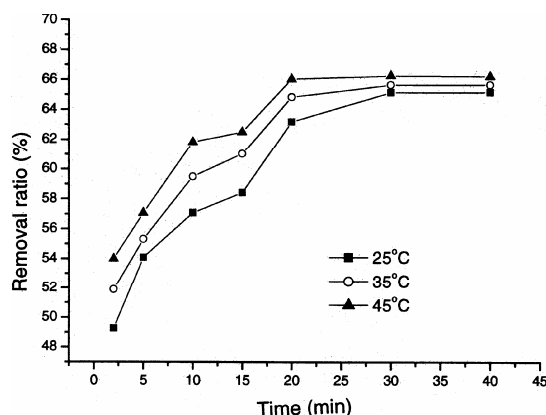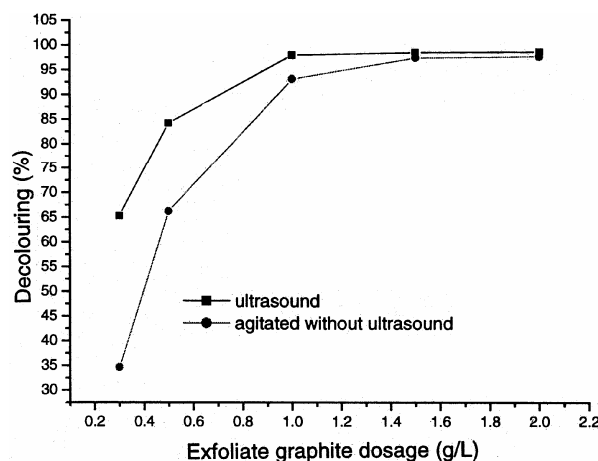

Fig. 3— Removal ratio of different treated Direct blue 78 aqueous solution. Initial concentration: 50 mg/L, temperature: 25°C, dosage of absorbent: 0.3 g/L, *p*H=1

use of ultrasound and adsorption, the mass transfer rate of adsorbate from the bulk solution to the surface of adsorbent, which usually limits the efficiency of adsorption process, can be largely enhanced[19]. The removal efficiency in presence of ultrasound increases with increase in initial dosage, which can be attributed to increased surface area and the availability of more adsorption sites. A removal ratio of 98.0% has been observed with the initial concentration of dye being 50 mg/L and the amount of exfoliated graphite 1.0 g/L. Increasing the dosage of adsorbent did not increase the removal ratios of Direct blue 78. So in the combined method, 1.0 g/L of exfoliated graphite was chosen as the optimum dosage.

Effect of initial concentration of dye

The effect of initial dye concentration on removal of Direct blue 78 by the combination of exfoliated graphite and ultrasound was investigated in the range of 50–285 mg/L of the initial dye concentrations. As shown in Fig. 6, different initial dye concentrations resulted in different removal ratios for a fixed exfoliated graphite dosage of 1.0 g/L. The dye removal decreased from 98.0 to 50.7% with an increase in the initial concentration of dye from 50 to 285 mg/L. Lower removal ratio at higher dye concentrations are due to the saturation of adsorption, though the actual amount of dye removed increased from 49 to 145 mg/L. It may be due to the high concentration of dye providing a high driving force to overcome all mass transfer resistance[20].
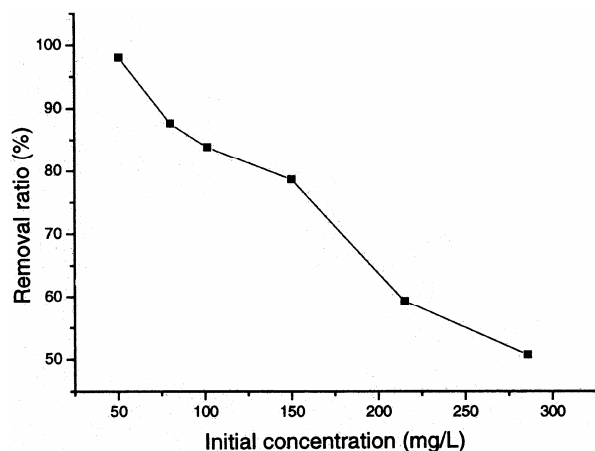
Effect of pH

The effect of the pH of the solution on removal efficiency of Direct blue 78 is shown in Fig. 7. It was observed that the removal ratios of Direct blue 78 in the presence of exfoliated graphite with ultrasound decreased gradually from pH 1 to 11. At low pH values, the surface of exfoliated graphite solids is positively charged and easily adsorbs Direct blue 78 ion having a negative charge[21]. In addition, it may be possible that the number of OH species produced by ultrasound increases on the surface of the exfoliated graphite particles in high acidic solution which favours the oxidation of organic matter. At high pH, the surface charge may get negatively charged, which does not favour the adsorption of negatively charged dye anions[22]. In addition, pH of the solution can influence the hydrophobic property of Direct blue 78. At very low pH, the molar fraction of the dissociated forms become very low; exfoliated graphite can also interact with dye molecules via hydrogen bonding and hydrophobic-hydrophobic mechanisms. The remarkable change in the removal ratio of Direct blue 78 indicated that low pH is in favourable for the adsorption of Direct blue 78 on exfoliated graphite.

Adsorption isotherm models and thermodynamics

For adsorption isotherms, dye solutions of different concentrations (50-300 mg/L) were irradiated under ultrasound with 1.0 g/L amount of exfoliated graphite at pH 1 at 25 and 45°C till the equilibrium was reached. Langmuir [Eq. (2)], Freundlich [Eq. (3)] isotherm models[23] were selected to describe the adsorption:

Fig. 6— Effect of initial concentration of Direct blue 78. Dosage of exfoliated graphite: 1.0 g/L, temperature: 25°C, contact time: 20 min.
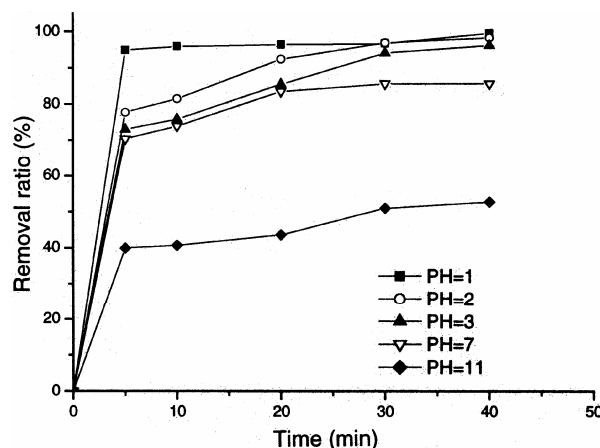

Fig. 7— Effect of pH. Dosage of exfoliated graphite: 1.0 g/L, temperature: 25°C.

$$\frac{1}{q_e} = \frac{1}{q_0 b C_e} + \frac{1}{q_0} \qquad \ldots(2)$$

$$\log q_e = \log K_f + \frac{1}{n}\log C_e \qquad \ldots(3)$$

where q_e (mg/g) is the adsorption capacity, C_e (mg/L) is the equilibrium concentration of solute, q_0 (mg/g) is the maximum capacity of adsorbate to form a complete monolayer on the surface, b (L/mg) is the Langmuir constant related to the heat of adsorption. When $1/q_e$ is plotted against $1/C_e$ and the data are regressed linearly, q_0 and b constants can be calculated from the slope and the intercept. The constant K_f is related to the adsorption capacity and $1/n$ is another constant related to the surface heterogeneity. When $\log q_e$ is plotted against $\log C_e$ and the data are treated by linear regression analysis, Freundlich and Langmuir plots are obtained
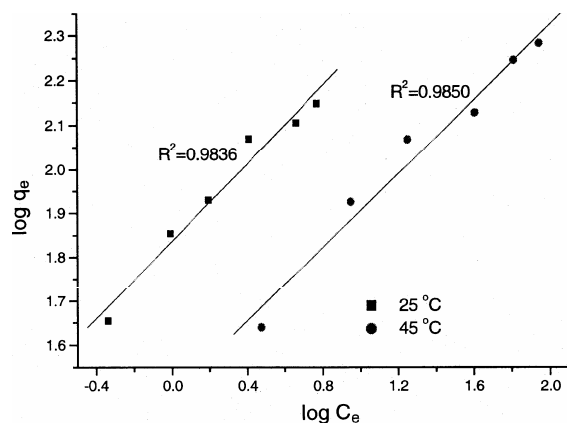

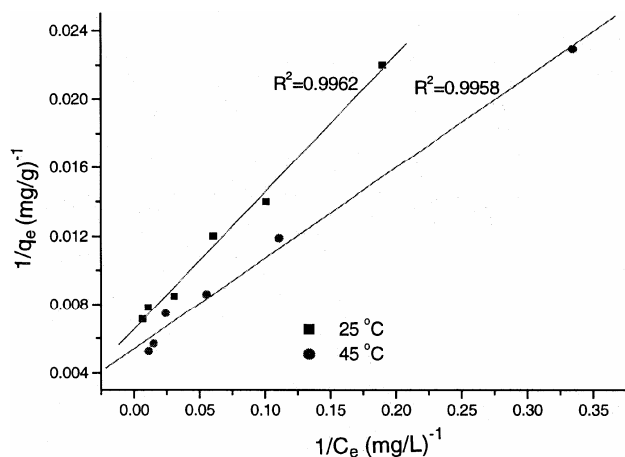Fig. 8— Freundlich isotherm of Direct blue 78 on exfoliated graphite

Fig. 9— Langmuir isotherm of Direct blue 78 on exfoliated graphite

(Figs 8 and 9), the values of Langmuir and Freundlich constants are listed in Table 1. Langmuir isotherm equation fits better than Freundlich isotherm equation for describing the isotherm data for the present system which means adsorption of dye onto exfoliated graphite is monolayer adsorption with a finite number of identical sites.

The thermodynamic data were evaluated from Langmuir isotherms using following equations:

$$\Delta G^\circ = -RT \ln b$$
$$\Delta H^\circ = R\,(T_1 T_2/T_2 - T_1)\,\ln(b_2/b_1)$$
$$\Delta S^\circ = (\Delta H^\circ - \Delta G^\circ)/T$$

where b, b_1 and b_2 are Langmuir constant at different temperature. The thermodynamic parameters of the adsorption systems are given in Table 2. The negative values of ΔG° confirm the feasibility of adsorption process at each temperature. The positive value of enthalpy change (ΔH°) suggests the endothermic nature of the process, while positive ΔS° value reflect the affinity of exfoliated graphite towards the dye[24].

Kinetics of adsorption

The kinetic data could be described with the well-known Lagergren first-order rate equation[25]:

$$\log (q_e - q_t) = \log q_e - \frac{k_{ad}}{2.303}t$$

Value of $\log (q_e - q_t)$ was calculated for each time interval at different temperatures, where q_e and q_t signify the amount adsorbed at equilibrium and at any time t. The plot of $\log (q_e - q_t)$ versus t (Fig. 10) exhibits straight lines at 25, 35 and 45°C and confirm the first-order rate kinetics for the ongoing

Table 1—The values of Langmuir and Freundlich constants for adsorption of Direct blue 78 on exfoliated graphite under ultrasound

Temperature (°C)	b (L/mg)	q_0 (mg/g)	K_f	$1/n$
25	0.08156	152.9	68.5630	0.43988
45	0.10181	185.5	30.7610	0.41700

Table 2 —The values of thermodynamic parameters for adsorption of Direct blue 78 on exfoliated graphite under ultrasound

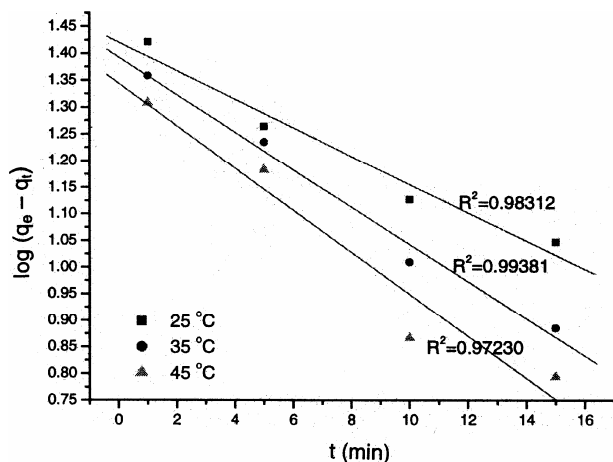| ΔG° (kJ/mol)	
25°C	-6.210
45°C	-6.040
ΔH° (kJ/mol)	8.738
ΔS° (J/K mol)	48.316

Fig.10— Lagergren's plot of Direct blue 78 adsorption on exfoliated graphite under ultrasound

adsorption process. The k_{ad} values evaluated, from Lagergren plots are found to be 0.06112, 0.08065 and 0.09104 min^{-1} at 25, 35 and 45°C, respectively. The higher value of k_{ad} at higher temperature suggests higher temperature is favourable for Direct blue 78 adsorption on exfoliated graphite under ultrasound and the adsorption is endothermic in nature.

Conclusion

The removal of Direct blue 78 with a combination of ultrasound and exfoliated graphite can be more useful in removing Direct blue 78 from aqueous solution in comparison with either individual method. Experimental results indicate that Direct blue 78 was readily discoloured nearly 100% by the combined ultrasound/exfoliated graphite at pH 1.0, dosage of exfoliated graphite 1.0 g/L, contact time 20 min and 45°C. The linear Langmuir and Freundlich isotherm models are fitting to represent the experimental data. The adsorption of Direct blue 78 over exfoliated graphite follows first-order kinetics. The results show that the combined ultrasound and exfoliated graphite can be an effective technology for treating wastewater containing organic dyes.

Acknowledgements

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