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Removal of reactive blue 52 dye from aqueous solution by adsorption on the surface of metal doped polyaniline nanocomposite

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Abstract:-*In this work, polyaniline-$CuCl_2$ composite has been used as adsorbent to remove reactive blue 52 dye from waste water. The effects of initial dye concentration, adsorbent dosage and temperature on the adsorption capacity of PANI- $CuCl_2$ for reactive blue 52 dye have been studied. The Langmuir and Freundlich adsorption models have been used for the mathematical description of adsorption equilibrium data. The best fit model is Langmuir isotherm with an R^2 value of 0.999. The change of Gibbs energy, enthalpy and entropy of adsorption has been evaluated. The adsorption process is exothermic in nature.*

Keywords: *Reactive blue 52, polyaniline composite, dye, adsorption.*

1. Introduction

Removal of colour bearing effluents from waste water is a growing need at present scenario. Synthetic dyes play vital role in various branches of textile, plastic, paper, food and cosmetics industries. Synthetic dyes are almost soluble in water which is very difficult to abate.[1] Chemical industries are extensively using over 10,000 tones synthetic dyes in their processes per year.[2] Among the varieties of dyes used, reactive blue 52 dye widely employed for wool, nylon and silk dyeing because of its favourable characteristics of bright colour, high solubility in water and low energy consumption. Untreated disposal of this coloured water enter into the receiving water bodies causes harmful effects such as allergic dermatitis, skin irritation, mutations and cancer to aquatic lives and humans.[3] Many technologies have been practiced for the treatment of dye containing effluents like flocculation, filtration, bio degradation, membrane filtration which are non-destructive and a new type of pollution arise which needs further treatment.[4] Among these technologies, 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 facets of heterogeneous catalysis.[5]

Varieties of adsorbents have been applied for the removal of toxic effluents like agricultural waste, polymers,[6, 7] activated charcoal,[8] clay[9] etc. In recent years π-conjugated polymers was tested in the adsorption of dye effluent. PANI considered to be one of the most prime classes of polymers due to characterized electrochemistry, simple protonation reversibility, fabulous redox recyclability[10], good environmental stability[11], easy doping[12], and easy preparation, exhibit different nano structure morphologies. PANI can be used as an adsorbent for the removal of anionic dyes or cationic dyes when the backbone of the polymer is positively charged or neutral respectively.[13-15] PANI usually combined with inorganic materials to form composites with high physical and chemical characteristics. Researchers designed the conducting polymers as in the form of nanomaterials due to their enhanced properties, different from the properties of corresponding macroscopic form which offers high surface area and improved electrical conductivity. Recently, doped PANI nano compoites was employed as sorbent for dye removal from aqueous medium under action of UV and visible light.[16] Cu^{2+} enhances the photocatalytic activity, perusal of literature reveals that little exploration of adsorption study reported using this adsorbent[17-20].

The present paper was devoted to study the adsorption of reactive blue 52 dye (fig.1) (Drimaren Blue X-3LR) as a model onto Cu doped PANI composite assisted by UV light. Physical characteristics of the dye is listed in table 1.

2. Materials and methods

Instruments

In the experimental studies, MAPADA-V-1100 D spectrophotometer was used for determination of dye concentrations. RIS 24-BL orbital shaker with 6 AMP UV lamps used for agitating the solution. R-8C laboratory centrifuge was used for centrifugation process. Equip-Tronics digital pH meter model EQ-610 was used in pH measurements for adsorption experiments.

Chemicals and Reagents

Reactive blue 52 (RB 52) was purchased from Geigy Co. Ltd . 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.

Preparation of Dye Solution

1000mg/L stock solution was prepared by dissolving 1g of dye in 1000 ml distilled water. Different concentrations (10-30 mg/L) of dye solutions were prepared by successive dilution from this stock solution.

Preparation of PANI-$CuCl_2$

PANI was prepared by chemical oxidation coupled with polymerization where ammonium persulphate was used as an oxidant. Required amount of ammonium persulphate dissolved in distilled water was added into solution of aniline (5ml) dissolved in 1.5M HCl .

The solution mixture was stirred at 400rpm for 5hours at room temperature. A colour change from white through blue to dark green was observed. After the polymerization leading to green emeraldine salt form of PANI granules, the solution was filtered, washed, and dried.

$CuCl_2$ at various doping levels prepared in 5ml distilled water were added into the solution mixture as described earlier prior to the stirring. The solution was then stirred at 400rpm and at room temperature for five hours. After the polymerization, the solution was filtered, washed, and dried leading to doped PANI samples[21].

Experimental procedure

The adsorption of reactive blue 52 onto PANI doped with 8% $CuCl_2$ was investigated using batch experiments. Various weights of doped polyaniline (0.025-0.175g) were agitated in 100 ml of dye solution with a concentration of 20 mg/L. The suspensions were shaken at 250 rpm for 120 min at room temperature, and pH of the solution is 5.48. At the end of pre-determined time intervals, the adsorbate was taken and centrifuged. Then the sample has been placed inside a cell of UV-Visible spectrophotometer.

The percentage removal of dye solution has been calculated by the following formula:

$$(\text{Adsorption }\%) = \frac{C_o - C_e}{C_o} X\ 100 \qquad (1)$$

Where C_o is the initial concentration of the dye and C_e is the equilibrium concentration of the dye (mol/L)

3. Results and Discussion

Characterization of the Adsorbent and Adsorbate

The FTIR spectra of before and after adsorption of PANI-$CuCl_2$ are shown in the figures 2a and 2b. The characteristic bands at 1568 cm^{-1} arise mainly from both C=N and C=C stretching for quinoid form, while the band at 1417 cm^{-1} is attributed to the C-C aromatic ring stretching of the benzenoid unit. The peaks at 1302 cm^{-1} and 811cm^{-1} can be assigned to C-N stretching of the secondary aromatic and aromatic C-H out-of-plane bending vibration respectively. The adsorption bands lies below 1000cm^{-1} are the characteristics of mono substituted benzene[22]. No significant changes observed before and after adsorption indicating that the removal of RB 52 may occur via physisorption.

SEM Analysis

The Scanning Electron Microscopy (SEM, ZEISS) images of PANI-$CuCl_2$ composite before and after adsorption of reactive blue 52 are shown in Fig.3a and 3b. Doped polyaniline(Fig. 3a) offers high surface area suitable for retaining the dye. The dye molecules are adsorbed directly on the positively charged PANI sites via delocalized π-electrons of the aromatic rings and the negative charge of SO_3^- group of the dye. Also, the adsorption could take place via hydrogen bond formation between the N-H linkage in PANI and dye. The rough surface of the sorbent can be seen, showing that the surface has more adsorption sites to remove the dye.

Effect of Contact time

Contact time is an important parameter because this factor determines the adsorption kinetics of an adsorbate at a given initial concentration. The effect of contact time for RB 52 by PANI-$CuCl_2$ was investigated for 120 minutes as shown in Fig.4. At the beginning adsorption rate is faster as the dye ions are adsorbed by the exterior surface of the PANI-$CuCl_2$ composite. When the adsorption of the exterior surfaces reaches saturation, the ions exerted onto the pores of the adsorbent and are adsorbed by the interior surface of particle. This phenomenon takes relatively long contact time.

Effect of initial dye concentration

The effect of initial dye concentration on adsorption efficiency onto PANI-$CuCl_2$ has been explored as shown in fig.5, table 2. This experiment was examined by varying initial dye concentration of reactive blue 52(10-30 mg/L) in presence of 1 g of PANI-$CuCl_2$ composite for two hours at room temperature. It can be noticed from the figure that the

percentage of RB 52 has decreased with the increase in initial concentration of dye solution because the actual amount of dye adsorbed per unit mass of adsorbent has increased with increase in dye concentration. The increase in initial dye concentration causes an increase in the interaction between dye molecules and PANI-$CuCl_2$ surface but available sites of adsorbent become fewer. Hence adsorption gets decreased.

Effect of Temperature

The effect of temperature was studied by varying the temperature from 30 to 45˚C. It can be noted from the fig.6 that as the temperature increases the removal percentage of dye decreases. This explains the exothermic nature of the adsorption system.

Effect of adsorbent dosage

Fig.7 shows that the adsorption of dye increases with increase in the amount of adsorbent. The number of binding sites on the adsorbent surfaces increases with the amount of adsorbent materials. Thus greater number of dye molecules can bind if the amount of adsorbent is more.

Isotherm studies

Assumptions of isotherms were made according to the equations (2)-(5)

$\frac{C_{eq}}{q_{eq}} = \frac{1}{K_L} + \frac{C_{eq}}{q_{eq}}$; (2a) Langmuir isotherm

Where $K_L = Q_0 X\ b$

$R_L = \frac{1}{1+bC_i}$ (2b)

$\ln q_{eq} = \ln K_f + \frac{1}{n} \ln C_{eq}$ (3) Freundlich isotherm

$q_{eq} = B \ln A_T + B \ln C_e$ (4) Temkin isotherm

where $B = \frac{RT}{b_T}$

$\ln q_e = \ln q_{max} - K_J C_e$ (5) Jovanovic isotherm

Isotherm models are shown in the following figures (From Fig. 8 to Fig.11), values are reported in table 3.

Adsorption Kinetics

The kinetic study of the adsorption processes often used to describe the efficiency of adsorption and feasibility of scale of operation. The kinetic data modeled with pseudo-second-order kinetic equation was examined by the linear plots of (t/q_t) Vs t is shown in Figure 12. The adsorption correlation coefficient R^2 was approximately close to unity and rate of the reaction appeared to be controlled by the chemical process.

Intraparticle diffusion

In the batch mode adsorption process, initial adsorption occurs on the surface of the adsorbent, Weber and Morris suggest the following kinetic model to investigate the adsorption is intra particle diffusion or not. The relationship given as equation (6)

$q_t = K_i \sqrt{t} + I$ (6)

where K_i is the Intraparticle diffusion rate constant, $\sqrt{t}$ square root of contact time, I is an intercept proportional to the boundary layer thickness(Figure 13).

Thermodynamic Parameters for adsorption process

Thermodynamic parameters for adsorption process have been calculated using Langmuir constant (K_L). These parameters have been calculated at different temperature values as shown in table 4. Parameters are as follows change in enthalpy (ΔH), the change in free energy (ΔG), and the change in entropy (ΔS) associated with adsorption process.

The change in free energy (ΔG) associated with adsorption process can be calculated from this equation:

$\Delta G = -RT \ln K_L$ (7)

where: ΔG is change in free energy (KJ/mol), R is general gas constant, which equals 8.314J/mol.k, T is absolute temperature (K), K_L is Langmuir constant (L/mol).

Equations (7) and (8) are used to calculate the values of ΔS, ΔH:

$\ln K_L = -\Delta H/RT + \Delta S/R$ (8)

$\Delta G = \Delta H - T\Delta S$ (9)

When the value of ΔH for RB 52 dye is negative this indicates that the adsorption process is an exothermic process. The negative value of ΔG has increased with temperature increase, indicating the feasibility and spontaneity of the adsorption process onto PANI-$CuCl_2$, while the positive value of ΔS revealed the increase in randomness at the solid-solution interface during the adsorption process.

Conclusion

We have investigated the adsorption behavior of anionic dye on doped polyaniline. It is characterized by FTIR and SEM techniques. Adsorption of the anionic dye RB 52 was significantly high. This may be due to the interaction of SO_3^- group in the anionic dye, which is responsible for the electrostatic interaction by the positively charged surface of doped polyaniline. The adsorption kinetic of RB 52 was found to follow pseudo second order model. The temperature has a

reverse effect on the percentage of dye removal, suggesting that exothermic process. This is an economical and efficient method for removal of anionic dye from water.

Nomenclature

1. C_{eq} - Equilibrum concentration of dye solution (mg/L)
2. Q_{eq} - Amount of dye adsorbed by catalyst at equilibrium (mg/g)
3. K_L - Langmuir adsorption equilibrium Constant
4. b - Langmuir Isotherm Constant (L/mg)
5. Q_0 - Maximum monolayer coverage capacity(mg/g)
6. C_i - Adsorbate Initial Concentration (mg/L)
7. K_f - Freundlich Isotherm constant (mg/g)
8. n - Adsorption Intensity
9. A_T - Temkin Isotherm equilibrium binding constant (L/g)
10. B_T - Temkin Isotherm Constant
11. R - Universal gas constant (8.314 J/mol /K)
12. T - Temperatureat 298K
13. B - Constant related to heat of sorption (J/mol)
14. K_J - Jovanovic Isotherm Constant (mg/g)

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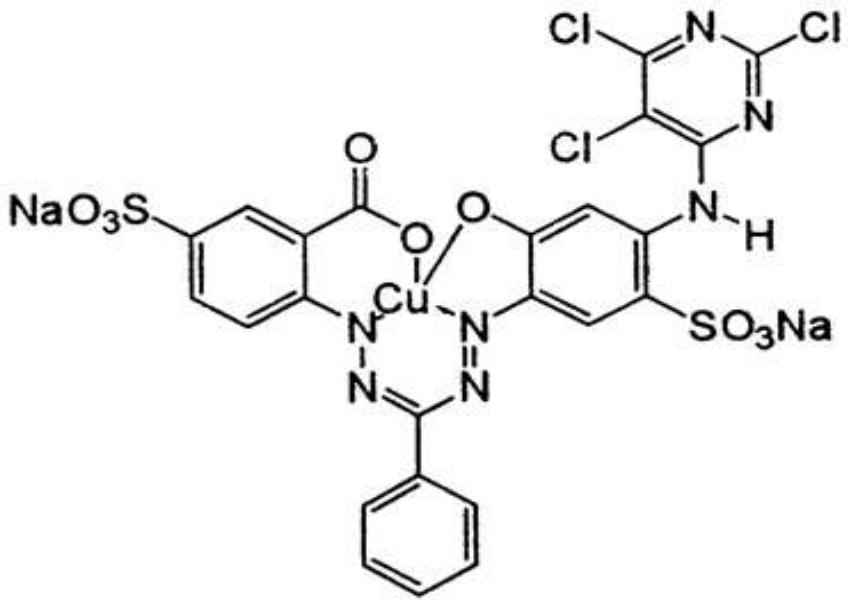

Fig.1 Chemical structure of Reactive Blue52

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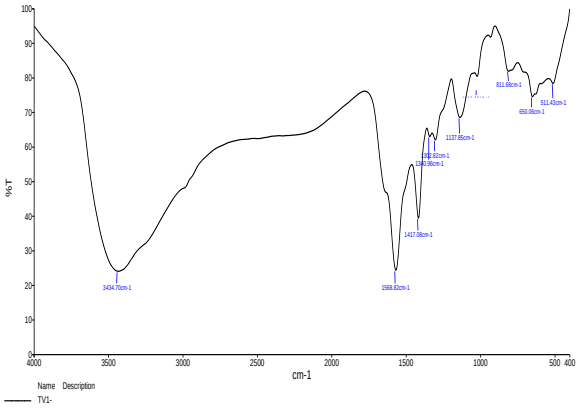

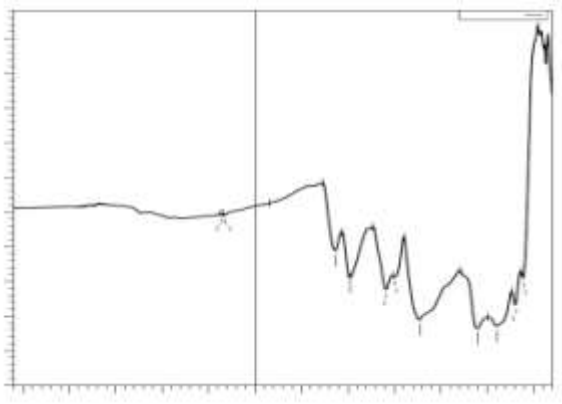

Fig.2a before adsorption **Fig.2b after adsorption of RB 52**

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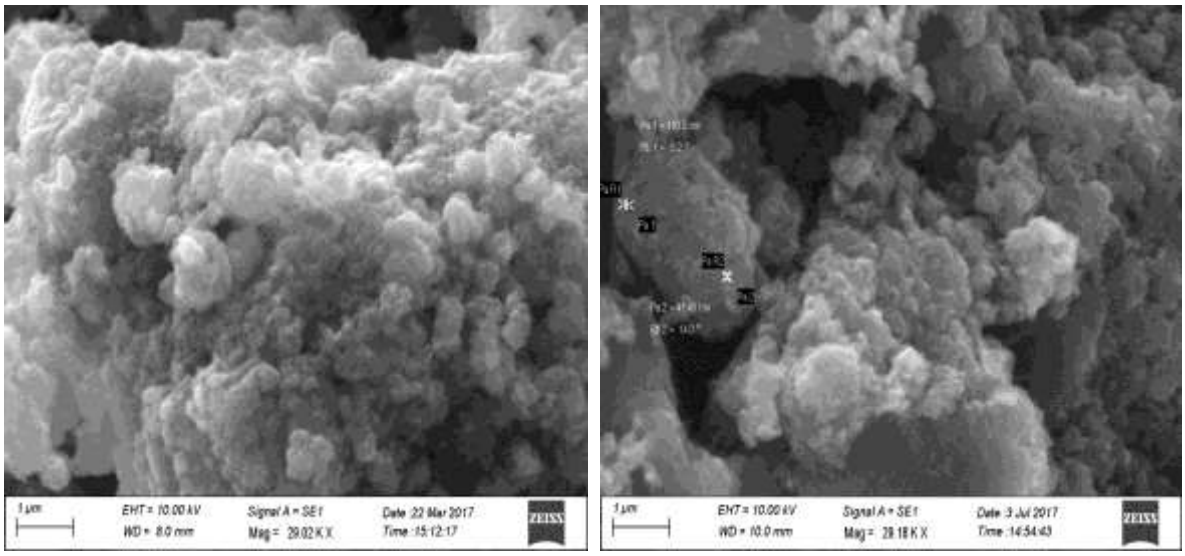

SEM images of PANI-$CuCl_2$ composite before (3a) and after adsorption of RB 52(3b)

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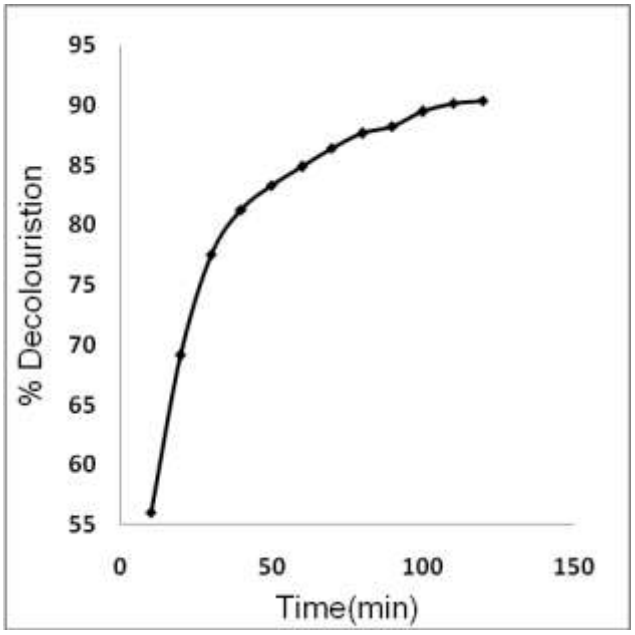

Fig.4 Effect of contact time of RB 52 dye on % removal

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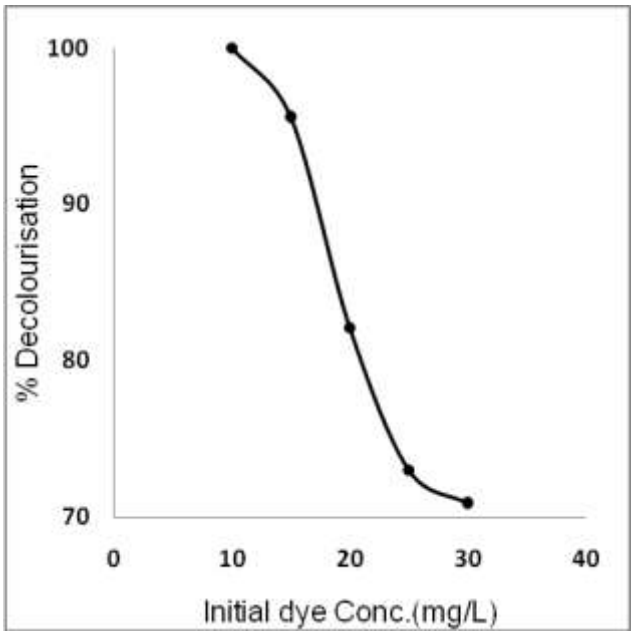

Fig.5 Effect of Initial Dye Conc. Of RB 52 dye

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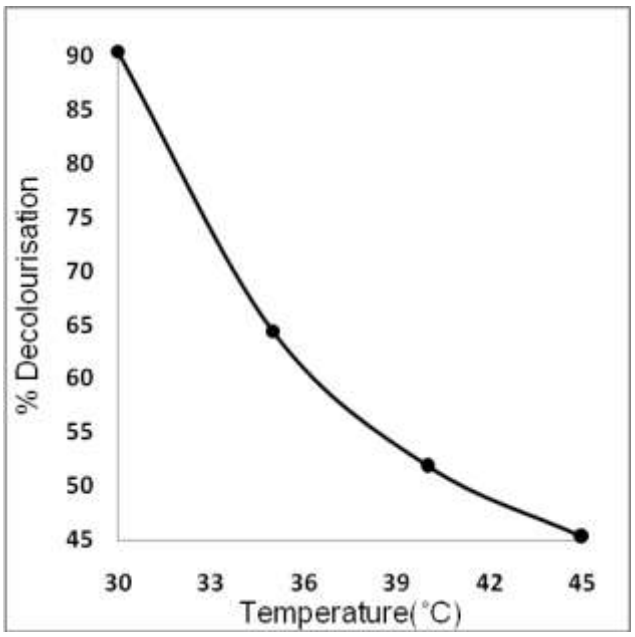

Fig.6. Effect of Temperature on % Removal

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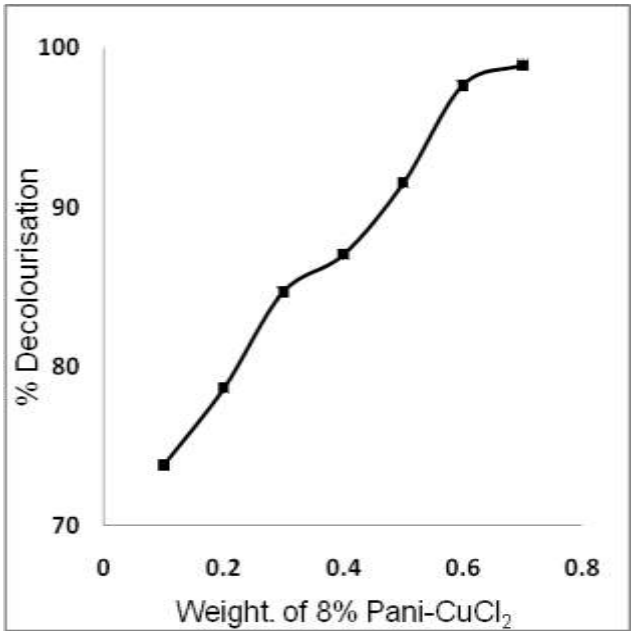

Fig.7. Weight of 8% Pani-$CuCl_2$

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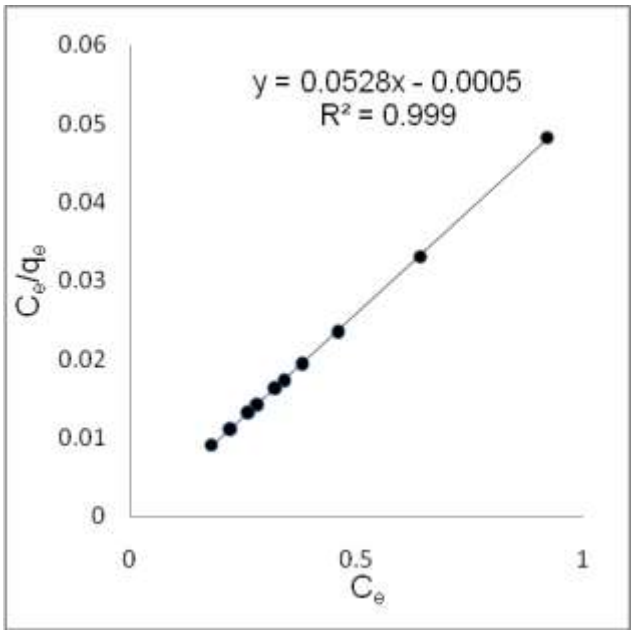

Fig.8 Langmuir isotherm model for RB 52

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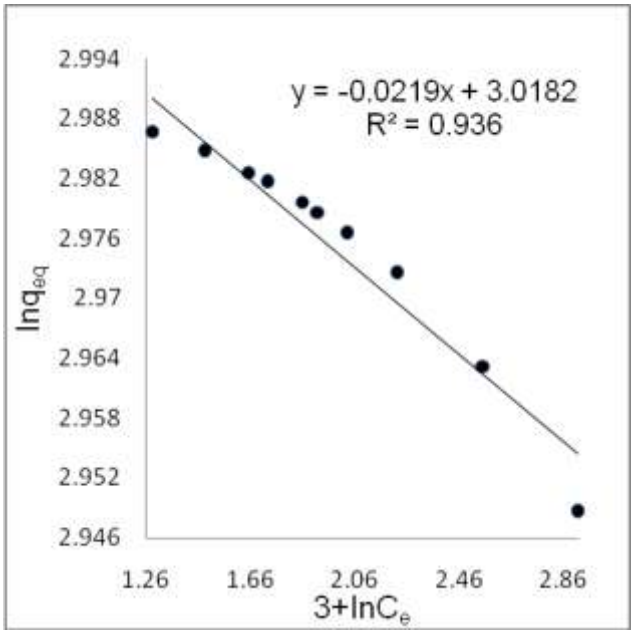

Fig.9 Freundlich isotherm model for RB 52

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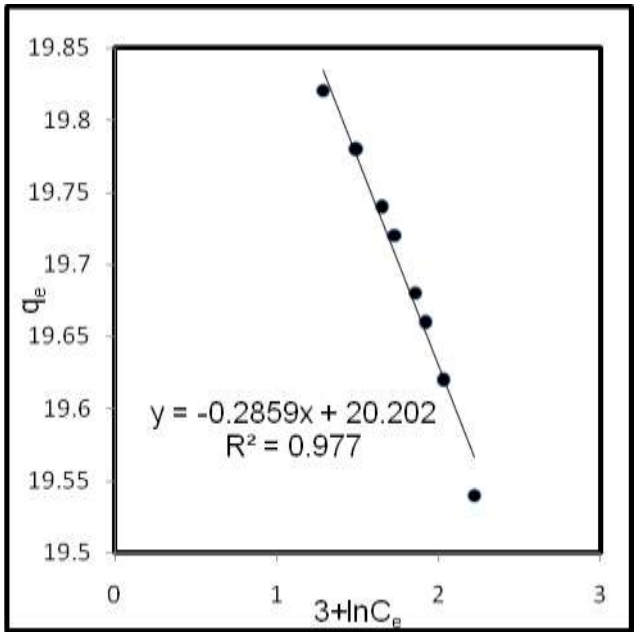

Fig.10 Temkin isotherm model for RB 52

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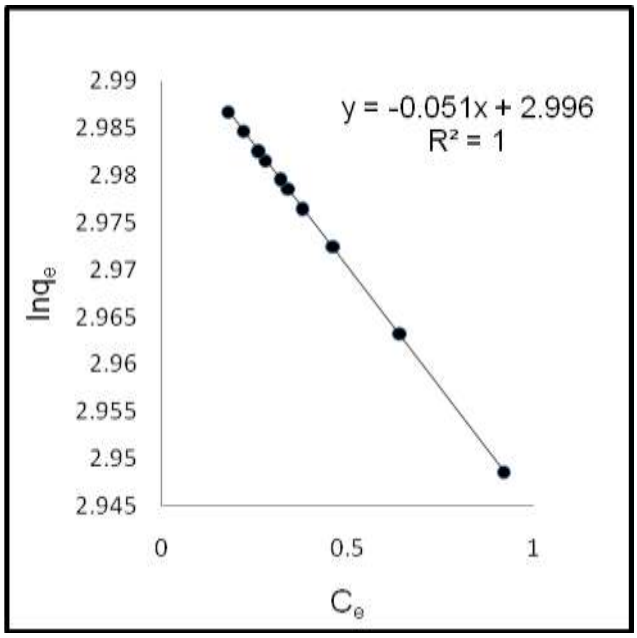

Fig.11 Jovanovic isotherm model for RB 52

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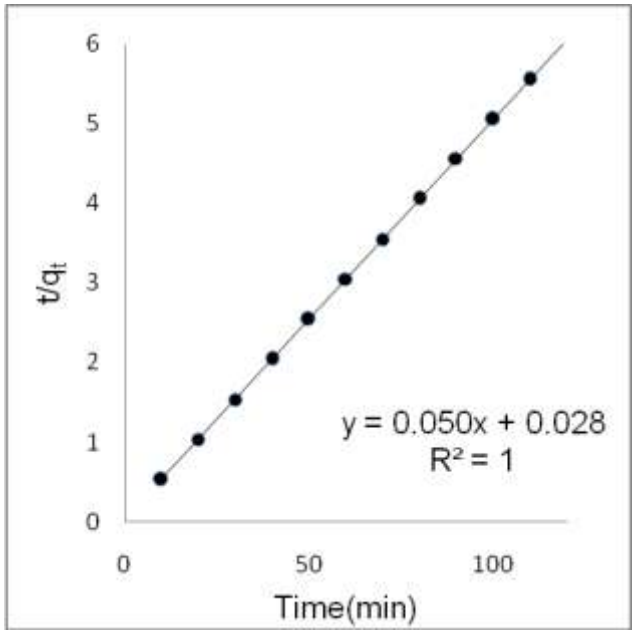

Fig.12 Pseudo second order model for RB 52

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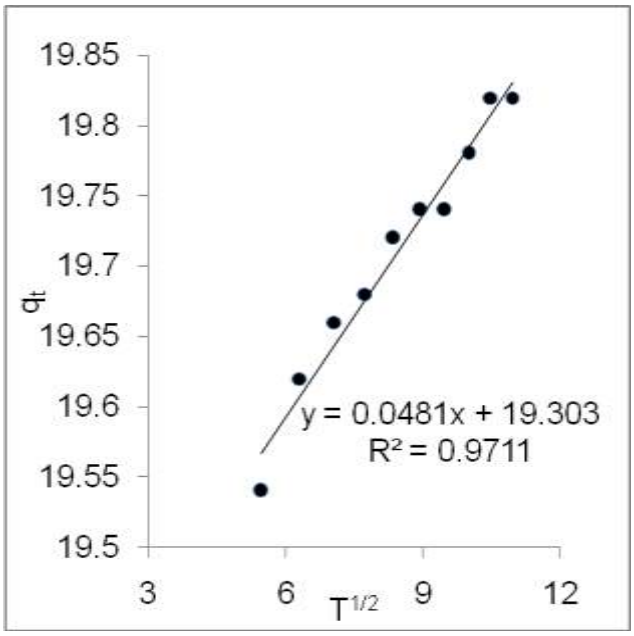

Fig.13 Intraparticle Diffusion Model for RB 52

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Table 1
Characteristics of Reactive blue 52 dye

Parameter	Value
1. Chemical formula	$C_{24}H_{11}Cl_3CuN_7Na_2O_9S_2$
2. Molecular Weight	821.40
3. Cas No.	12225-63-7
4. Physical form	Blue powder
5. Solublity	Soluble in water
6. λ_{max} (nm)	615
7. C.I. Name	Azo Dye

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Table 2

Initial dye concentrations with % removal

Initial dye Conc. (mg/L)	**% Removal**
10	99.99
15	95.53
20	82.12
25	73.04
30	70.83

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Table 3

Langmuir, Freundlich, Temkin and Jovanovic Isotherm Constants for the adsorption of RB 52 onto PANI-$CuCl_2$

Dye	**Langmuir Isotherm**				**Freundlich Isotherm**			
RB52	**Q_0**	**K_L (L/mg)**	**R_L**	**R^2**	**1/n**	**N**	**K_f(mg/g)**	**R^2**
	18.94	2000	0.0005	0.99	0.022	45.6	20.45	0.93
	Temkin Isotherm				**Jovanovic Isotherm**			
	A_T (L/mg)	**b_T (J/Mol)**	**B**	**R^2**	**K_J**	**Q_{max}**		**R^2**
	192.1	8811.3	0.2859	0.97	0.0514	8.14		1.0

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Table 4

The Thermodynamic parameters of RB 52 dye adsorption process on the surface of PANI-$CuCl_2$

T(K)	**1/T (K)**	**K_L (L/mol)**	**ln K_L**	**ΔG (KJ/mol)**	**ΔH (KJ/mol)**	**ΔS (J.mol /K)**
303	0.00330	2000	7.6	-19.15	$-23.3x10^{-3}$	63.1
308	0.00325	2000	7.6	-19.46		
313	0.00319	2000	7.6	-19.78		
318	0.00314	2000	7.6	-20.09		

