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Identification of Water Polluting Organic Dyes by Tomato Plant Root and Silica through Adsorption Mechanism from Aqueous Solution

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The organic dyes directly pollute the soil, water, plants and all living systems in the environment. In which, water polluting dyes are identified through adsorption mechanism by using anionic dyes such as indigo carmine and congo red. For this study, tomato plant root powder and silica are chosen as adsorbents. The adsorption parameters are optimized for maximum adsorption. The positive ΔSº values for adsorption of anionic dyes indicate that the high disorder at adsorption interface. The ΔGº values are not much increased with increase of temperature indicates the adsorption is almost over at room temperature. The adsorptions of both dyes are followed Freundlich and Langmuir isotherms and pseudo second order kinetics. The negative values of ΔHº less than 40 kJ/mol indicated that the adsorption is physisorption. The high recovery of anionic dyes from tomato plant root and silica is a supportive evidence for the water polluting nature of anionic dyes.

Key Words: Organic dyes, Adsorption, Silica, Tomato plant root, Water polluting.

INTRODUCTION

Effluents from the dyeing and dye manufacturing industries are the important sources of water pollution, because dyes in water undergo chemical as well as biological changes which consume dissolved oxygen and destroy aquatic life. Moreover, some dyes and their degradation products may be carcinogen and toxic[1,2]. Therefore, it is necessary to treat the dye effluents prior to discharge into the river. Because of serious efforts of researchers, numbers of methodologies have been developed to manage water pollution. These methods include coagulation, froth floatation, ion exchange, sedimentation, solvent extraction, adsorption, electrolysis, chemical oxidation, chemical precipitation and membrane process[3-6]. Among these methods adsorption is the most convenient method for treating the waste water. Activated carbon is the most commonly used adsorbent for the removal of various pollutants from wastewater[7,8].

Among the various anionic dyes, indigo caramine (IC) and congo red (CR) are well-known dyes used for various purposes like stain, a dermatological agent, a veterinary medicine, an additive to poultry feed to inhibit propagation of mold, intestinal parasite and extensively used in textile and paper industries. These dyes are harmful to all living systems.

Adsorbents used for the adsorption of IC in the literature survey are TiO_2 impregnated activated carbon[9], granular activated carbon[10], chitin and chitosan[11], amino functionalized acrylamide-maleic acid hydrogels[12], bottom ash and de-oiled soya[13], aqueous biphasic extraction chromatographic[14], charcoal from extracted residue of coffee beans[15], charcoal from rice bran[16], activated carbon[17], Mn-supported TiO_2[18], ZSM-5 with manganese and lanthanum[19] and hen feathers[20].

Congo red adsorption studies are reported on β-cyclodextrin and starch based polymers[21], yeast-based biosorbent[22], coal-based mesoporous activated carbon[23], *Azadirachta indica* leaf powder[24], activated carbon prepared from coir pith[25] and waste red mud[26].

On the basis of literature survey, the dye treatment methods are not yet identified the water polluting organic dyes. In the present investigation, to identify the water polluting nature of organic dyes, tomato plant root (TPR) powder and silica have been used as an adsorbent to study the adsorption mechanism and to evaluate the water polluting nature of anionic IC and CR dyes. Moreover, on the basis of literature survey, TPR powder and silica are not yet used as the adsorbent for the adsorption of the anionic dyes IC and CR.

EXPERIMENTAL

The dyes used in this study are indigo carmine (Merck India Ltd.) having molecular formula $C_{16}H_8N_2O_8S_2Na_2$, Molecular weight 466.36, λ_{max}-610 nm and congo red having molecular formula $C_{32}H_{22}N_6O_6S_2Na_2$, molecular weight 696.67, C.I. No. 22120. The structures of indigo carmine and congo red are given in Figs. 1 and 2, respectively.

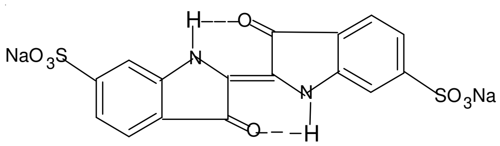


Fig. 1. Structure of indigo carmine (IC)

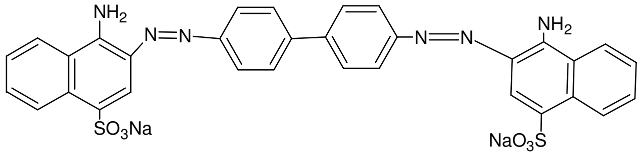
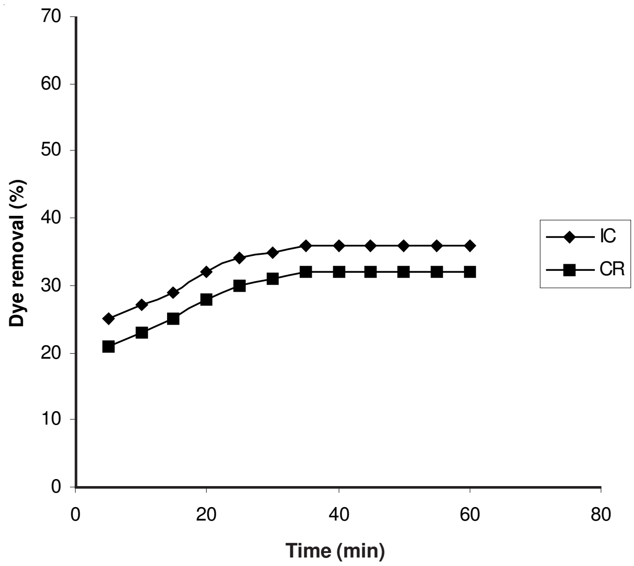


Fig. 2. Structure of congo red (CR)

Preparation of stock solutions of IC and CR: The stock solution of 1000 mg L^{-1} is prepared by dissolving 1 g of dyes IC and CR in a standard measuring flask separately. The working solutions of required concentration are prepared by successive dilution of stock solution. The dye concentration is analyzed by UV-spectrophotometer (Elico model SL-171).

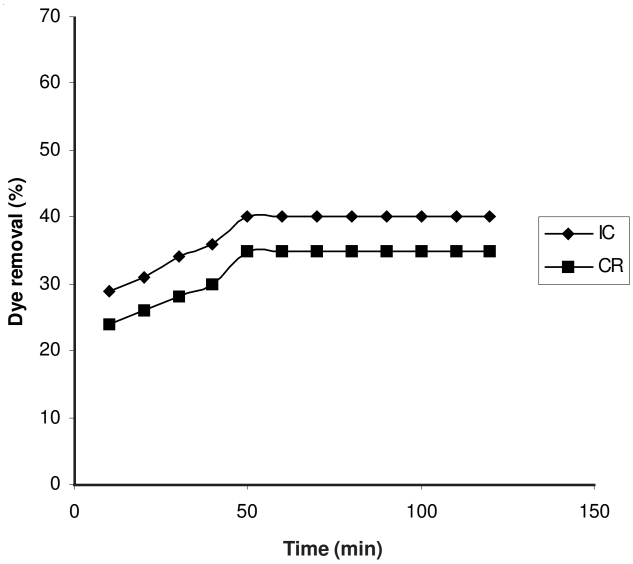
Batch adsorption studies: The dried adsorbent (0.25 g) is added with 50 mL of IC and CR solution in 100 mL conical flasks separately. The mixture is stirred on magnetic stirrer (Remi-model-1MH) and at the end of the experiment the solution is centrifuged off. The final concentrations of the solutions are measured spectrophotometrically. The contact time is studied up to 1 h to find the equilibrium time. The adsorption process of IC and CR on silica and TPR powder is studied in the concentration range of 100-600 mg/L. The temperature effect of IC and CR is studied in the range of 30-70 ºC. The adsorbent dosages are studied in the range of 200-1000 mg L^{-1} of dye solution.

Desorption studies: The dye adsorbed TPR powder and silica are used in the desorption studies. The dye adsorbents 200 mg is added with 50 mL of water in 100 mL conical flasks separately. The solutions are stirred for 1 h at room temperature in a magnetic stirrer (Remi-Model MLH). At the end of the experiment, the solutions are centrifuged off. The final concentrations of the solutions are measured spectrophotometrically.



Temperature 30 ºC, concentration 100 ppm, dosage 250 mg/50 mL

Fig. 3a. Effect of contact time for the adsorption of indigo carmine and congo red on tomato plant root powder



Temperature 30 ºC, concentration 100 ppm, dosage 250 mg/50 mL

Fig. 3b. Effect of contact time for the adsorption of indigo carmine and congo red on silica

RESULTS AND DISCUSSION

Effect of contact time and adsorption mechanism: Adsorption equilibrium attained within 35 minutes for the IC and CR on TPR powder and on silica both dyes takes 50 min to attain the equilibrium at room temperature. Further increase of contact time not increased the adsorption has shown in Fig. 3a-b. The removal of IC was 36 % and CR was 33 % on TPR and the removal of IC was 40 % and CR was 35 % on silica. This low adsorption may be due to the physisorption of anionic IC and CR dyes on the basic surface of the TPR powder and silica (Figs. 4 and 5).

Effect of initial dye concentration: The effect of dye concentration in the range of 100-600 mg L^{-1} of IC and CR on TPR powder and silica are shown in the Fig. 6a-b. Adsorption of IC and CR on TPR decreased with increase of initial dye concentration from 36-25 and 33-23 %, respectively. Further, the adsorption of both dyes on silica decreased with increase of initial dye concentration from 40-32 and 35-25 %, respectively. This may be due to saturation of active sites and surface area on the surface of the TPR and silica.

Effect of pH: The pH effects for the adsorption of anionic dyes on TPR and silica is shown in Fig. 7a-b. The pH of anionic dye solution are varied from 2-10. The adsorption of anionic dyes on TPR and silica was more in the pH range 2-6. The dye's original pH is 7-9. In this original pH range adsorption was poor may be due to the repulsion between the negative charge appear on the dyes and the OH group present on the TPR and silica surface. The pH was reduced to acidic condition by using dil. HCl. In acidic condition, dyes are protonated. Hence the protonated dyes are attracted towards the OH group appear on the TPR (cellulose) and silica surface. Therefore adsorption increased at lower pH.

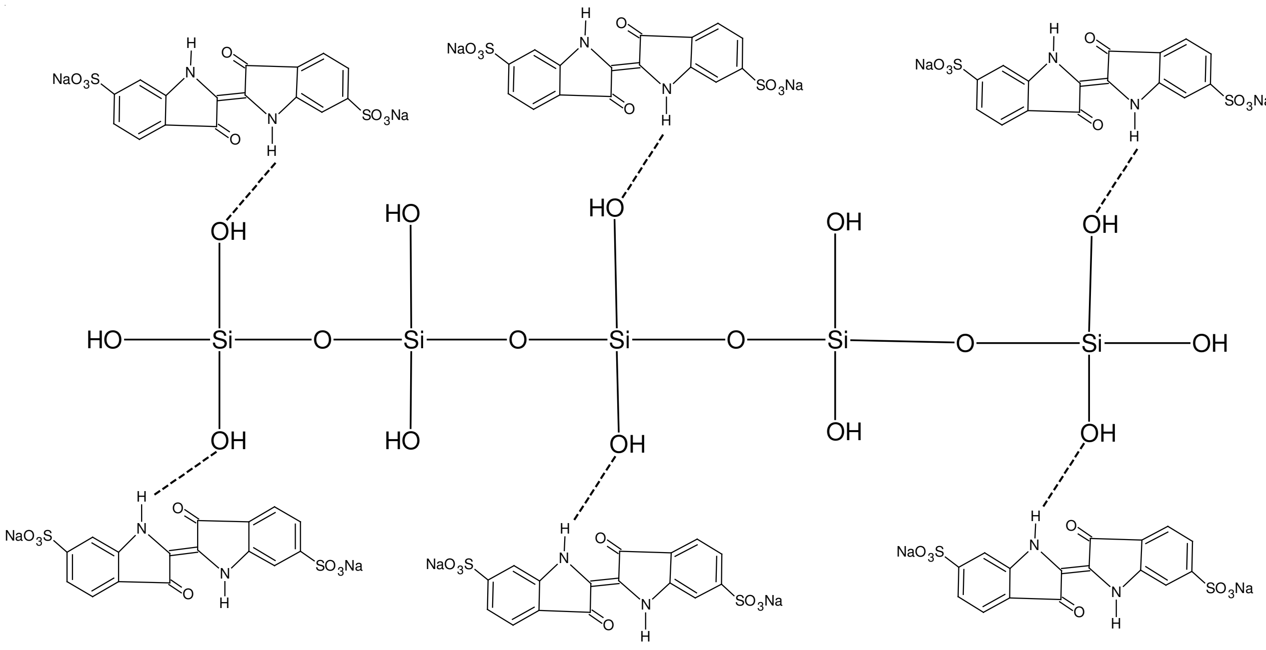


Fig. 4. Adsorption mechanism of the anionic indigo carmine on basic surface of silica

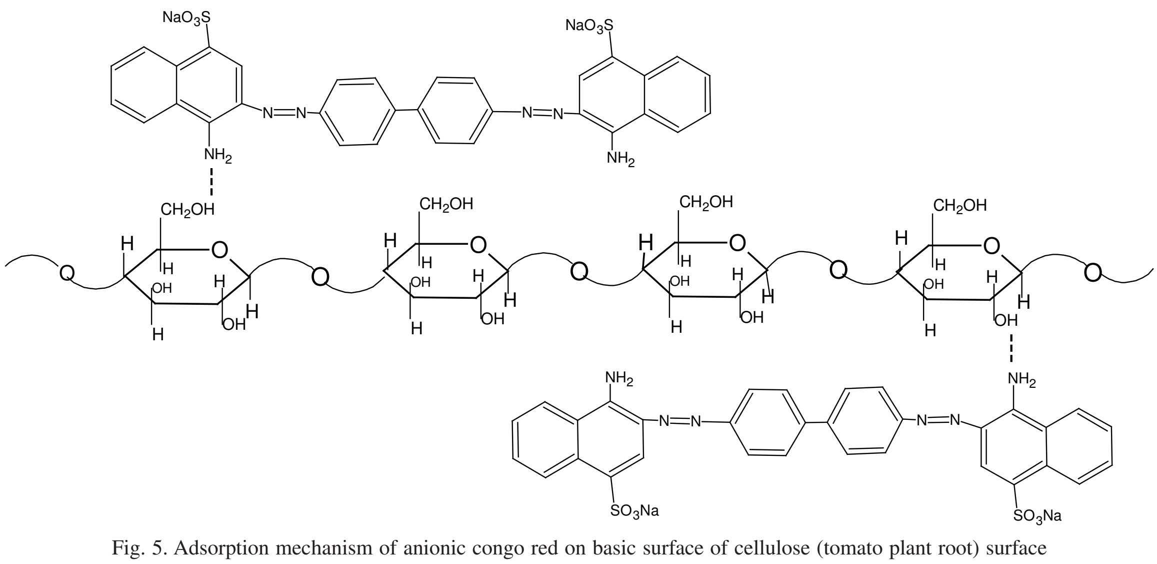
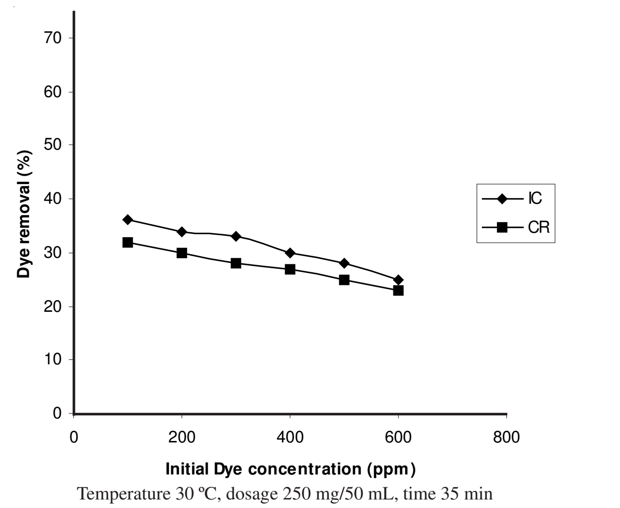
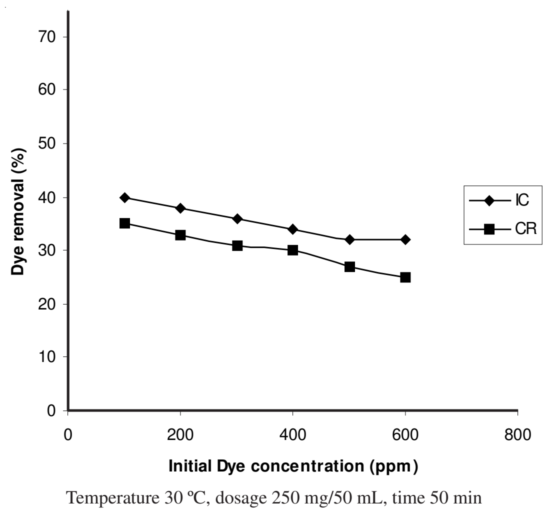


Fig. 5. Adsorption mechanism of anionic congo red on basic surface of cellulose (tomato plant root) surface



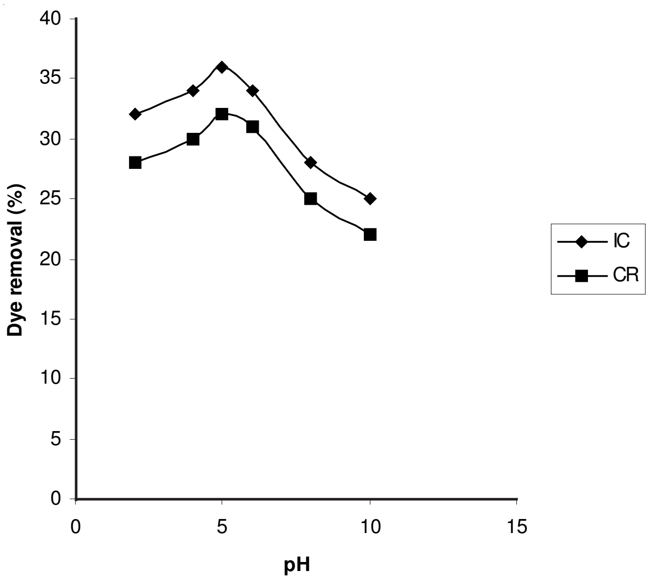
Temperature 30 ºC, dosage 250 mg/50 mL, time 35 min

Fig. 6a. Effect of dye concentration for the uptake of indigo carmine and congo red on tomato plant root powder



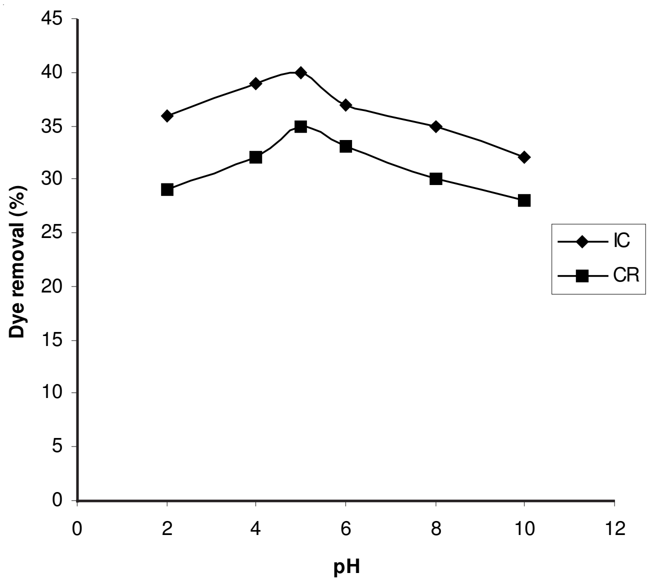
Temperature 30 ºC, dosage 250 mg/50 mL, time 50 min

Fig. 6b. Effect of dye concentration for the uptake of indigo carmine and congo red on silica



Temperature 30 ºC, dosage 250 mg/50 mL, time 35 min, concentration 100 ppm

Fig. 7a. Effect of pH on the uptake of indigo carmine and congo red on tomato plant root powder

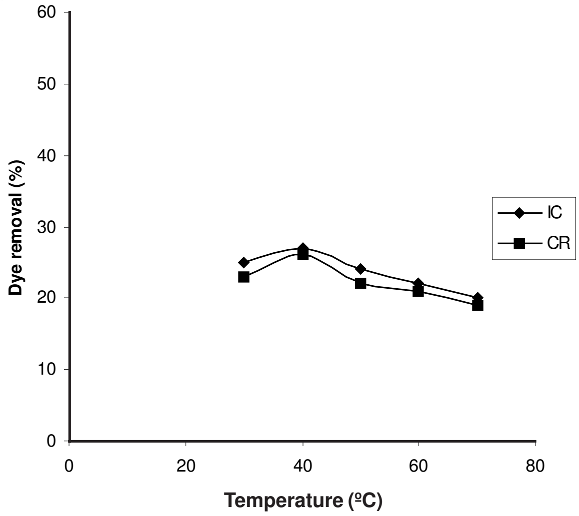


Temperature 30 ºC, dosage 250 mg/50 mL, time 50 min, concentration 100 ppm

Fig. 7b. Effect of pH on the uptake of indigo carmine and congo red on silica

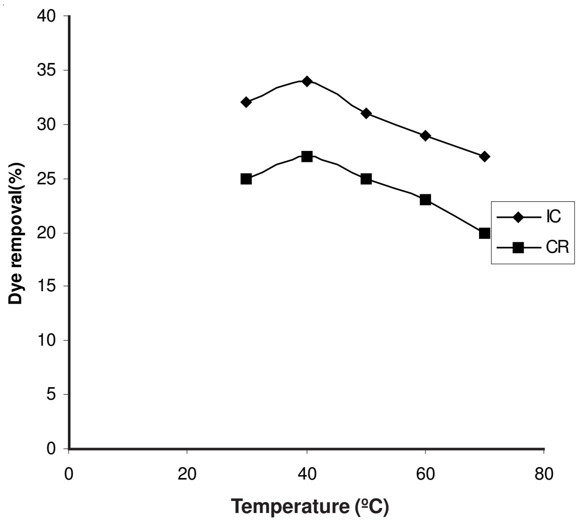
Effect of temperature: The effect of temperature for the uptake of both dyes (IC and CR) on TPR and silica at 30-70 ºC has shown in the Fig. 8a-b. The adsorption of dyes slightly increased from 30-40 ºC and further increase of temperature decreased the adsorption. The decrease might be due to the collapse of hydrogen bond (physisorption-shown in Figs. 4 and 5) between the anionic dyes and the adsorbents (TPR and silica).

Effect of adsorbent dosage: The effect of adsorbent dosage on the dyes adsorption has shown in the Fig. 9a-b. The percentage adsorption increased with increase of adsorbent dosage. It is apparent that by increasing the adsorbent dosage increased the number of valuable adsorption sites as well as the surface area. Therefore, adsorption increased with increase of adsorbent dosage.



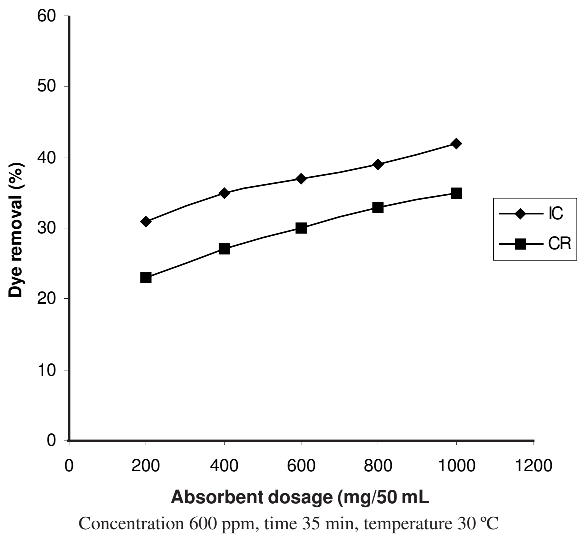
Concentration 600 ppm, time 35 min, dosage 250 mg

Fig. 8a. Effect of temperature for the uptake of indigo carmine and congo red on tomato plant root powder



Concentration 600 ppm, time 50 min, dosage 250 mg

Fig. 8b. Effect of temperature for the uptake of indigo carmine and congo red on silica

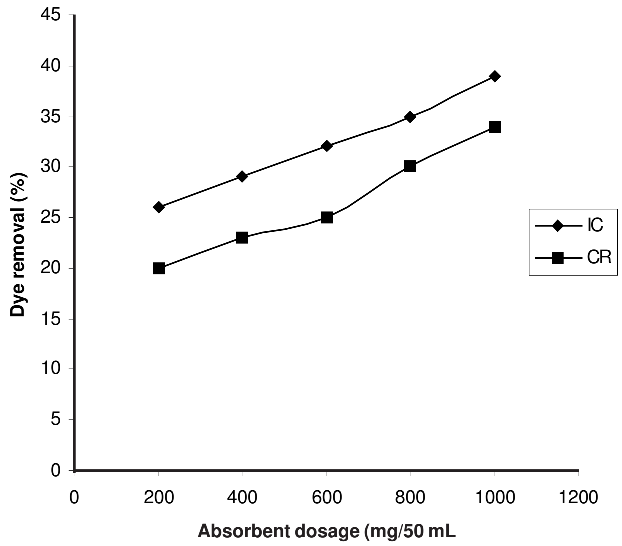


Concentration 600 ppm, time 35 min, temperature 30 ºC

Fig. 9a. Effect of adsorbent dosage for the uptake of indigo carmine and congo red on tomato plant root powder

TABLE-1
LANGMUIR AND FREUNDLICH ADSORPTION ISOTHERM FOR ADSORPTION OF ANIONIC DYES (INDIGO CARMINE AND CONGO RED) ON SILICA AND TOMATO PLANT ROOT POWDER

Adsorbent	Dyes	Langmuir adsorption isotherm			Freundlich adsorption isotherm		
		Q_{max}	K_L	R^2	K_F	n	R^2
Tomato plant root powder	Indigo carmine	75.08	0.0017	0.998	0.34	1.34	0.984
	Congo red	69.07	0.0015	0.999	0.25	1.29	0.994
Silica	Indigo carmine	97.22	0.0015	0.989	0.31	1.24	0.998
	Congo red	74.58	0.0016	0.999	0.30	1.31	0.990



Concentration 600 ppm, time 50 min, temperature 30 ºC

Fig. 9b. Effect of adsorbent dosage for the uptake of indigo carmine and congo red on silica

Adsorption isotherms: Congo red and indigo carmine dyes adsorption isotherm at different concentrations studied and observed that both are well matched with the Langmuir (Fig. 10a-d) and Freundlich adsorption isotherms (Fig. 11-d). The Langmuir equation represented as

$$\frac{C_e}{Q_e} = \frac{1}{Q_{max}K_L} + \frac{C_e}{Q_{max}}$$

Modified Langmuir equation represented as

$$1/Q_e = 1/Q_{max}K_L + /Q_{max}$$

where, Q_e is the equilibrium concentration of dye on the adsorbent, C_e is the equilibrium concentration of dye in solution, Q_{max} is the monolayer adsorption capacity, K_L is the Langmuir adsorption constant.

The Freundlich equation represented as

$$\ln Q_e = \ln K_F + \left(\frac{1}{n}\right)\ln C_e$$

where, K_F = Freundlich constant; n = number of layer of adsorption.

The adsorption parameters are given in Table-1. The R^2 value for both the adsorption model of IC and CR on TPR powder and on silica close to 1 indicated that the adsorption of both dyes followed the Langmuir and Freundlich adsorption isotherms. The value of n is not more than 1 proved that it is a mono layer adsorption.

Adsorption kinetics: The adsorption kinetics of IC and CR on TPR and silica has been studied in regular time interval to determine the kinetics of the adsorption. The equation is

$$\frac{t}{Q_t} = \frac{1}{k}Q_e^2 + \frac{t}{Q_e}$$

where, k is the rate constant, Q_e is the amount of dye adsorbed per unit mass of the adsorbent at equilibrium, Q_t is the amount of dye adsorbed per unit mass of the adsorbent at time t.

The plot of t/Q_t *versus* t gives straight lines for IC and CR adsorption on TPR and silica (Fig. 12a-b). The linear regression coefficients near to 1 indicated that the adsorption followed the pseudo-second order kinetics on TPR powder and silica. The k values can be calculated from the intercepts of these plots are given in Table-2.

TABLE-2
PSEUDO SECOND ORDER KINETICS RATE CONSTANT FOR ADSORPTION OF ANIONIC DYES (INDIGO CARMINE AND CONGO RED) ON SILICA AND TOMATO PLANT ROOT POWDER

Adsorbent	Dyes	R^2 value	Pseudo second order rate constant (k)
Tomato plant root powder	Indigo carmine	0.995	3.572×10^{-2}
	Congo red	0.989	3.364×10^{-2}
Silica	Indigo carmine	0.999	3.931×10^{-2}
	Congo red	0.998	3.362×10^{-2}

Adsorption thermodynamics: The thermodynamics parameters like free energy (ΔGº), enthalpy (ΔHº) and entropy (ΔSº) of adsorption on TPR powder and silica calculated by using Van't Hoff relationship.

$$\log K_c = \frac{\Delta S^o}{2.303R} - \frac{\Delta H^o}{2.303RT}$$

The equilibrium constant (K_c) calculated from the following equation

$$K_c = \frac{C_{Ae}}{C_e}$$

where, C_{Ae} is the adsorbed dye concentration at equilibrium, C_e is the equilibrium concentration of dye in solution.

The enthalpy and entropy can be calculated from Van't Hoff plot shown in the Fig. 13a-b. The ΔGº, ΔHº and ΔSº values calculated for the adsorption of CR and IC on TPR powder and silica given in Table-3. The positive ΔSº values for adsorption of anionic dyes (IC and CR) shown that the more disorder at the adsorption interface. The ΔGº values are not much increased with increase of temperature indicated the adsorption is almost over at room temperature. The negative values of ΔHº less than 40 KJ/mol indicated the physisorption of both dyes.

Dye recovery: Recovery of adsorbed dyes on silica and TPR powder has been carried out in the presence water at 80 ºC (Table-4). The high recovery of anionic dyes from TPR powder

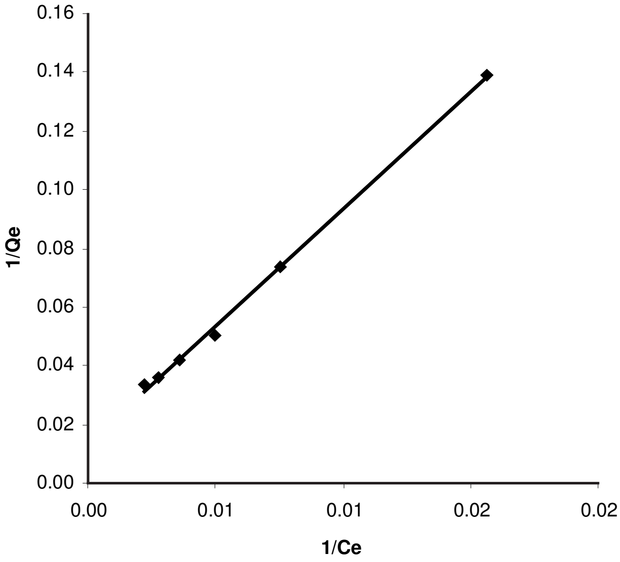


Fig. 10a. Langmuir adsorption isotherm for the adsorption of indigo carmine on tomato plant root powder

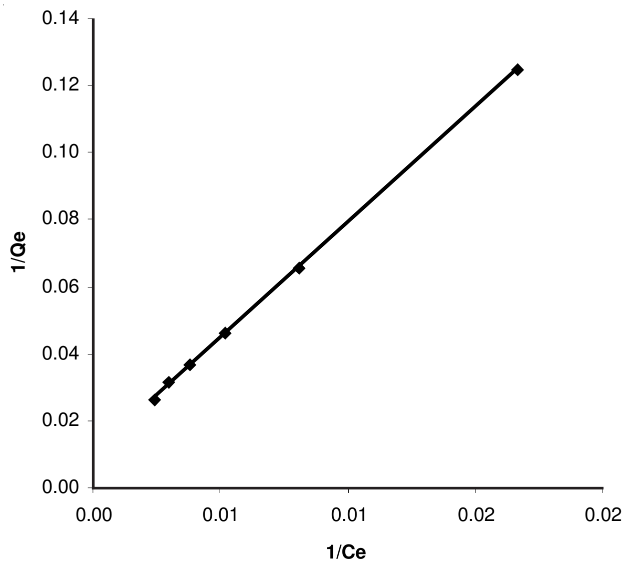


Fig. 10b. Langmuir adsorption isotherm for the adsorption of congo red on tomato plant root powder

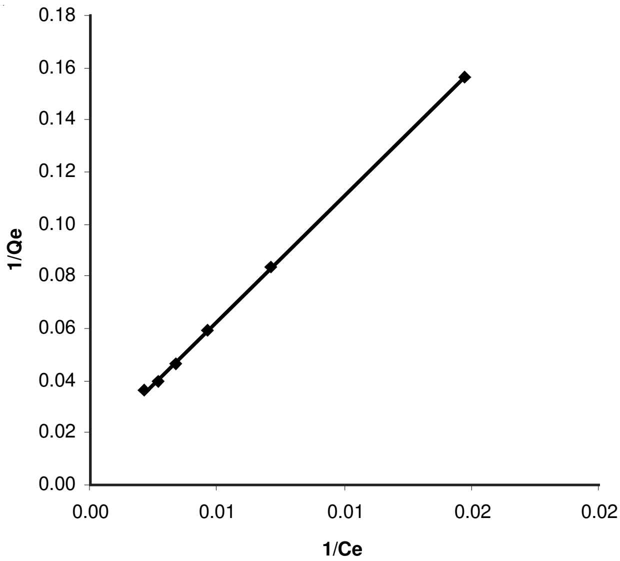


Fig. 10c. Langmuir adsorption isotherm for the adsorption of congo red on tomato plant root powder

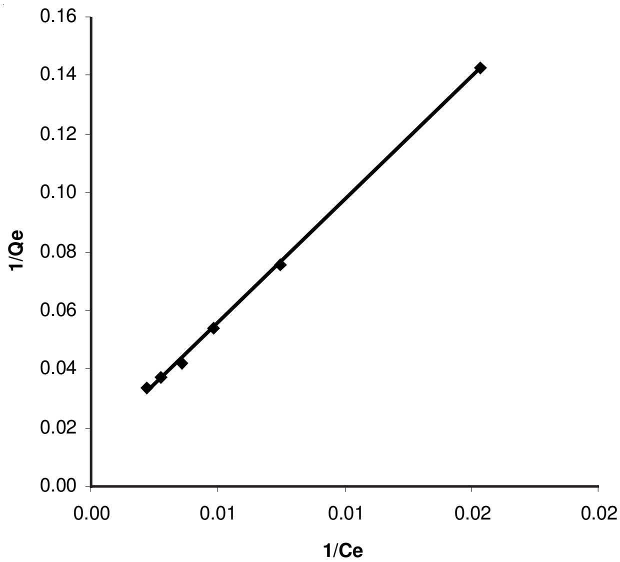


Fig. 10d. Langmuir adsorption isotherm for the adsorption of congo red on silica

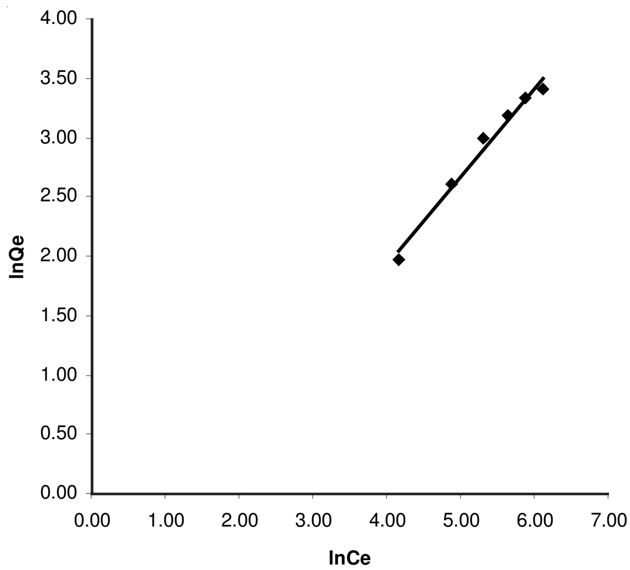


Fig. 11a. Freundlich adsorption isotherm for adsorption of indigo carmine on tomato plant root powder

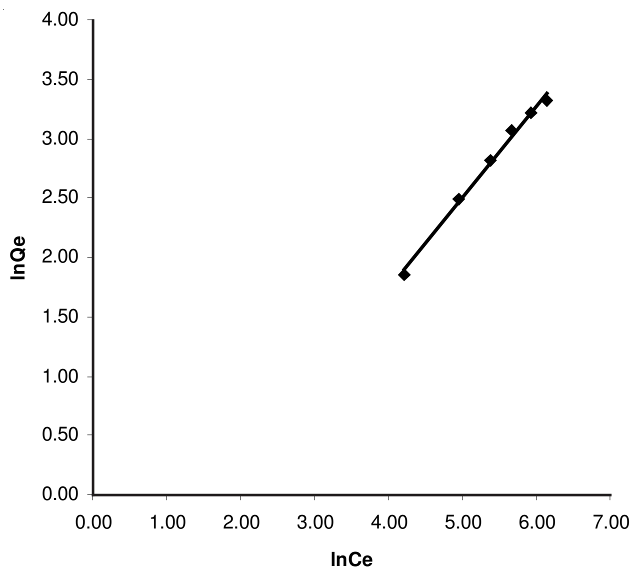


Fig. 11b. Freundlich adsorption isotherm for adsorption of congo red on tomato plant root powder

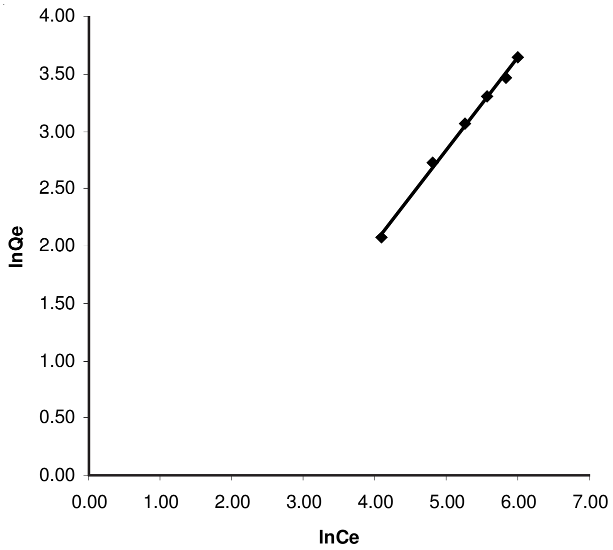


Fig. 11c. Freundlich adsorption isotherm for adsorption of indigo carmine on silica

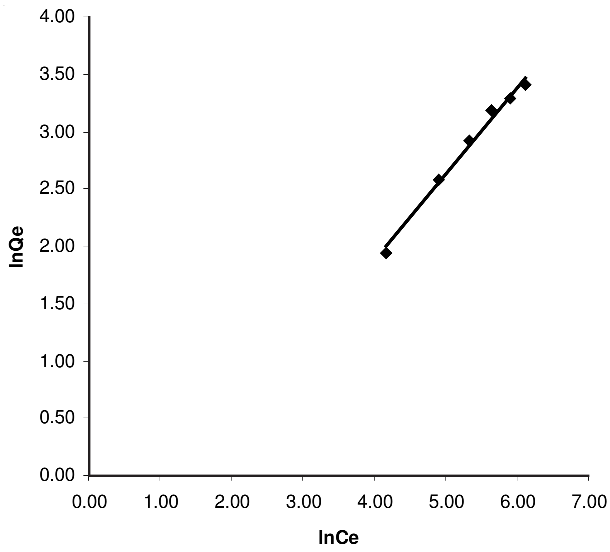


Fig. 11d. Freundlich adsorption isotherm for adsorption of congo red on silica

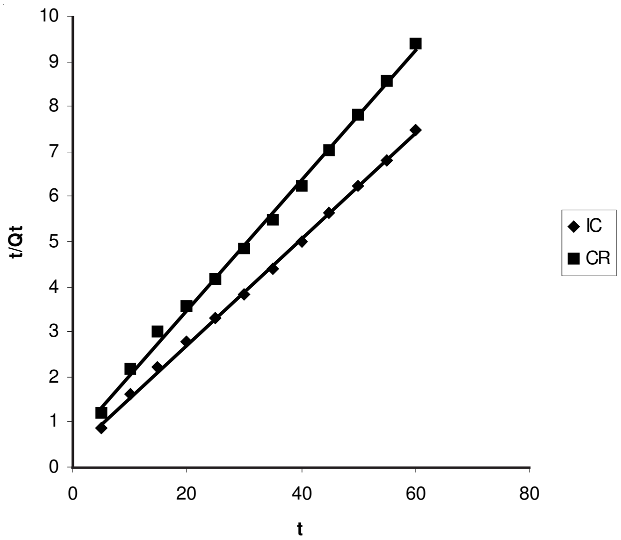


Fig. 12a. Kinetic studies for the adsorption of indigo carmine and congo red on tomato plant root powder

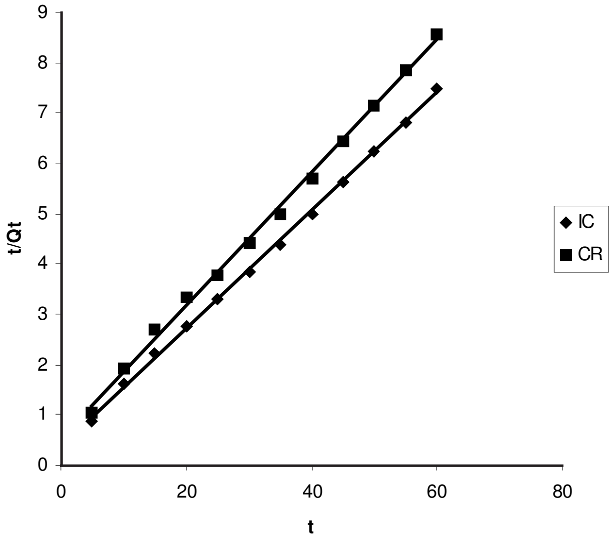


Fig. 12b. Kinetic studies for the adsorption of indigo carmine and congo red on silica

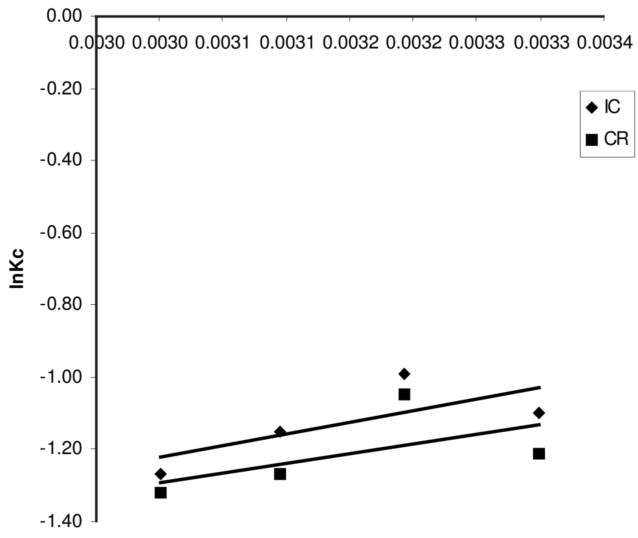


Fig. 13a. Van't Hoff Plot for the adsorption of indigo carmine and congo red on tomato plant root powder

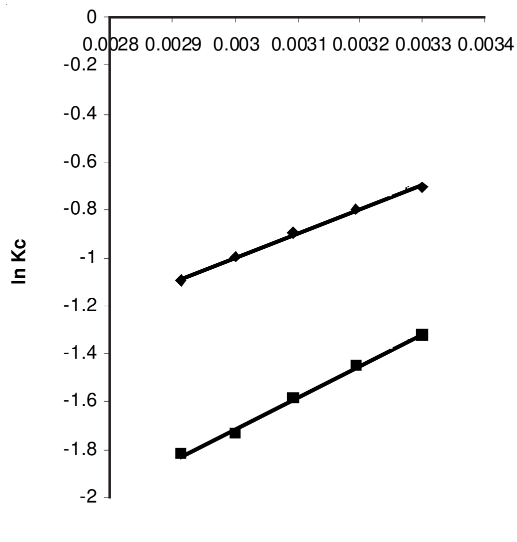


Fig. 13b. Van't Hoff Plot for the adsorption of indigo carmine and congo red on silica

TABLE-3
THERMODYNAMIC PARAMETER VALUES FOR ADSORPTION OF ANIONIC DYES (INDIGO CARMINE AND CONGO RED) ON TOMATO PLANT ROOT POWDER AND SILICA

Adsorbent	Dyes	Temperature (K)	ΔG° (KJ/mol)	ΔH° (KJ/mol)	ΔS° (J/mol K)
Tomato plant root powder	Indigo carmine	303	2.7689	-7.20396	32.14276
		313	2.5895		
		323	3.0969		
		333	3.5057		
		343	3.9550		
	Congo red	303	3.0454	-6.4741	30.54021
		313	2.7232		
		323	3.4004		
		333	3.6698		
		343	4.1368		
Silica	Indigo carmine	303	1.8998	-6.07594	25.6678
		313	1.7269		
		323	2.1497		
		333	2.4800		
		343	2.8376		
	Congo red	303	2.7689	-6.66514	30.2868
		313	2.5895		
		323	2.9516		
		333	3.3468		
		343	3.9550		

and silica may be attributed to the physisorption of dyes on TPR and silica. The high recovery indicated that these dyes may not toxic to plant roots (TPR) or soil (silica). However, the plant materials and silica are the best adsorbent for the specific recovery of anionic dyes from the dye effluent. Thus, the recovery study proved that IC and CR strongly pollute the water than the soil and plant.

TABLE-4
DESORPTION OF INDIGO CARMINE AND CONGO RED FROM TOMATO PLANT ROOT POWDER AND SILICA AT 80 °C

Adsorbent	Dye	Water (mL)	Adsorption (mg/g)	Desorption (mg/g)
Tomato plant root	Indigo carmine	50	168	143
	Congo red	50	140	123
Silica	Indigo carmine	50	156	132
	Congo red	50	136	126

Conclusion

Though IC and CR adsorption on TPR powder and silica attained within 50 min. The adsorption data well matched with the Langmuir and Freundlich adsorption isotherm models and followed pseudo second order kinetics. The values of ΔH° indicated that the adsorption not much increased with increase of temperature due to the less interaction (physisorption) between anionic dyes and the adsorbents (silica and TPR powder). The recovery of both dyes from the adsorbents in water at 80 °C was very high, but the adsorption was poor. The above studies proved that the anionic dyes have strong affinity towards water. Thus, the anionic dyes are polluting the water than plant and soil.

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