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Adsorption Of Rhodamine B Dye And Co^{2+} Ions Onto Tamarind Seed Powder

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Abstract

The present work describes adsorption of Rhodamine B dye and Co^{2+} ions from its aqueous solution onto tamarind seed powder (TSP). Initial concentration, pH, adsorbent dose and contact time with various temperature have been studied, in which pH was found to be most effective. The adsorption data were mathematically analyzed using adsorption isotherm like Freundlich and Langmuir isotherm to study adsorption mechanism of Rhodamine B dye and Co^{2+} ions onto this seed powder. The highest removal efficiency of TSP (1.2 g) is 99.33 % for Rhodamine B dye at pH 5 within 20 min and 88.43 % removal of Co^{2+} ions at pH 3 within 20 min. Langmuir isotherm was found to be most applicable. The reaction was found to be pseudo second order.

Keywords: Tamarind, Rhodamine B, Langmuir isotherm.

Abbreviations

TSP Tamarind Seed Powder

1. Introduction

One of the most important issues currently facing human beings is the environmental pollution. In the last few years it was increased exponentially and in terms of its effects on living creatures reached alarming levels. Hazardous heavy metals and dyes are the pollutants that have direct effect on living beings. Water of high quality is needed for agriculture, industrial, domestic and commercial uses. All these sources are thrown billions of gallons of waste to fresh water bodies every day. The requirement for water is increasing while all the water resources are becoming slowly unfit for use due to improper waste disposal. The task of providing proper treatment facility is difficult for all polluting sources and also expensive, hence there is pressing demand for innovative technologies which are low cost, require low maintenance and are energy efficient. Various methods are available for removal of such dyes and heavy metals like coagulation (Stephenson & Sheldon 1996), precipitation (Stephenson & Sheldon 1996), reverse osmosis (Forgacs et al., 2004), photo-degradation (Wu et al., 1999), electrochemical oxidation (Kusvuran et al., 2004), ozonation (Robinson et al., 2001) and adsorption.

Adsorption technique is economically favourable and technically easy to separate as the requirement of the control system is minimum. Activated carbon is commonly used as an adsorbent for the removal of dyes and heavy metals (Wu et al., 1999). But it is costly, and therefore, it is very important to develop an alternative low-cost adsorbent. Various low-cost adsorbents by various workers are clay materials, zeolites, siliceous materials, coffee husk-based activated carbon, decreased coffee bean, marine algae, chitosan and ion exchange resin have been used for the removal of dyes and heavy metals from aqueous solution (Kyzas et al., 2012; Ahmad & Rahman 2011; Baek et al., 2010). Present study demonstrates use of natural material TSP for the removal of Rhodamine B dye and Co^{2+} ions from their aqueous solutions.

2. Materials and Methods

2.1 Preparation of adsorbent

Tamarind used in the present study was collected from the local market of Nashik, Maharashtra, India. It was first cleaned and washed with tap water and then with distilled water several times to remove dust like impurities. The cleaned seed was oven dried at 60 ^{0}C for 24 h and then husk of seed was removed. The seed was powdered, pulverized and stored in a plastic bottle for further use. No other chemical or physical treatments were used prior to adsorption experiments.

2.2 Preparation of adsorbate

Rhodamine B dye and Co^{2+} ions used in the present study were of commercial pure and were used without further purification. Stock solutions were obtained by dissolving the required quantity of dyes and heavy metals in double-distilled water. Experimental dyes and heavy metal solutions were prepared by diluting the stock solution with suitable volume of distilled water to the desired concentration.

2.3 Adsorption Experiment

Adsorption studies were carried out in batch systems by adding 200 mg of adsorbent in 50 ml of adsorbate solution of known concentration. The concentrations of adsorbate in the solutions before and after adsorption were estimated using a UV–Visible spectrophotometer analysis (Camspec M550). The % removal efficiency is calculated as follows:

$$\% \text{ removal} = \frac{\mathrm{Co}-\mathrm{Ce}}{\mathrm{Co}} \times 100$$

Where C_o and C_e are the initial and final concentration respectively.

Results and Discussion

Fourier Transform Infrared (FTIR) Spectroscopy

Figure 1 depicts FT-IR spectrum (4000-400 cm^{-1}) for TSP. The peaks observed at the positions 3205.69 cm^{-1} and 2978.09 cm^{-1} confirms presence of amino and carboxylic acid group. The peaks at 1668.43 cm^{-1} and 1400.32 cm^{-1} are due to primary amine and nitro compound and also 1022.27 cm^{-1} of primary alcohol (C-O) stretching.

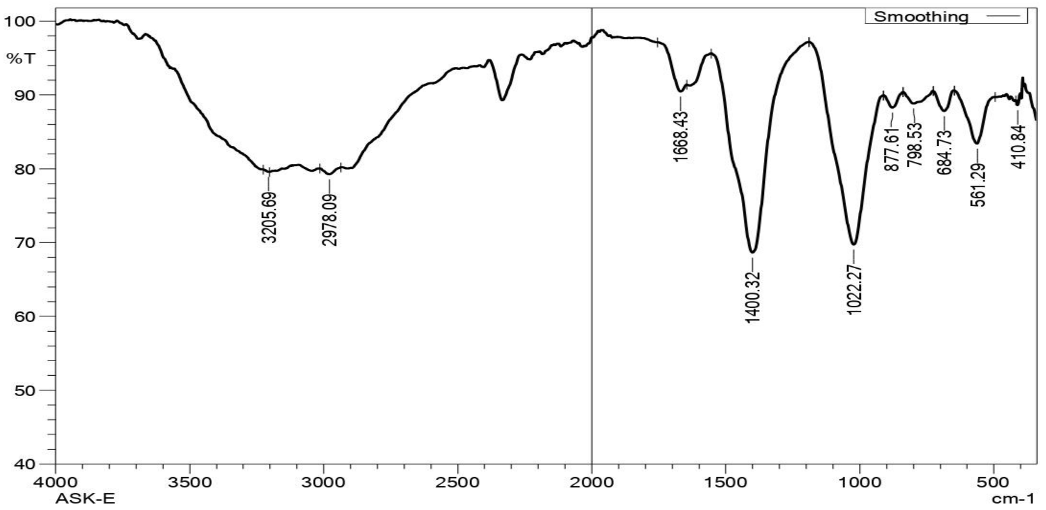

Fig. 1 FT-IR spectrum of TSP.

X-ray Powder Diffraction (XRD)

X-ray diffraction pattern of the TSP is shown in Fig. 2. The XRD- pattern obtained shows diffraction peaks which indicating that the crystalline size is small. The (hkl) plane obtained from XRD patterns are shown in Fig.2.

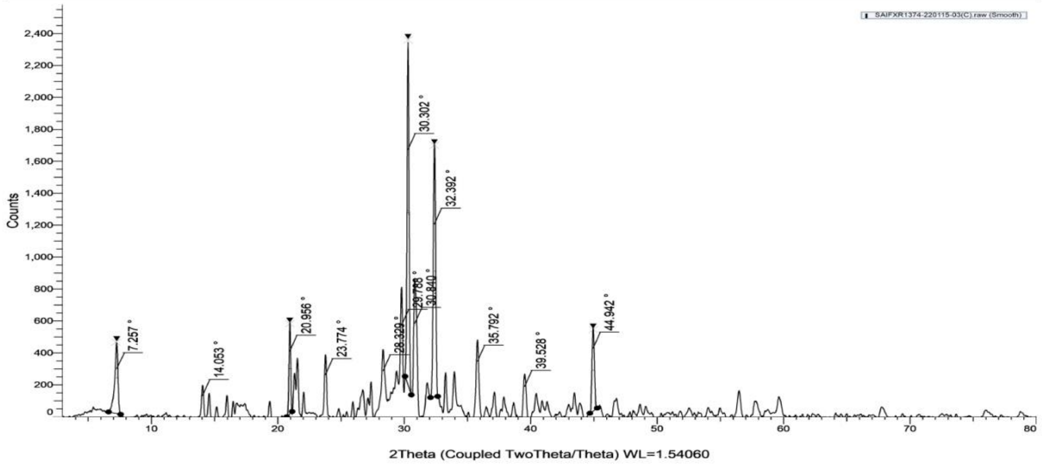

Fig. 2 XRD analysis of TSP.

Brunauer - Emmett - Teller (BET) Surface Area

Figure 3 depicts N_2 adsorption/desorption isotherm for TSP. It shows that the N_2 adsorption/desorption isotherm for TSP satisfies IV N_2 adsorption/desorption isotherm with H1 hysteresis. The surface area (S_{BET}) estimated by this method was found to be 21.74 m^2/g

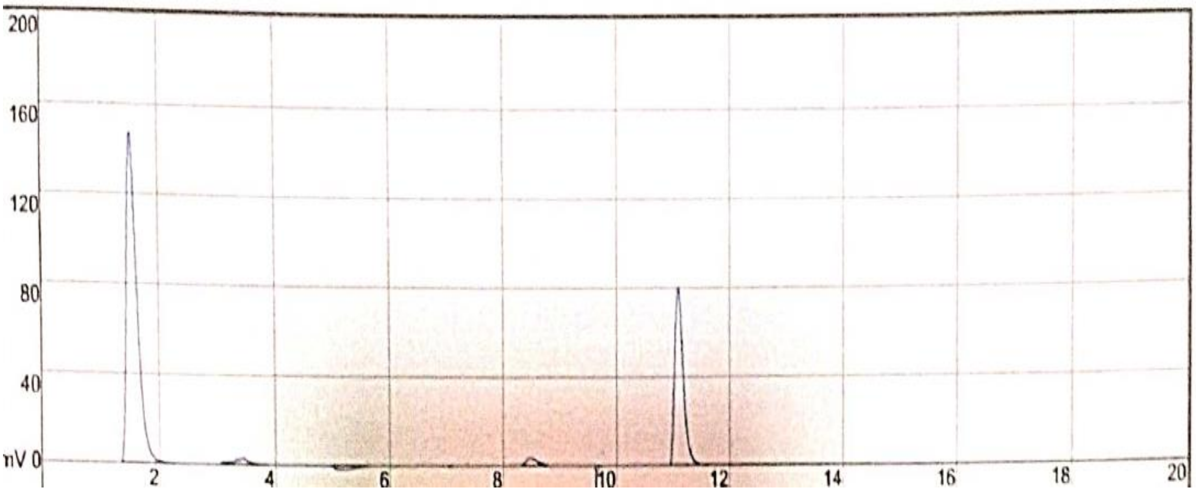

Fig. 3 BET Surface area of TSP.

Determination of pHzpc

The zero point charge (pHzpc) was evaluated by using a standard technique (Sartape et al. 2013). It is important to know the adsorption mechanism by determining the zero point charge of the adsorbent (Govindasmay et al. 2009). It was worked out by adjusting the pH of a solution containing 0.01 M NaCl between 1 and 11 using NaOH and HCl, and then, 0.1 g of Jackfruit seed powder was added to 50 ml of the solution. The obtained pH was recorded after stabilizing the initial pH after 24 h. The graph of final pH versus initial pH (Fig. 4) was used to identify pH_{ZPC} , which is the point in which both initial and final pH values are equal (Govindasmay et al. 2009). In this study, the pH_{ZPC} of the TSP was found to be 5.14.

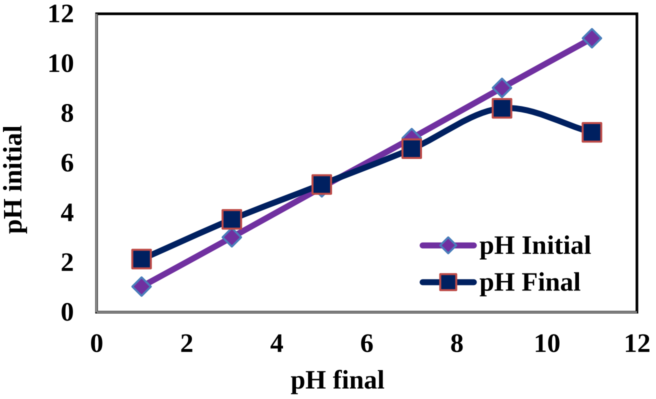

Fig. 4 Determination of pHzpc of TSP.

Effect of initial concentration

The effect of initial concentration was performed by adding known amount of adsorbent in 50 ml of aqueous solution at different concentrations for 120 min. The solutions were shaken properly and then filtered at proper time interval and residual concentration was measured using spectrophotometric method.

The solution adsorbed at equilibrium q_e (mg/g) was calculated using following equation,

$$q_e = \frac{(Co - Ce)V}{M}$$

Where, C_o and C_e (mg/L) are the liquid phase concentration of dye and metal ions at initial concentrations and equilibrium conditions, V (L) is volume of the aqueous solution and m (g) is mass of adsorbent. The function of initial concentration is the rate of adsorption. The effect of initial concentration on the adsorption of Rhodamine B dye and Co^{2+} ion are shown in Fig. 5. Figure 5 indicates that higher adsorption was found to take place at lower concentrations (2 mg/L for dye and 40 mg/L for metal ion). This may be due to the interaction of dye and metal ion present in solution with binding sites (Azouaou et al., 2010; Mausumi et al., 2006; Mohammad Mehdi et al., 2011). At higher concentration, more dyes and metal ions are left unadsorbed in solution due to the saturation of adsorption sites. At lower concentration, the percentage uptake was higher due to larger surface area of adsorbent being available for adsorption. When the concentration became higher, the percentage removal decreased since the available sites for adsorption became less due to saturation of adsorption sites.

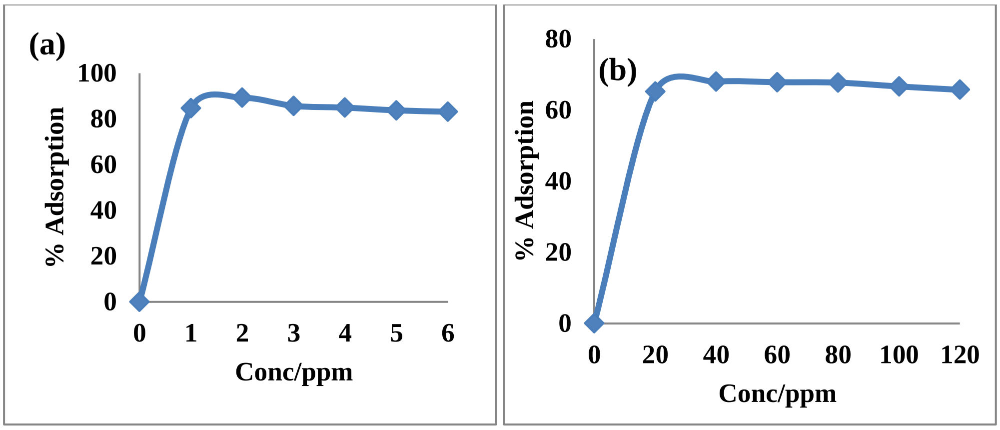

Fig. 5 Variation of concentration of (a) Rhodamine B dye and (b) Co^{2+} ions onto TSP.

Effect of pH

The pH of the aqueous solution is an important adsorption controlling parameter in the adsorption process. The effect of pH solution on the adsorption of Rhodamine B dye and Co^{2+} ion is shown in Fig.6.The effect of pH was studied by varying pH range from 1 to 13. Then pH was adjusted by using 0.1 N NaOH and 0.1 N HCl solutions. The initial concentrations of Rhodamine B dye were 2 mg/L and for Co^{2+} ions were 40 mg/L. Other parameters such as adsorbent dose, temperature and contact time remained constant. The percentage removal of dye and heavy metal was calculated as

$$\% \text{ removal} = \frac{(\mathrm{Co}-\mathrm{Ce})}{\mathrm{Co}} \text{ X } 100$$

Where, $C_0$and C_e (mg/L) are the initial and final concentrations of solution respectively.

The maximum removal efficiency by TSP for Rhodamine B dye is 89.56 % at pH 5 and for Co^{2+} ions is 76.13 % at pH 3 respectively.

At lower pH values the H^+ concentration is high and therefore protons can compete with the dyes and metal ions for surface sites. When pH increases, there is a decrease in positive surface charge due to the protonation of the sorbent functional group, which results in a lower electrostatic repulsion between the positively charged metal ion and the surface of the adsorbent (Azouaou et al., 2010; Babu & Gupta 2008; Gupta & Rastogi 2007). As pH value is higher, more exchangeable cations contained in the adsorbent can be exchanged with dye and metal ion due to weak competitive adsorption of H^+ ions.

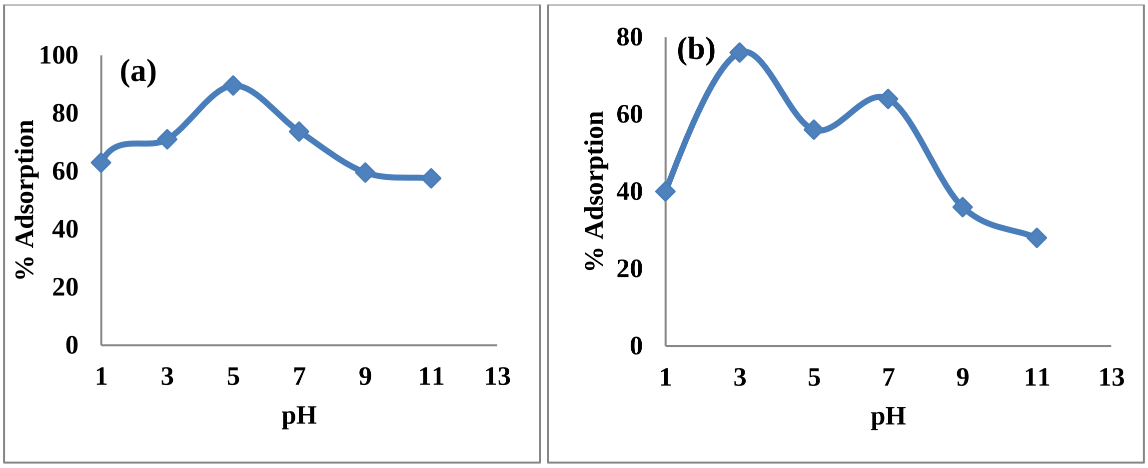

Fig. 6 Effect of pH of (a) Rhodamine B dye and (b) Co^{2+} ions onto TSP.

Effect of Adsorbent Dose

The effect of adsorbent dose was studied by changing the amount of TSP (0.2 g to 1.2 g) by keeping initial concentration, temperature and pH constant for 120 min. The results obtained for effect of adsorbent dose is shown in Fig. 7. It was found that percentage removal increases with increase in amount of TSP (Azouaou et al., 2010; El-Said et al., 2010; Saifuddin & Kumaran 2005). It was observed that, the removal efficiency by TSP was increased from 88.55 to 95.29 % for Rhodamine B dye and 60.11 to 80.21 % for Co^{2+} ions, where the adsorbent dose increased from 0.2 to 1.2 g. After 0.6 g of dose, the percent adsorption of each dye and metal were increased slowly. This is because; as the dose increased, there was an increment of active sites present in the adsorbent. As a result, there is fast superficial adsorption onto adsorbents surface that produce lower concentration for dye and metal solution, compared to the concentration of dye and metal, at lower dose of adsorbent. The maximum removal was found at 1.2 g, so that, 1.2 g of adsorbents maintained to be as equilibrium dose, used for all subsequent experiments and considered to be sufficient for the removal of Rhodamine B dye and Co^{2+} ions.

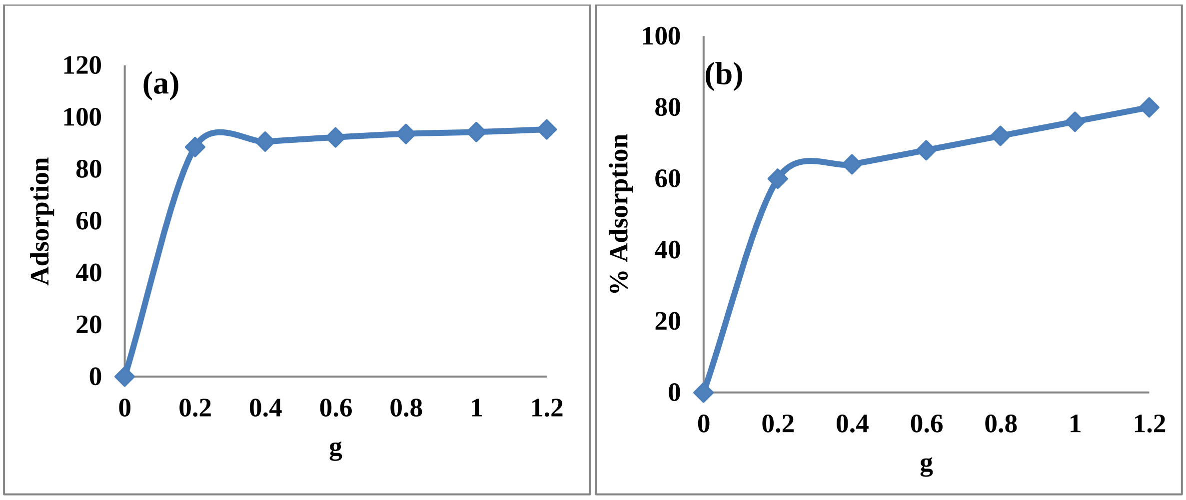

Fig. 7 Effect of adsorbent dose of (a) Rhodamine B dye and (b) Co^{2+} ions onto Tamarind seed powder

Effect of Contact Time with Temperature

The effect of contact time was studied by varying contact time and keeping initial concentration, pH and adsorbent dose constant for 60 min (Fig. 8). Figure 8 shows that the percentage uptake increases with time and after some time, it reaches a constant value where no more dye and metal ion can be removed from the solution. This effect was initially observed within first 20 min in presence of adsorbent. The percentage removal of Rhodamine B dye and Co^{2+} ion by TSP reached equilibrium within 30 min. The variation of the contact time on removal of Rhodamine B dye and Co^{2+} ions is reported and results obtained are shown in Fig. 8. It is clearly seen from the figures that maximum adsorption was found at 20 min. indicates complete adsorption. Hence, optimal contact time was chosen 20 min for Rhodamine B and Co^{2+} using TSP. A careful inspection of Fig. 8 (a-f) shows that adsorption of Rhodamine B dye is found highest 99.33 % and 88.43 % for Co^{2+} ion. Further, in comparison with adsorbent we observed that TSP is better choice as an adsorbent for removal of Rhodamine B dye and Co^{2+} ions.

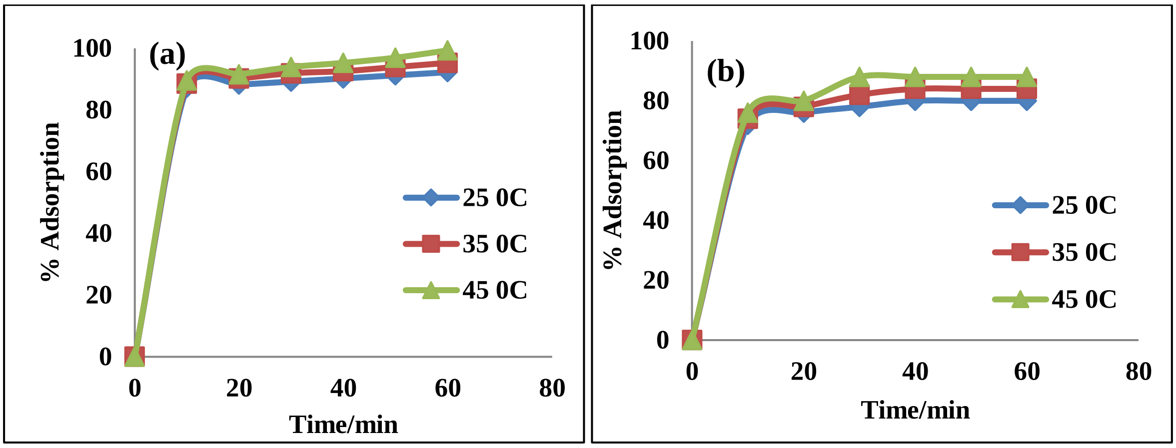

Fig. 8 Effect of contact time of (a) Rhodamine B dye and (b) Co^{2+} ions onto TSP with temperature.

ADSORPTION ISOTHERMS

Langmuir isotherm

Langmuir isotherm model is based on assumption that a saturated monolayer of adsorbate molecules is present on the adsorbent surface, the adsorption energy is constant and there is no migration of adsorbate molecules in the surface plane when maximum adsorption capacity occurs. The linear form of Langmuir adsorption equation is

$$\frac{1}{Q_e} = \frac{1}{Q_0} + \frac{1}{Q_0 k_L C_e}$$

Where C_e(mg/L^{-1}) - is the equilibrium concentration of adsorbate, Q_e(mg/g) - is the amount of metal adsorbed per gram of the adsorbent at equilibrium, Q_0(mg/g) - is the maximum monolayer coverage capacity, K_L(L/mg) - is the Langmuir isotherm constant.

The values of $K_L$and q_m were computed from the slope and intercept of the Langmuir plot of $1/Q_e$ versus $1/C_e$(Langmuir, 1918). The essential features of the Langmuir isotherm may be expressed in terms of equilibrium parameter R_L, which is a dimensionless constant referred to as separation factor or equilibrium parameter (Webber & Chakravarti 1974).

$$R_L = \frac{1}{1+(1+K_L C_0)}$$

The values of slope and intercept can be determined from linear plots of experimental data ($1/Q_e$) versus ($1/C_e$) for Rhodamine B dye and Co^{2+} ions (Fig. 9).R_L value indicates the adsorption nature to be either unfavourable if R_L >1, linear if R_L = 1, favourable if $0 < R_L < 1$ and irreversible if R_L = 0. R^2 values are also tabulated for the observed linear relationship to be statistically significant. If the value of R^2 is near to 1, it shows that this isotherm is applicable for adsorption studies. Table 2 shows the Langmuir isotherm constants and their correlation coefficients. The adsorption of Rhodamine B and Co^{2+} onto surface of TSP was favourable as R_L values calculated were in between 0 and 1 (Table 2).

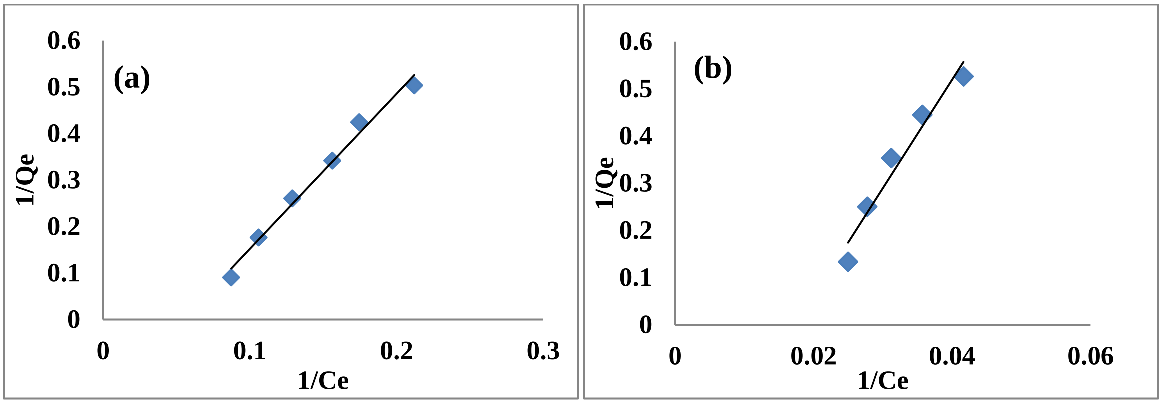

Fig. 9 Langmuir isotherm plot of (a) Rhodamine B dye and (b) Co^{2+} ions onto TSP.

Freundlich isotherm

The Freundlich isotherm model is an empirical relationship and is based on an assumption that the adsorption energy of a metal ion binding to a site of an adsorbent depends on whether the adjacent sites are already occupied or not. The linear form of Freundlich adsorption equation is

$$\log Q_e = \log k_f + \frac{1}{n}\log c_e$$

Where k_f (mg/g) - Freundlich isotherm constant, n is the adsorption intensity. The constant k_f - approximate indicator of adsorption capacity, while 1/n - function of the strength of adsorption in the adsorption process (Voudrias et al., 2002). If n = 1 then the partition between the two phases are independent of the concentration. If value of 1/n is below one it indicates a normal adsorption. On the other hand, 1/n being above one indicates cooperative adsorption (Mohan & Karthikeyan 1997).k_f and n are parameters characteristic of the sorbent–sorbate system, which must be determined by data fitting, whereas linear regression is generally used to determine the parameters of kinetic and isotherm models (Guadalupe et al., 2008). The value of 1/n indicates that adsorption is favourable and value more than 1 implies cooperative adsorption. The values of the constants can be determined from the intercept and slope of the linear plots of the experimental data of (ln Q_e) versus (ln C_e) for Rhodamine B dye and Co^{2+} ions (Fig.10) as shown in Table 2.

Comparing the data in Table 2, the Langmuir isotherm model showed the best fit with the highest R^2 value of 0.99 for Rhodamine B dye and Co^{2+} ion as compared to the Freundlich isotherm model. In addition, the values of 1/n are less than 1. Figure 10 shows Freundlich plot for adsorption of Rhodamine B dye and Co^{2+} ion.

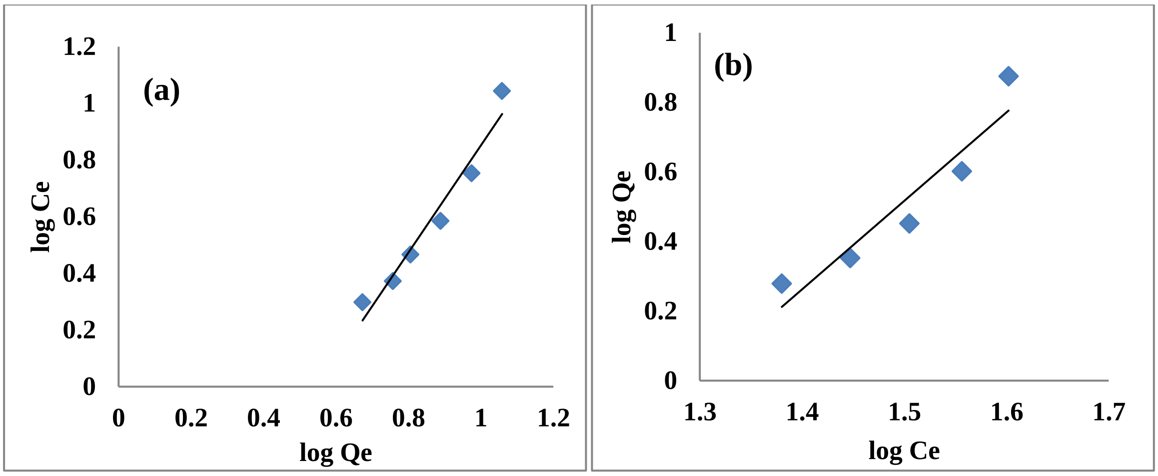

Fig. 10 Freundlich isotherm plot of (a) Rhodamine B dye and (b) Co^{2+} ions onto TSP.

Table 2 Langmuir and Freundlich Isotherm model constants and correlation coefficients for the adsorption of Rhodamine B dye and Co^{2+} ion on TSP.

Tamarind seed powder							
	Langmuir constants				**Freundlich constants**		
Dye/Metal	**K_L (L mg^{-1})**	**R_L**	**Q_0**	**R^2**	**K_F**	**n**	**R^2**
Rhodamine B	0.05428	0.1346	55.24	0.987	10.9395	0.5238	0.854
Co^{2+}	0.0174	0.2673	25.13	0.952	0.000502	0.3931	0.890

ADSORPTION THERMODYNAMICS

Following equations (Laidler & Meiser1999) are used to evaluate thermodynamic parameters such as standard Gibbs free energy (ΔG), entropy change (ΔS) and enthalpy (ΔH).

$$\Delta G = - RT \ln K_a \qquad (1)$$

$$\Delta G = \Delta H - T\Delta S \qquad (2)$$

$$\text{Thus, } \ln K_a = - (\Delta H/RT) + (\Delta S/R) \qquad (3)$$

Where, $K_a = C_a/C_e$ (distribution coefficient) C_a = metal ion concentration after adsorption ($mg.g^{-1}$) and C_e = metal ion concentration ($mg.L^{-1}$) at equilibrium.

The well known thermodynamic aspects including ΔH, ΔS and ΔG for the adsorption of Rhodamine B dye and Co^{2+} ions on TSP were evaluated using equation 2. The plot between ln K_a and 1/T gives ΔH and ΔS in terms of slope and intercept (Fig. 11) and data obtained is incorporated in Table 3. A careful inspection of Table 3 reveals that ΔG value for dyes and metal ions is negative suggests that the process of adsorption is spontaneous. ΔH values calculated for adsorption process of Rhodamine B is dye 57.4663 $kJ.mol^{-1}$ and Co^{2+} ions is 13.3024 $kJ.mol^{-1}$ The values of ΔH indicate the process is physical sorption and it is endothermic in nature. The ΔS values for adsorption of Rhodamine B dye found to be 0.2041 and for Co^{2+} ions are found to be 0.05107 $kJ.mol^{-1}$. The positive values of ΔS confirm the increase in entropy because of adsorption.

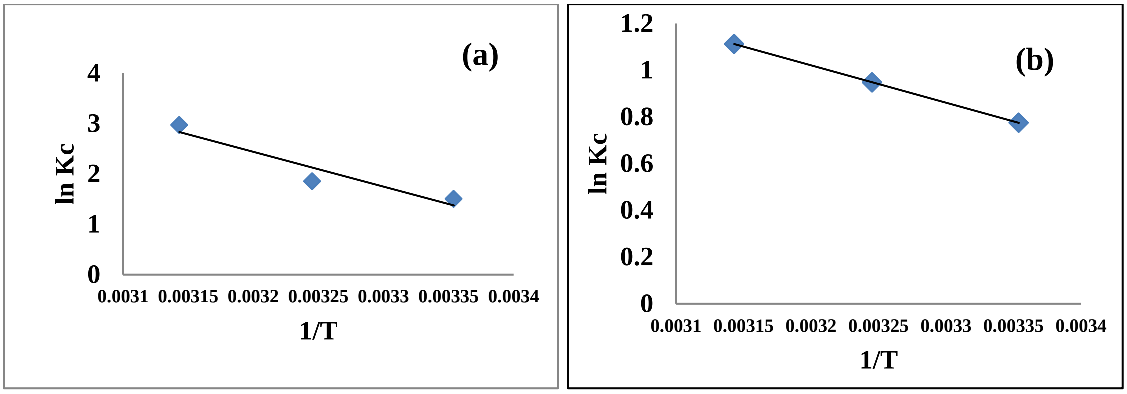

Fig. 11 Plot of ln K_a Vs 1/T for adsorption of (a) Rhodamine B dye and (b) Co^{2+} ions on TSP.

Table 3 Thermodynamic parameters of the present study, temperature (298.15, 308.15, 318.15) K, for Rhodamine B dye and for Co^{2+} ions Gibbs free energy ΔG, Distribution coefficient K_a, Enthalpy change ΔH and Entropy change ΔS

Dye/Metal	**Temperature/K**	**K_a**	**Δ G**	**Δ H/ ($kJmol^{-1}$)**	**ΔS/ ($kJmol^{-1}$)**
Rhodamine B	298.15	1.5070	- 3735.68	57.4663	0.2041
	308.15	1.8532	- 4747.94		
	318.15	2.9733	- 7864.66		
Co^{2+}	298.15	0.7748	- 1920.76	13.3024	0.05107
	308.15	0.9478	- 2428.45		
	318.15	1.1124	- 2942.42		

ADSORPTION KINETICS

In order to define the adsorption kinetics of Rhodamine B dye and for Co^{2+}ion, the kinetic parameters were studied for the adsorption processes for the contact time ranging from 10 to 120 min and pseudo first order and second order were applied to experimental data as shown in Fig.12 and Fig.13.

The first order kinetic equation is,

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}\, t$$

Where q_e and q_t are the adsorption capacity at equilibrium and at time t respectively and k_1 is the rate constant of the pseudo first order adsorption process.

The second order kinetic equation is,

$$\frac{t}{q_t} = \frac{1}{k_2} + \frac{1}{q_e}\, t$$

The comparison of experimental adsorption capacities (q_{exp}) and the predicted values (q_{cal}, k_1, k_2) from pseudo first order and pseudo second order are given in Table 4. The pseudo first order was not satisfactory to explain the experimental data, whereas calculated q_{cal} values derived from pseudo second order model for sorption of dyes and metal ions were very close to each other to the experimental (q_{exp}) values. The second order equation appeared to be the better fitting model than pseudo first order because it has higher R^2 value.

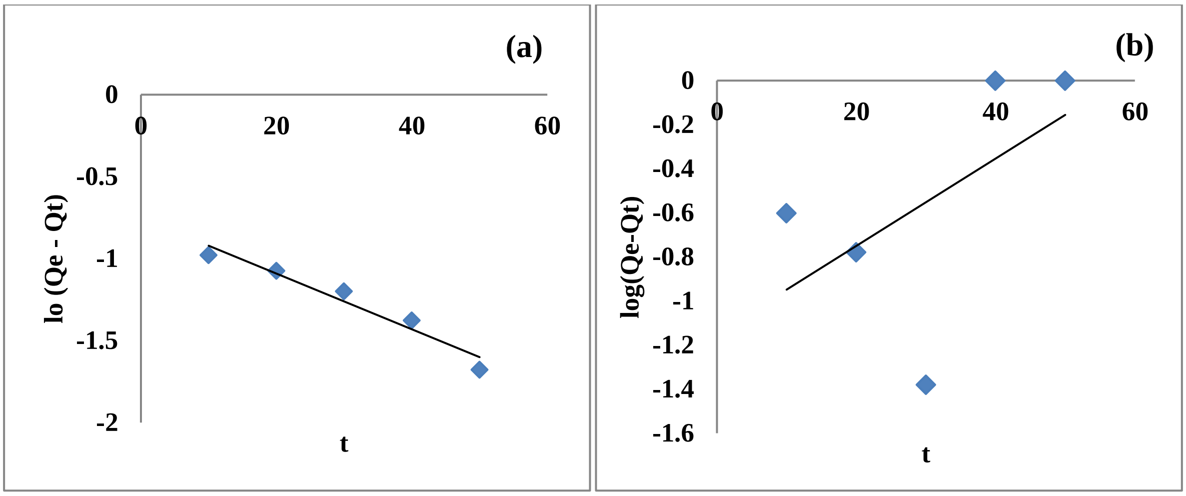

Fig. 12 Pseudo first order plot of (a) Rhodamine B dye and (b) Co^{2+} ions on TSP.

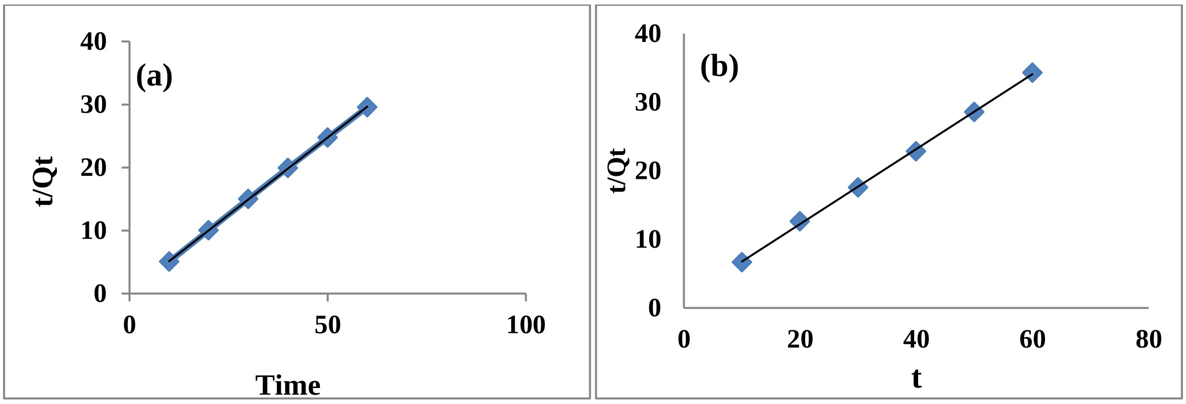

Fig. 13 Pseudo second order plot of (a) Rhodamine B dye and (b) Co^{2+} ions on TSP.

Table 4 Kinetic parameter calculated by applying pseudo-first and second-order for the adsorption of Rhodamine B dye and Co^{2+} ions on TSP.

Tamarind seed powder								
	pseudo first order kinetic model				**pseudo second order kinetic model**			
Dyes/Metals	**q_e (exp)**	**q_e (mg g^{-1})**	**k_1 (min^{-1})**	**R^2**	**q_e (exp)**	**q_e (mg g^{-1})**	**k_2(g mg^{-1} min^{-1})**	**R^2**
Rhodamine B	1.9219	0.3288	-0.005758	0.951	1.9219	2.0408	1.0913	0.999
Co^{2+}	1.75	0.07145	0.04376	0.291	1.75	1.8315	0.2281	0.999

CONCLUSIONS

Natural material, TSP was identified as an effective adsorbent for the removal of Rhodamine B dye and Co^{2+} ions from their aqueous solutions. TSP was effective toward removing dyes and heavy metals from their aqueous solutions. The adsorption process best fitted to the Langmuir isotherm model. The kinetic data showed that the pseudo second order model is applicable. It could be used as low cost, efficient and effective adsorbent for water purification.

References

Ahmad, M.A., Rahman, N.K. (2011) Equilibrium, kinetics and thermodynamic of Remazol Brilliant Orange 3R dye adsorption on coffee husk-based activated carbon. Chem Eng J., **170**, 154–161.

Al-Degs, Y., Khraisheh, M.S., Allea, M. Ahmad (2003) Effect of carbon surface chemistry on the removal of reactive dyes from textile effluent, Water Res., **34**, 927–935.

Azouaou, N., Sadaoui, Z., Djaafri, A., Mokaddem, H. (2010) Adsorption of cadmium from aqueous solution onto untreated coffee grounds: Equilibrium, kinetics and thermodynamics. Journal of Hazardous Materials, **184**, 126–134.

Babu, B.V., Gupta, S. (2008) Adsorption of Cr (IV) using activated neem leaves: kinetic studies. Adsorption, **14**, 85-92.

Baek, M.H., Ijagbemi, C.O., Jin, O.S., Su, Kim D. (2010) Removal of Malachite Green from aqueous solution using degreased coffee bean. J. Hazard Mater **176**, 820–828.

Dikpati, M., Peter, A.G., Keith, B.M. (2008) Penetration of Dynamo-generated Magnetic Fields into the Sun's Radiative Interior Mausumi. The Astrophysical Journal, **638**, 564.

Faria, P.C., Orfão, J.J., Pereira, M.F. (2004) Adsorption of anionic and cationic dyes on activated carbons with different surface chemistries, Water Res., **38**, 2043–2052. doi:http://dx.doi.org/10.1016/j.watres.2004.01.034. 15087185.

Forgacs, E., Tibor, C., Gyula, O. (2004) Removal of synthetic dyes from wastewaters: a review. Environ Int., **30**, 953–971.

Guadalupe, R., Reynel-Avila, H.E., Bonilla. Petriciole A., Cano Rodrı´guez, I., Velasco-Santos, C., Martı´nez Herna´ndez, A.L. (2008) Recycling poultry feathers for Pb removal from wastewater: kinetic and equilibrium studies. Proc World Acad Sci Eng Technol, **2**(11), 338–346.

Gupta, V.K., Rastogi, A. (2007) Biosorption of lead from aqueous solutions by green algae Spirogyra species: kinetic and equilibrium studies. Journal of Hazardous Material, **152**, 407-414.

Kusvuran, E., Gulnaz, O., Irmak, S., Matanur, O., Yavuz, H., Erbatur, O. (2004) Comparison of several advanced oxidation processes for the decolorization of Reactive Red 120 azo dye in aqueous solution. J Hazard Mater., **109**, 85–93.

Kyzas, G.Z., (2012) A decolorization technique with spent greek coffee grounds as zero-cost adsorbents for industrial textile wastewaters. Materials, **5**, 2069–2087.

Langmuir, I., (1918) The adsorption of gases on plane surfaces of glass, mica and platinum. J Am Chem Soc. **40**, 1361–1403.

Mohan, S.V., Karthikeyan, J. (1997) Removal of lignin and tannin colour from aqueous solution by adsorption onto activated charcoal. Environ Pollut., **97**(1-2), 183-187.

Movahedi, M.M., Yousefy, M. Exploring effective factors in ergonomic system responsiveness to managers and employees' requirements: a case study. Iranian journal of development & evolution management.

Robinson, T., McMullan, G., Marchant, R., Nigam, P. (2001) Remediation of dyes in textile effluent: a critical review on current treatment technologies with a proposed alternative. Bioresour Technol. **77**, 247–255.

Saifuddin, M.N., Kumaran, P. (2005) Removal of heavy metal from industrial waste water using Chitosan coated oil palm shell charcoal. Environ. Biol. **8**(1), 1-13.

Stephenson, R.J., Sheldon, J.B. (1996) Coagulation and precipitation of mechanical pulping effluent 1: Removal of carbon and turbidity. Water Res., **30**, 781–792.

Voudrias, E., Fytianos, F., Bozani, E. (2002) Sorption–desorption isotherms of dyes from aqueous solutions and wastewaters with different sorbent materials. Glob Nest, **4**, 75–83

Webber, T.W., Chakravarti, R.K. (1974) Pore and solid diffusion models for fixed bed adsorbers. J Am Inst Chem Eng., **20**, 228–238.

Wu, K., Xie, Y., Zhao, J., Hidaka, H. (1999) Photo-Fenton degradation of a dye under visible light irradiation. J Mol Catal A Chem., **144**, 77–84