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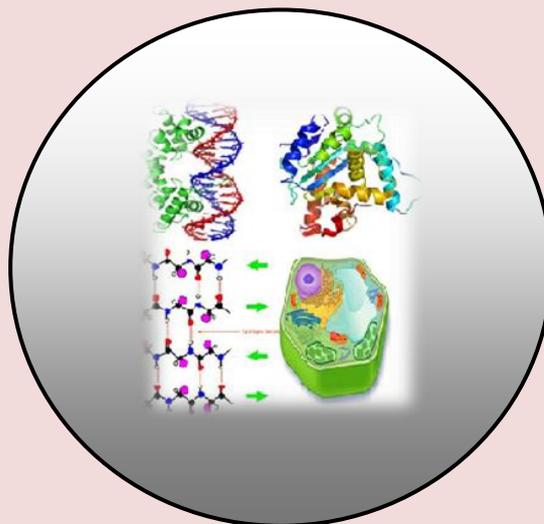
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## ***Syzygium cumini* Seed Powder as an Efficient Adsorbent for Removal of Dyes and Heavy Metal Ions from their Aqueous Medium**

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### **ABSTRACT**

*Present study focused on the efficient removal of dyes (Basic Blue 9, Acid Blue 9 and Mordant Black 11) and heavy metal ions ( $Pb^{2+}$ ,  $Cd^{2+}$  and  $Sn^{2+}$ ) by adsorption onto low cost natural adsorbent *Syzygium cumini* seed powder (SCSP) from their aqueous medium. The existence of surface functional groups like  $-OH$ ,  $-H$ ,  $-C=O$  and surface morphology of SCSP were analyzed by spectroscopic and electron microscopic technologies. The effect of various parameters such as initial concentration of adsorbate, pH, adsorbent dose and contact time were studied. The adsorption capacity of seed powder increases with contact time and a plateau reached at equilibrium. Various isotherms including Langmuir and Freundlich were applied for the equilibrium adsorption data. The kinetic study of dyes and heavy metal ions follow pseudo-second order kinetics. SCSP showed highest removal efficiency towards Basic blue 9 (95.63 %) and  $Pb^{2+}$  ion (59.44 %).*

*Keywords: Adsorption, Removal, Dyes, Heavy Metals and Isotherms.*

### **Abbreviations**

BB = Basic blue 9

AB = Acid blue 9

MB = Mordant Black 11

SCSP = *Syzygium Cumini* seed powder

SC = *Syzygium Cumini*

### **INTRODUCTION**

Water is the most ubiquitous material in nature and most vital for domestic purposes such as drinking, cooking, washing, bathing etc. Environmental pollution is currently one of the most important issues facing by humanity. It was increased exponentially in the past few years and reached to alarming levels in terms of its effects on living creatures (Renge et al., 2012). Rise in industrial and agricultural activities have resulted in the generation of various types of toxic pollutants, which are the main cause of water pollution on a global scale. However, years of increased industrial, agricultural and domestic activities have resulted in the generation of large amount of waste water containing number of toxic pollutants which are polluting the available fresh water continuously (Amit Bhatnagar et al., 2011).

Due to the discharge of non-biodegradable dyes and heavy metals such as BB, MB, AB, cadmium, lead, tin ions etc. into water stream, the industrial pollution is continuously said to be a potential threat for water quality. Consumption of such polluted water causes various health problems. As they are carcinogenic and cause adverse health conditions, water is to be treated thoroughly before consumption. Many conventional methods for heavy metal removal from aqueous solution were found which includes coagulation (Stephenson and Sheldon 1996), precipitation (Stephenson and 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 suggested 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 2012; Ahmad and Rahman 2011; Baek et al., 2010). Present study demonstrates use of new natural material, SCSP for the removal of dyes (BB, AB and MB) and heavy metal ions ( $Pb^{2+}$ ,  $Cd^{2+}$  and  $Sn^{2+}$ ) from their aqueous solutions.

## MATERIAL AND METHODS

Basic Blue 9 (BB9), Acid Blue 9 (AB9), Mordant Black 11 (MB11), Lead Nitrate [ $Pb(NO_3)_2$ ], Cadmium Chloride ( $CdCl_2$ ) and Stannous Chloride ( $SnCl_2$ ) were used without further purification. All syntheses and stock solutions were prepared by dissolving appropriate amounts of corresponding chemicals in distilled water. The entire chemicals used are of analytical grades purchased from sigma Aldrich having purity  $\geq 98.5\%$ .

### Preparation of Adsorbent

The seeds of waste SC fruits were washed with distilled water to get rid of dust and other deposits. The seeds was dried in the oven at  $45\text{ }^\circ\text{C}$ . The dried seeds and its husk were separated. The separated seeds were ground in mortar and pestle to obtain fine powder as an adsorbent.

## RESULTS AND DISCUSSION

### Characterization of adsorbents

#### Fourier Transform Infrared spectroscopy (FT-IR)

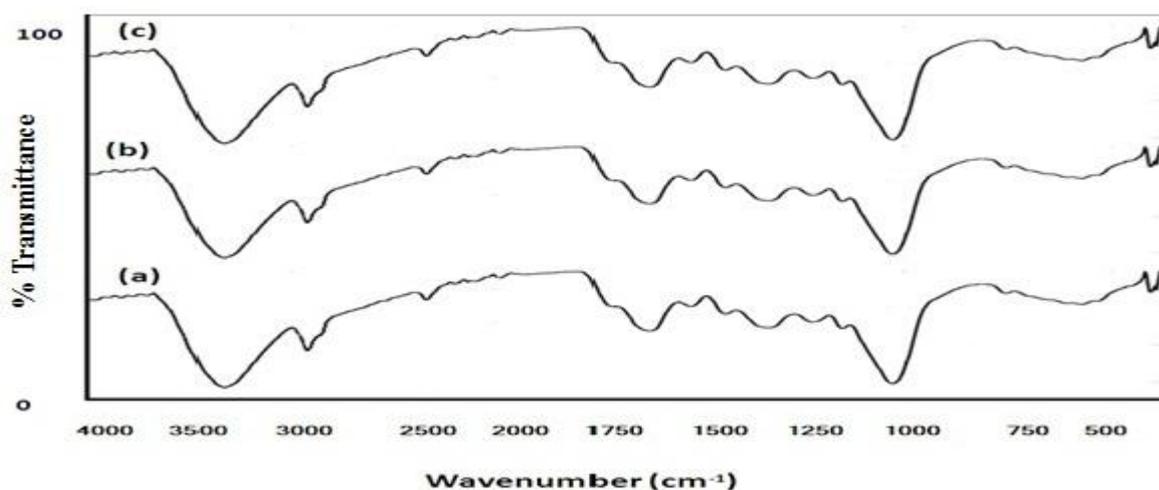


Figure 1. FT-IR spectrum of (a) SCSP, (b) SCSP after dye adsorption and (c) SCSP after metal adsorption.

FT-IR spectra of SCSP before and after dyes and heavy metals adsorption are shown in Fig. 1. Figure 1, shows broad and intense peaks at  $3302$  and  $3325\text{cm}^{-1}$  correspond to stretching of O-H group due to intra and inter molecular hydrogen bonding of carboxylic acids, alcohols and phenols.

The bands at 2920 and 2924  $\text{cm}^{-1}$  show C-H stretching of aliphatic acids. The peak observed at 2854  $\text{cm}^{-1}$  is due to the symmetric stretching vibration of  $\text{CH}_2$  and is due to C-H bond of aliphatic acids. The band at 1705  $\text{cm}^{-1}$  is because of the stretching vibration of C=O bond due to non-ionic carboxyl groups like -COOH or -COOCH<sub>3</sub>. Bands appearing at 1612, 1624, 1627, 1450 and 1338  $\text{cm}^{-1}$  corresponds to ionic carboxylic group. The band at 1153, 1161, 1006, 1014 and 1029  $\text{cm}^{-1}$  were may be due to the presence of >C=S group.

IR of SCSP before and after adsorption of dyes and metals are same, indicates that adsorption is of physical nature.

### Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES)

The composition of SCSP was evaluated using elemental analysis (ICP-AES) and results obtained are shown in table 1.

Table 1. Elemental analysis of adsorbent.

Adsorbent	Ca	Fe	Mg	Mn	Na
	ppm	ppm	ppm	ppm	ppm
<i>Syzygium Cumini</i> seed powder	295.66	15.16	702.09	113.23	62.36

### Determination of zero point charge (ZPC)

Figure 2 shows determination of  $\text{pH}_{\text{zpc}}$  of SCSP. 50 ml of 0.1 M KCl was taken in various stoppered bottles; 5 ml of buffer solution of various pH ranging from 1 to 11 were added to each bottle then 0.2 g of SCSP powder was added to each bottle and its initial pH were measured using digital pH-meter (Equiptronics Make, Model No. EQ. 614 A). The bottles were kept for 24 hrs and the final pH of the solutions was measured.  $\text{pH}_{\text{zpc}}$  is the point where the curve  $\text{pH}_{\text{final}}$  versus  $\text{pH}_{\text{initial}}$  intersects where  $\text{pH}_{\text{final}} = \text{pH}_{\text{initial}}$ .

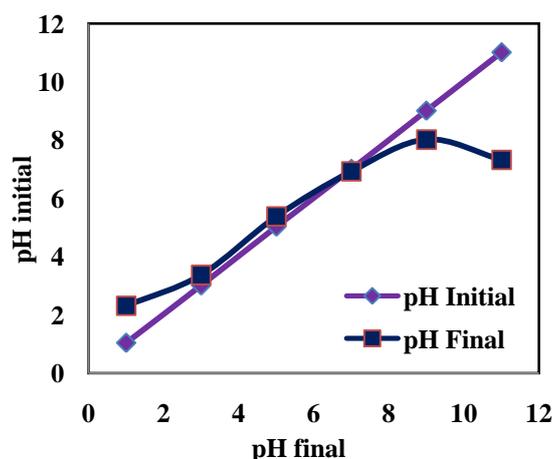


Figure 2. Determination of  $\text{pH}_{\text{zpc}}$  of adsorbent (SCSP).

The combined effect of all functional groups of adsorbents determines the value of  $\text{pH}_{\text{zpc}}$ , i.e., the pH at which the net surface charge on adsorbents was zero. At  $\text{pH} < \text{pH}_{\text{zpc}}$ , the adsorbents surface has a net positive charge, while at  $\text{pH} > \text{pH}_{\text{zpc}}$ , the surface has a net negative charge.

### BATCH ADSORPTION STUDIES

#### Effect of initial adsorbate 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,

$$q_e = \frac{(C_0 - C_e)V}{M} \quad \text{-----} \quad (1)$$

Where,  $C_0$  and  $C_e$  (mg/L) are 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.

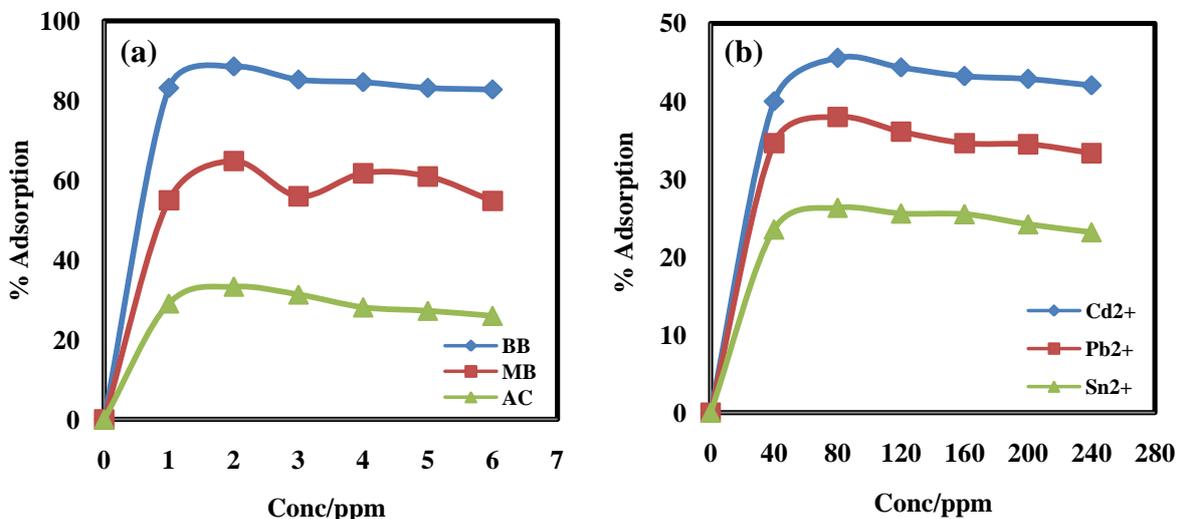


Figure 3. Effect of concentration of (a) dyes and (b) heavy metals onto SCSP.

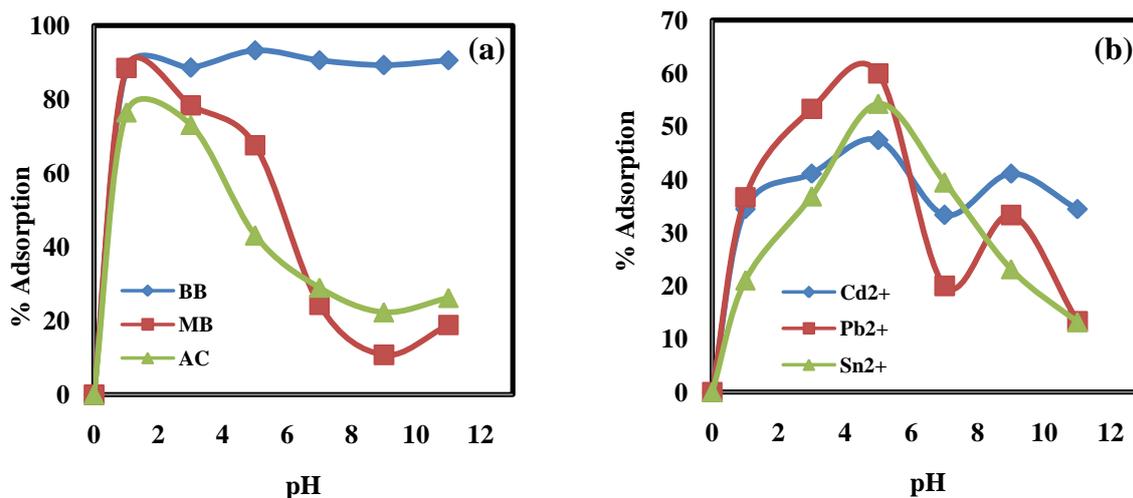


Figure 4. Effect of pH of (a) dyes and (b) heavy metals onto SCSP.

The percentage removal of dyes and heavy metals was calculated as

$$\% \text{ removal} = \frac{(C_0 - C_e)}{C_e} \times 100 \quad \text{-----} \quad (2)$$

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

The effect of initial concentration on the adsorption of dyes and heavy metals are shown in Fig. 3 which indicates that higher adsorption was found to take place at lower concentrations (2 mg/L for dyes and 40 mg/L for metal ions). This may be due to the interaction of all dyes and metal ions 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 (Senthilkumar et al., 2010).

When the concentration became higher, the percentage removal decreased since the available sites for adsorption became less due to saturation of adsorption sites.

### 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 dyes and heavy metal ion is shown in Fig. 4. The effect of pH was studied by varying pH range from 1 to 13. Then pH was adjusted by using various standard buffer solutions. The initial concentrations of dyes (BB, AB and MB) were 2 mg/L and for metal ions ( $\text{Pb}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Sn}^{2+}$ ) 40 mg/L. Other parameters such as adsorbent dose, temperature and contact time were kept constant.

The maximum removal efficiency by SCSP for BB is 93.26 % at pH 5, 88.48 % for MB at pH 1, 76.47% for AB at pH 1 and for  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$  and  $\text{Sn}^{2+}$  is 47.42 %, 60% and 54.26 % at pH 5 respectively.

At lower pH values the  $\text{H}^+$  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 and Gupta 2008; Gupta and Rastogi 2007). As pH value is higher, more exchangeable cations contained in the adsorbent can be exchanged with dyes and metal ions due to weak competitive adsorption of  $\text{H}^+$  ions.

### Effect of adsorbent dose

The effect of adsorbent dose was studied by varying the amount of adsorbent (0.2 g to 1.2 g) and by keeping initial concentration, temperature and pH constant for 120 min. The results obtained for effect of adsorbent dose is shown in Fig. 5.

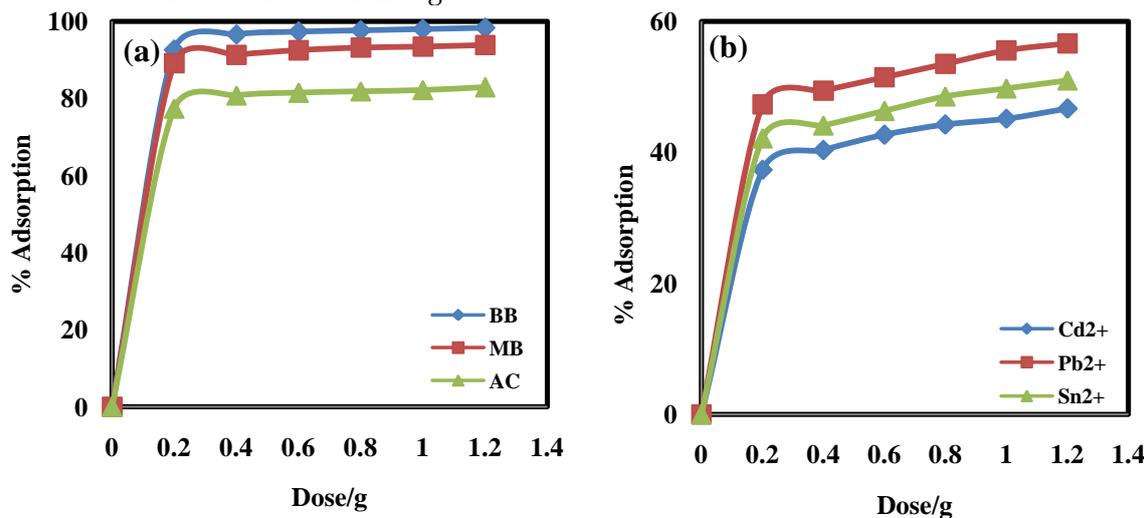


Figure 5. Effect of adsorbent dose of (a) dyes and (b) heavy metals onto SCSP.

It was found that percentage removal increases with increase in amount of adsorbent (Azouaou et al., 2010; El-Said et al., 2010; Saifuddin and Kumaran 2005). It was observed that, the removal efficiency by SCSP was increased from 92.59 to 98.31 % for BB, 89.15 to 93.87 % for AB, 77.37 to 82.89 % for MB, 37.33 to 46.66 % for  $\text{Cd}^{2+}$ , 47.33 to 56.63 % for  $\text{Pb}^{2+}$ , 42.13 to 50.98 % for  $\text{Sn}^{2+}$ , 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 each dyes and metal solution, compared to the concentration of each 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 all dyes and metals.

### Effect of Temperature

The adsorption of the dyes and metal ions on SCSP was studied at various temperatures 25, 35 and 45 °C for 1 hour. The results obtained are shown in Fig. 6. The dyes and metal ions solutions were measured into 6 labelled beakers each containing 0.2 g of the adsorbent. At the end, the content of each beaker was filtered and the residual concentrations of metal ions in the filtrates were determined using UV spectrophotometer. Increase in temperature from 25 °C to 45 °C was found to result in a steady increase in the removal efficiency of the adsorbent for the dyes and metal ions. This is probably due to the effect of temperature on the interaction between the adsorbent and the adsorbate.

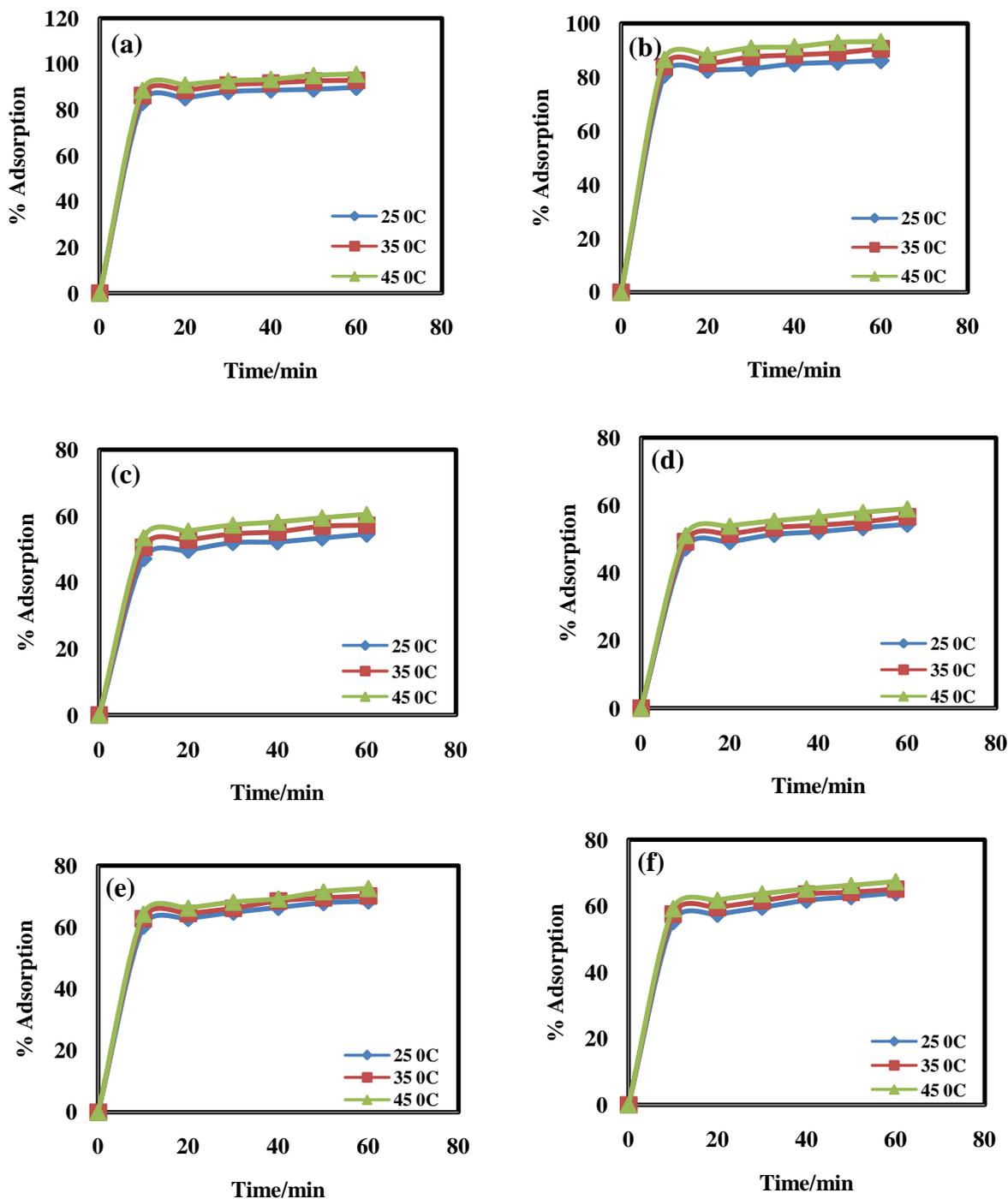


Figure 6. Effect of contact time for dyes (a) BB (b) MB, (c) AB and heavy metals (d) Cd<sup>2+</sup>, (e) Pb<sup>2+</sup>, (f) Sn<sup>2+</sup> onto SCSP at various temperature.

### Effect of contact time

The effect of contact time was studied by varying contact time and keeping initial concentration, pH and adsorbent dose constant for 60 min (Fig. 6) which 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. The percentage removal of dyes and metal ions by SCSP reached equilibrium within 30 min. The variation of the contact time on removal of dyes (BB, AB and MB) and metal ions ( $Pb^{2+}$ ,  $Cd^{2+}$  and  $Sn^{2+}$ ) is reported and results obtained are shown in Figure 6. 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 dyes and metal ions using SCSP. A careful inspection of Fig. 7 (a, b) shows that adsorption of all dyes on SCSP is found highest 95.63 % for BB, 90.25 % for MB, 80.89 % for AB, 48.66 % for  $Cd^{2+}$ , 59.44 % for  $Pb^{2+}$  and 55.63 % for  $Sn^{2+}$ .

In case of metal ions,  $Pb^{2+}$  adsorbs more (69.47 %) as compared to  $Cd^{2+}$  and  $Sn^{2+}$  because electronegativity of  $Pb^{2+}$  is highest (2.33) with respect to  $Sn^{2+}$  (1.96) and  $Cd^{2+}$  (1.69). This trend is also explained on the basis that more the ionic size, enthalpy of hydration decreases. Hence enthalpy of hydration shows that,  $Pb^{2+}$  ions possess higher accessibility to the adsorbent surface and follow the order  $Pb^{2+} > Sn^{2+} > Cd^{2+}$ .

In case of dyes, BB adsorbs more (95.63 %) as compared to MB and AB and seed powder bind basic dyes more favorably than acidic and azo dyes. This might be due to the presence of O-H group which then facilitate the adsorption of basic dyes.

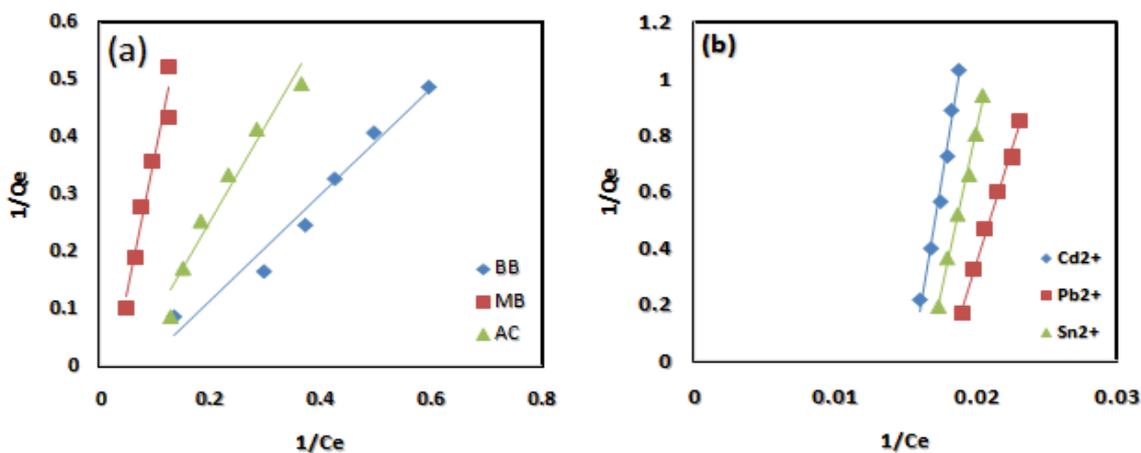


Figure 7. Langmuir adsorption isotherm for adsorption of (a) dyes and (b) heavy metal ions onto SCSP.

### ADSORPTION ISOTHERMS

#### Langmuir isotherm

Langmuir isotherm model is based on assumption that, a saturated monolayer of adsorbate molecules is found 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

$$\frac{1}{Q_e} = \frac{1}{Q_0} + \frac{1}{Q_0 K_L C_e} \text{----- (3)}$$

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 and Chakravarti 1974).

$$R_L = \frac{1}{1+(1+K_L C_0)} \text{----- (4)}$$

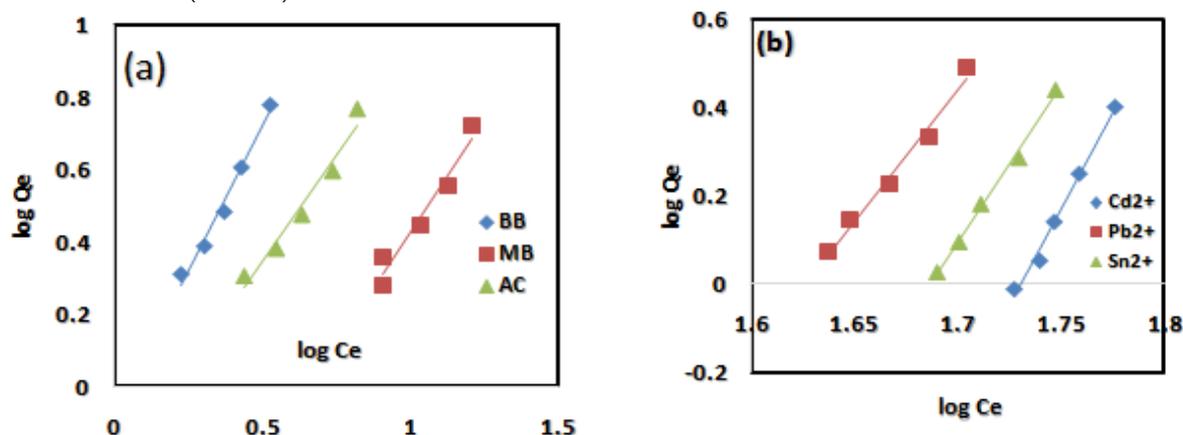
The values of slope and intercept can be determined from linear plots of experimental data ( $1/Q_e$ ) versus ( $1/C_e$ ) for the different dyes and heavy metal ions (Fig.7).

$R_L$  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 Langmuir and Freundlich Isotherm Model Constants and correlation coefficients for the adsorption of the different dyes and heavy metals on SCSP.**

<i>Syzygium Cumini</i> seed powder							
Dyes/Metals	Langmuir constants				Freundlich constants		
	$K_L$ (L mg <sup>-1</sup> )	$Q_o$	$R_L$	$R^2$	$K_F$	n	$R^2$
Basic Blue 9	0.0761	14.164	0.1039	0.966	1.1983	0.6274	0.981
Mordant Black 11	0.0207	10.152	0.2456	0.956	6.6603	0.8010	0.950
Acid Blue 9	0.0473	12.690	0.1484	0.953	1.7326	0.8562	0.963
Cd <sup>2+</sup>	0.01536	0.2195	0.2827	0.982	1.56 E+15	0.1139	0.990
Pb <sup>2+</sup>	0.01641	0.2638	0.2745	0.993	4.93 E+09	0.3377	0.981
Sn <sup>2+</sup>	0.01780	0.3529	0.2645	0.993	1.12 E+12	0.1399	0.994

Table 2 shows the Langmuir isotherm constants and their correlation coefficients. The adsorption of dyes and heavy metals onto surface of two adsorbents was favourable as  $R_L$  values calculated were in between 0 and 1 (Table 2).



**Figure 8. Freundlich adsorption isotherm for (a) dyes and (b) heavy metal ions onto SCSP.**

### 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

$$\log Q_e = \log k_f + \frac{1}{n} \log C_e \quad \text{----- (5)}$$

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, if  $1/n > 1$  indicates cooperative adsorption (Mohan and 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 different dyes and heavy metals (Fig.8) 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 most of the dyes and heavy metals as compared to the Freundlich isotherm model. In addition, the values of  $1/n$  are less than 1. Figure 8 shows Freundlich plot for adsorption of dyes and heavy metals.

### ADSORPTION THERMODYNAMICS

Following equations (Laidler and Meiser 1999) are used to evaluate thermodynamic parameters such as standard Gibbs free energy ( $\Delta G$ ), entropy change ( $\Delta S$ ) and enthalpy ( $\Delta H$ ).

$$\Delta G = -RT \ln K_a \text{ ----- (6)}$$

$$\Delta G = \Delta H - T\Delta S \text{ ----- (7)}$$

$$\text{Thus, } \ln K_a = -(\Delta H/RT) + (\Delta S/R) \text{ ----- (8)}$$

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

The well known thermodynamic aspects including  $\Delta H$ ,  $\Delta S$  and  $\Delta G$  for the adsorption of dyes and metal ions on SCSP were evaluated using eq. (6) to (8). The plot between  $\ln K_a$  and  $1/T$  gives  $\Delta H$  and  $\Delta S$  in terms of slope and intercept (Fig. 9) and data obtained is incorporated in Table 3.

**Table 3. Thermodynamic parameters, Gibb's free energy change ( $\Delta G$ ), distribution coefficient  $K_a$ , enthalpy change ( $\Delta H$ ) and entropy change ( $\Delta S$ ) for the removal of dyes(BB 9, AB 9 and MB 11) and heavy metal ions ( $\text{Pb}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Sn}^{2+}$ ) onto SCSP.**

Dyes/Metal ions	Temperature/K	$K_a$	$\Delta G/(\text{kJ mol}^{-1})$	$\Delta H/(\text{kJ mol}^{-1})$	$\Delta S/(\text{kJ mol}^{-1})$
Basic Blue 9	298.15	5.011	- 3995.16	54.80	0.2026
	308.15	7.254	- 5076.66		
	318.15	13.210	- 6826.95		
Mordant Black 11	298.15	9.099	- 5473.89	83.23	0.2899
	308.15	11.979	- 6361.88		
	318.15	16.786	- 7460.73		
Acid Blue 9	298.15	7.215	- 4898.69	52.17	0.1924
	308.15	11.208	- 6191.31		
	318.15	42.177	- 9897.64		
$\text{Pb}^{2+}$	298.15	0.6374	1116.126	4.56	0.00958
	308.15	0.7044	897.68		
	318.15	0.7862	635.94		
$\text{Cd}^{2+}$	298.15	0.6837	942.53	7.62	0.02371
	308.15	0.7333	794.47		
	318.15	0.7843	642.53		
$\text{Sn}^{2+}$	298.15	0.8461	414.06	3.28	0.0104
	308.15	0.8748	342.54		
	318.15	0.9196	221.48		

A careful inspection of Table 3 reveals that  $\Delta G$  value for dyes and metal ions is negative suggests that the process of adsorption is spontaneous.  $\Delta H$  values calculated for adsorption process of dyes are 54.80 for BB 9, 83.23 for MB 11 and 52.17  $\text{kJ.mol}^{-1}$  for AB 9 and metal ions are 7.62  $\text{kJ.mol}^{-1}$  for  $\text{Cd}^{2+}$ , for  $\text{Pb}^{2+}$  4.56 and 3.28  $\text{kJ.mol}^{-1}$  for  $\text{Sn}^{2+}$ . The values of  $\Delta H$  indicate the process is physical sorption and it is endothermic in nature.

The  $\Delta S$  values for adsorption of dyes are found to be 0.2026 for BB 9, 0.2899 for MB 11 and for AB 9 is 0.1924  $\text{kJ}\cdot\text{mol}^{-1}$  and for metal ions are found to be 0.02371 for  $\text{Cd}^{2+}$ , 0.00958 for  $\text{Pb}^{2+}$  and 0.0104  $\text{kJ}\cdot\text{mol}^{-1}$  for  $\text{Sn}^{2+}$ . The positive values of  $\Delta S$  confirm the increase in entropy because of adsorption.

### ADSORPTION KINETICS

In order to define the adsorption kinetics of dyes and heavy metal ions, 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. 10 and 11 respectively.

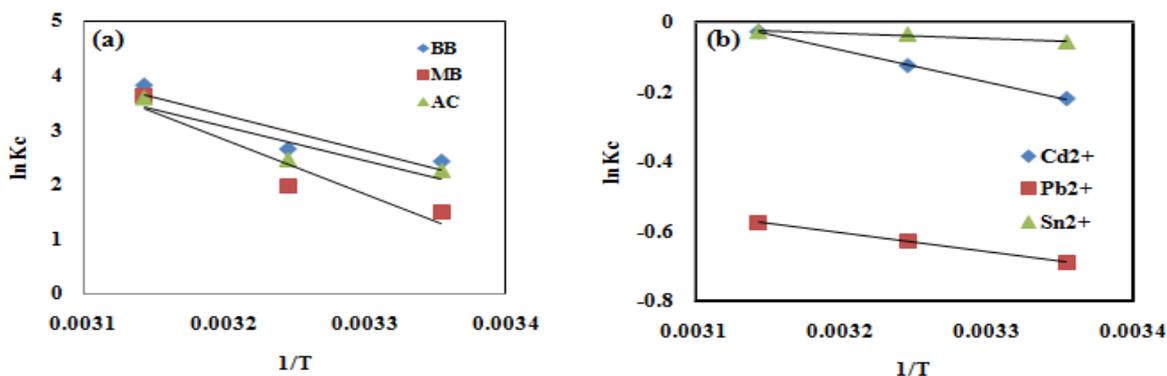


Figure 9. Plot of  $\ln K_a$  Vs  $1/T$  for adsorption of (a) dyes and (b) metal ions on SCSP.

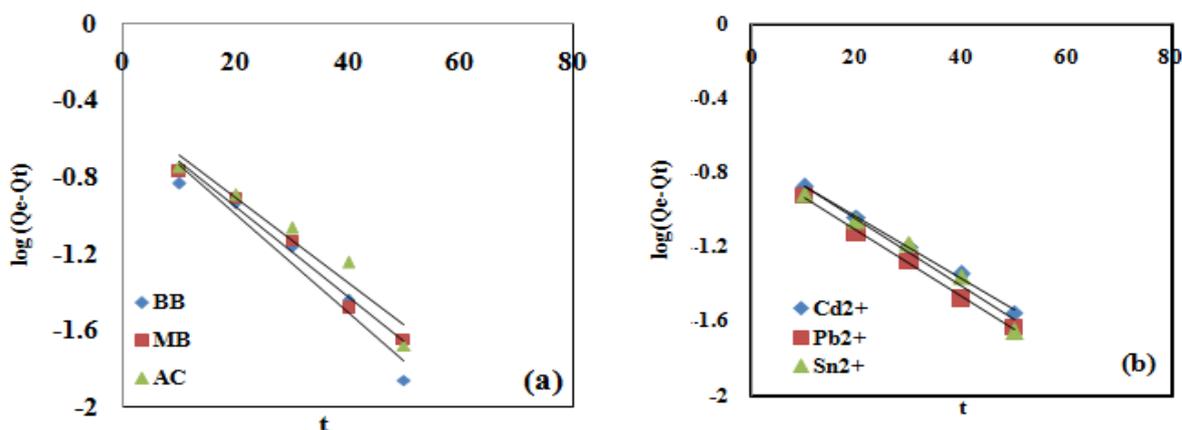


Figure 10. Pseudo first order plot of (a) dyes and (b) heavy metal ions onto SCSP.

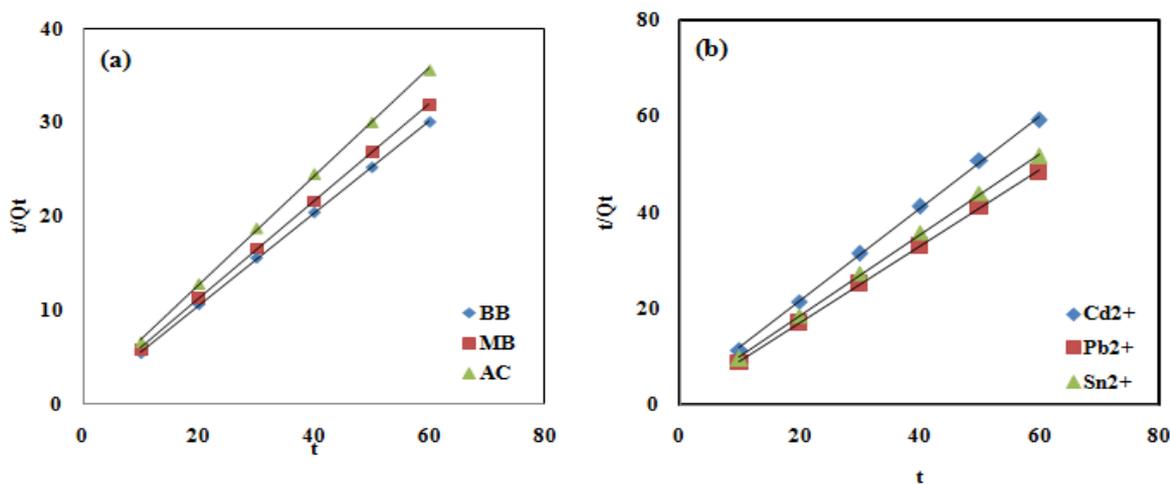


Figure 11. Pseudo second order plot of dyes (a) and heavy metal ions (b) onto SCSP.

The first order kinetic equation is,

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad \text{-----} \quad (9)$$

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,

$$\frac{t}{q_t} = \frac{1}{k_2} + \frac{1}{q_e} t \quad \text{-----} \quad (10)$$

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.

**Table 4. Kinetic parameter calculated by applying pseudo-first-order and pseudo-second-order for the adsorption of dyes and heavy metals on SCSP.**

Syzygium Cumini seed powder								
Dyes/ Metals	pseudo first order kinetic model				pseudo second order kinetic model			
	$q_e$ (exp)	$q_e$ (mg g <sup>-1</sup> )	$k_1$ (min <sup>-1</sup> )	R <sup>2</sup>	$q_e$ (exp)	$q_e$ (mg g <sup>-1</sup> )	$k_2$ (g mg <sup>-1</sup> min <sup>-1</sup> )	R <sup>2</sup>
Basic Blue 9	1.99	0.3288	- 0.057	0.951	1.99	2.04	1.091	0.999
Mordant Black 11	1.68	0.3435	- 0.050	0.941	1.68	1.73	0.2831	0.999
Acid Blue 9	1.88	0.3221	0.052	0.978	1.88	1.92	0.3154	0.999
Pb <sup>2+</sup>	1.23	0.1733	- 0.039	0.997	1.23	1.26	0.4866	0.999
Cd <sup>2+</sup>	1.01	0.1954	- 0.036	0.996	1.01	1.04	0.3941	0.999
Sn <sup>2+</sup>	1.15	0.1995	- 0.039	0.963	1.15	1.18	0.4126	0.999

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 in good agreement to that of 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.

## CONCLUSIONS

Low cost natural material, SCSP was identified as an effective adsorbent for the removal of dyes (BB, AB and MB) and heavy metals (Pb<sup>2+</sup>, Cd<sup>2+</sup> and Sn<sup>2+</sup>) from their aqueous solutions. SCSP was effective toward removing dyes and heavy metals from their aqueous solutions. The adsorption process best fitted to the Langmuir isotherm model. The adsorption of dyes and heavy metal ions follow pseudo-second order kinetics. It could be used as low cost, efficient and effective adsorbent for water purification.

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## REFERENCES

- Ahmad, M.A. and 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 and 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. and 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. and 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 and Kim, D. (2010). Removal of Malachite Green from aqueous solution using degreased coffee bean. *J Hazard Mater*, 176, 820–828.
- Bhatnagar, A., Vitor, J.P., Vilar, Cidália, M.S., Botelho and Rui A.R. Boaventura (2011). A review of the use of red mud as adsorbent for the removal of toxic pollutants from water and wastewater. *Environmental Technology*, 32(3), 231–249.
- Dikpati, M., Peter, A. G., and 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. and Pereira, M.F. (2004). Adsorption of anionic and cationic dyes on activated carbons with different surface chemistries. *Water Res.*, 38, 2043–2052.
- Forgacs, E., Tibor, C. and 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 Rodríguez, I., Velasco-Santos, C. and Martí nez Hernández, 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. and Rastogi, A. (2007). Biosorption of lead from aqueous solutions by green algae *Spirogyra* species: kinetic and equilibrium studies. *Journal of Hazardous Materials*, 152, 407–414.
- Kusvuran, E., Gulnaz, O., Irmak, S., Matanur, O., Yavuz, H. and Erbatır, 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. and 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. and Yousefy, M. (2011). Exploring effective factors in ergonomic system responsiveness to managers and employees' requirements: a case study. *Iranian journal of development and evolution management*. 3, 39–47.
- Renge, V. C., Khedkar, S. V. and Shradha, V. Pande (2012). Removal of heavy metals from wastewater using low cost adsorbents : A Review. *Scientific Reviews and Chemical Communications*, 2 (4), 580–584.
- Robinson, T., McMullan, G., Marchant, R. and 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. and Kumaran, P. (2005). Removal of heavy metal from industrial waste water using Chitosan coated oil palm shell charcoal. *Environ. Biol.*, 8(1), 1–13.
- SenthilKumar, M., Anandham, R., Gandhi, P.I., Sridar, R., Nalayini P. and Sa, T.M. (2010). Sulfur oxidizing bacteria: A novel bio-inoculant for sulfur nutrition and crop production. In: *Bacteria in Agrobiolgy, Agroecosystems*, Maheswari, D.K. (Ed.), Springer, Germany.
- Stephenson, R.J. and 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. and 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. and Chakravarti, R.K. (1974). Pore and solid diffusion models for fixed bed adsorbents. *J Am Inst Chem Eng*, 20, 228–238.
- Wu, K., Xie, Y., Zhao, J. and Hidaka, H. (1999). Photo-Fenton degradation of a dye under visible light irradiation. *J Mol Catal A Chem*, 144, 77–84.

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