ADSORPTION OF NAPHTHALENE FROM AQUEOUS SOLUTIONS BY DE-OILED RICE BRAN CHARCOAL AS A LOW COST ADSORBENT

BOHAR SINGH[1]*, TANDEEP SINGH[2], JOBANDEEP SINGH[1], RAJIV ARORA[3] AND B.S WALIA[4]

*[1]Department of Civil Engineering, Shaheed Bhagat Singh State Technical Campus,
Ferozepur 152 004, India*
[2]School of Architecture and Built Environment, Deakin University, Geelong, Australia
[3]Department of Chemical Engineering, Shaheed Bhagat Singh State Technical Campus, Ferozepur 152 004, India
[4]Maharishi Markandeshwar Engineering College, Mullana 133 207, India

ABSTRACT

Poly aromatic hydrocarbons are toxic to the living bodies even though present in trace amounts. In this study, De-oiled rice bran charcoal was used as adsorbent for the adsorption of naphthalene in aqueous solution. The De-oiled rice bran charcoal was characterized using XRD and SEM-EDX. The batch experiments were performed to optimize the parameters for the maximum adsorption of the naphthalene and the parameters included were - pH, initial naphthalene concentration, amount of adsorbent, contact time and temperature of the naphthalene solution. A dose of 9.0 g L^{-1} of biosorbents in solutions with an initial pH of 6.0, an initial naphthalene concentration of 50 mg L^{-1} and a contact time of 75 minutes resulted in the maximum naphthalene removal efficiency. The Freundlich isotherm gave a better fit than the Langmuir isotherm indicating that the biosorption was potentially multilayer. The adsorption kinetics were also studied, and it was found that the adsorption followed pseudo-second order kinetics, which implied that the biosorption was mainly a chemisorption process. The results indicate that De-oiled rice bran charcoal is an effective low-cost adsorbent for the removal of naphthalene ions from aqueous solutions due to its high naphthalene uptake capacity.

KEY WORDS : Adsorption, De-oiled rice bran charcoal, Naphthalene, Dye removal, Isotherms, Wastewater Treatment

INTRODUCTION

Polycyclic aromatic hydrocarbons are the organic compounds which consist of only hydrogen and carbon and are made of multiple aromatic rings. Naphthalene is one of the simplest chemical of this class which consists of double aromatic rings and the three ring compounds phenanthrene and anthracene. Polycyclic Aromatic Hydrocarbons (PAH) establish a critical class of very dangerous and long living environmental pollutants. For acknowledgement of their poisonous quality and high versatility in the environment, a safe tolerance limit of PAHs in the potable water has been recommended by World Health Organization (WHO, 2006), and these compounds have been incorporated in the list of important pollutants to be observed in industrial effluents by the European Environmental Agency (EEA). In spite of all this, they have been detected in a variety of waters as well as wastewaters (Douben, 2003 and Williams, 1990), because they are related to a number of industrial processes like incomplete combustions of fuel and coke making (Cabal, 2009).

Polycyclic aromatic hydrocarbons are largely lipopholic, chemically inert, and can be dissolved in a large number of organic solvents. Hence, their biological activities and characteristics may differ in

the environment (Barr and Aust, 1994). Polycyclic aromatic hydrocarbons have gained a large consideration because of their ill-effects related to human health like skin problems, bladder, lungs, colon and breast cancer (Boffetta *et al.,* 1997; Marti-Cid *et al.,* 2008). Due to these adverse effects polycyclic aromatic hydrocarbons have been put in to the class of highly toxic materials by different agencies (Matina *et al.,* 2014). PAHs having smaller molecular weights like naphthalene on dissolving in water pose a heavy threat to aquatic life and impart toxic effects to many living organisms.

PAHs are universally dispersed in the diverse types of biosphere such as atmosphere, lithosphere and hydrosphere because of their large use in the industries. Polycyclic aromatic hydrocarbons are discharged into the surroundings by different means which are extensively differentiated into anthropogenic sources e.g. paint, oil refinery, carpet and chemical industry. Refineries are the prime sources for discharge of PAH compounds in the atmosphere. Volcanic eruption and forest fire are amongst the other normal means of polycyclic aromatic hydrocarbon compounds. PAH has for quite some time been of worldwide concern due to its stubbornness credited to delocalized pibonds and fused benzene ring bringing about harmful and carcinogenic potential. PAHs have affinity for lipids and hence get effectively dispersed into the aquatic food chains bringing about biomagnification and bioaccumulation of PAHs (Ke *et al.,* 2010). Various innovations have been done amid the recent decades for the cleaning of persistent PAHs from surroundings. Chemical and physical treatment technologies are common however they are not much eco-friendly. To conquer the adverse effects of chemical and physical techniques on the ecosystem, biological means like biodegradation or biosorption are more appropriate. Biological techniques are economical and environment friendly to disinfect effluents and soils.

Naphthalene is a polycyclic aromatic hydrocarbon (PAH) that has a large number of uses in many industrial units and is a noteworthy component experienced by the coal and tar based industries. It has been identified in soil, oil tainted sediments, and both urban and industrial wastewater. Naphthalene has also periodically been isolated as pollutant at waste sites. To save the aquatic life, the allowable concentrations of naphthalene are 0.6 and 2.3 mg L^{-1} on chronic and acute toxicity, respectively. Naphthalene is highly

dangerous by hypodermic route, and naphthalene poisoning may occur by ingestion of extensive dosages, breathing or skin absorption (Vipulanandan and Ren, 2000). Deliberate disclosure to naphthalene and its derivatives have been held responsible to cause a number of disorders and also disturbance of the metabolism of human beings (Amoore and Hautala, 1983; Agarry *et al.,* 2013).

Different chemical treatment methods have been reported in literature to remove naphthalene from water such as electrochemical separation, solvent extraction, precipitation, distillation, reverse osmosis, ion exchange etc. (Kong *et al.*, 2014). While some of these techniques are expensive and difficult to operate (such as reverse osmosis, electrochemical separation, solvent extraction, etc.), the others are energy intensive processes (such as distillation) and also these methods are responsible for generating toxic sludge & secondary pollution (Guo *et al.*, 2009; Tasar *et al.*, 2014; Guyo *et al.*, 2015).

Adsorption is known to be one of the most promising techniques for removal of naphthalene. Adsorption can happen due to association within any two different phases like liquid-solid, liquid-liquid and gas-liquid interfaces (Barakat, 2011). Furthermore, adsorption has emerged to be considered as a realistic separation technique for bulk separation or purification in the newly created material production methods. Pore structures and surface characteristics of the adsorbents are major properties for determination of rate properties and adsorption equilibrium required for the design of plant. New adsorbents are being continuously explored with introduction of latest applications for adsorption technique. For the design of adsorption operations, the fundamental factor is adsorption equilibrium.

When the adsorption occurs with suspended adsorbent molecules in a container, adsorbate gets transferred to the adsorption sites available in adsorbent molecule from the bulk liquid phase. During such situations the concentration in the fluid phase or changes in adsorbed amount can be determined by using differential equations explaining mass balances in molecule, at the external periphery and between the fluid phase and particle. Diffusion parameters should be determined by a general kinetic system.

The objective of the present study was to evaluate charcoal prepared from de-oiled rice bran, completely chemical free and environmental friendly as a low cost biosorbent for the removal of

naphthalene from aqueous solution. The removal efficiency was investigated by a series of experiments under different experimental conditions such as solution pH, contact time, initial concentration temperature and biosorbent dosage.

MATERIALS AND METHODS

Materials

Naphthalene ($C_{10}H_8$) having molecular weight 128.17 g mol^{-1}, 99% purity was procured from Merck, India. Because of low solubility of naphthalene (polycyclic aromatic hydrocarbon) in water, a water-methanol solution was used to prepare an aqueous solution. A stock solution was prepared by dissolving 1.0 g of naphthalene in 1.0 L of deionized water-methanol solution, the later consisting of 950 mL deionized water and 50 mL methanol. This was used to prepare working solutions of different concentrations (25, 50, 75, 100, 125, 150 mg L^{-1}) by diluting it with deionized water.

Rice-bran was obtained from Bhagwati Lacto Rice Mills, Ferozepur (India). The oil from rice bran was removed by soxhlet extraction. The de-oiled rice bran was first washed with distilled water to remove the soil, sand and any other undesirable material and then, dried at 50 °C in an air oven for 24 hours. The de-oiled rice bran was further reduced to 1-2 mm size by grinding. These particles were pyrolysed in a furnace at 500 ºC for 2.5 hours (Singh *et al.*, 2018). The produced char was grinded, sieved through 100 mesh sieve. It was then stored in an air tight container and labeled as 'De-oiled Rice Bran Charcoal (DRBC).

Experimental Set-up

The experiments were conducted in 250 mL Erlenmeyer flasks with the working volume of 100 ml of aqueous naphthalene solution. The pH of the solution was adjusted to the desired value by adding 0.1 M NaOH or HCl. After the required amount of adsorbent dose was added, the flasks were shaken for the specified time period in a temperature-controlled incubation shaker at 120 rpm. The flasks were withdrawn from the shaker after the required time of operation. The supernatant and the spent adsorbent were separated by centrifugation at 6000 rpm for 15 minutes using the centrifuge (R24 REMI Centrifuge, Mumbai, India). The residual naphthalene concentration in the supernatant was analyzed by measuring the solution absorbance at λ = 290 nm using a UV–visible spectrophotometer (Model–EI-2375 of Electronics India). All experiments were carried out in triplicate and the average values are presented.

The amount of equilibrium absorption Q_e (mg/g) of the naphthalene was calculated by:

$$Q_e = \frac{c_0 - c_e}{w} V$$
.. (1)

The percentage removal of naphthalene was calculated as:

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

where, C_o and C_e (mg/L) are initial concentration and equilibrium concentration respectively, V is the volume of the solution (L) and w is the mass of the adsorbent (g).

The process parameters such as solution pH, adsorbent dose, initial naphthalene concentration, time and temperature were chosen as the independent input variables and the efficiency of naphthalene removal as the dependent output variable.

RESULTS AND DISCUSSION

Characterization of adsorbent

The X-ray diffraction studies were done by XRD analyzer (Pan analytical X'pert Pro diffractometer, D/max rA) at 45 kV and 40 mA (Cu Kα = 1.50406 Å). The XRD pattern of de-oiled rice bran charcoal adsorbent is illustrated in Figure 1. The XRD pattern indicates the amorphous structure of adsorbent with a small sharp peak at 2θ = 26.62°, one mid-size peak at 29.44 and few smaller peaks at 39.43 and 48.59.
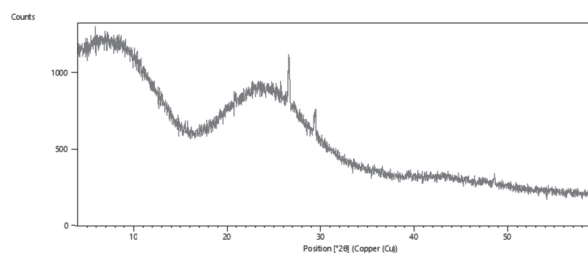

Fig. 1.   XRD analysis of de-oiled rice bran charcoal carbonized at 500 ºC

Morphological structures of the adsorbent was drawn using scanning electron microscope (SEM) JSM-6510 LV, JEOL and elemental composition was performed by energy-dispersive X-ray spectroscopy (EDS) INCax-act, Oxford Instruments. SEM-EDS made it possible to visualize the surface morphology

of adsorbent. Figure 2(a) and 2(b) of microscopy SEM shows a porous aspect of 10-30 ìm sized adsorbent particles which facilitate materials adsorption. In addition, spectrum EDX (Figure 3) shows the presence of various elements as Calcium, Magnesium, Sodium, Silicon and Potassium.
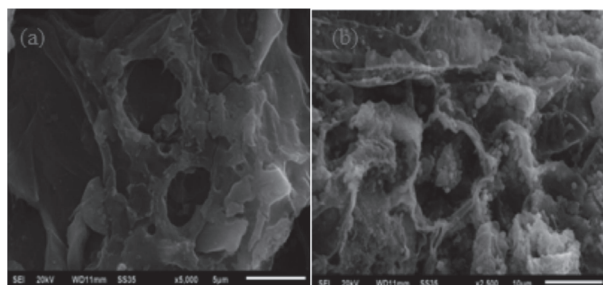

Fig. 2. SEM images of de-oiled rice bran charcoal carbonized at 500 °C at different magnifications of (a) 5000 (b) 2500
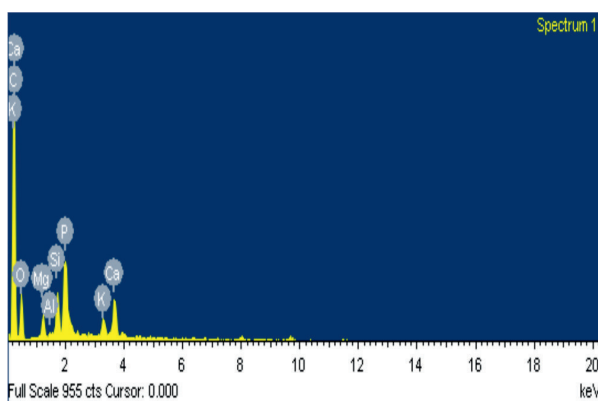

Fig. 3. EDX image of de-oiled rice bran charcoal carbonized at 500 °C

Effect of solution pH

As pH of the solution effect the surface charge of the adsorbent and furthermore the ionization of adsorbate and thus is an imperative parameter to perform the adsorption procedure. The effect of pH on the adsorptive disposal of naphthalene by carbonized de-oiled rice bran was investigated by varying pH values from 5.0-9.0 (Figure 4). It is observed that the adsorption of naphthalene increases from 90.20% to 94.00% as the pH of the solution is increased from 5.0 to 6.0. Thereafter, removal efficiency decreases slightly with further increase in pH of the medium. Hence, an ideal value of pH 6.0 is adopted for further biosorption investigations on naphthalene. It was also observed that a continuous rise in the adsorption capacity and removal efficiency of naphthalene occurred with an increase in pH from 5.0 to 6.0 and decreased at the pH > 6.0 (Figure 4). The highest removal efficiency took place at pH 6.0 and reached 94.00%. The electrostatic interaction within the sorbate and biosorbent is controlled by pH of the wastewater. The surface characteristics of a biosorbent rely on the available functional groups and also on its point of zero charge (pHPZC) or iso-electric point. At lower pH the external surface charges are positive on the biosorbent, therefore at lower pH less biosorption of naphthalene occurs. The minimum naphthalene adsorption was observed at pH 5.0. Anionic adsorption was favored at pH below pHPZC whereas cationic adsorption above pHPZC (Savova *et al.*, 2001). With the increase in pH, the biosorbent surface exhibits more negative charge and the naphthalene adsorption reached to maximum extent at an optimum value of pH 6.0. Hence, the highest adsorption capacity exists at pH value 6.0, and above pH 6.0, it decreased.
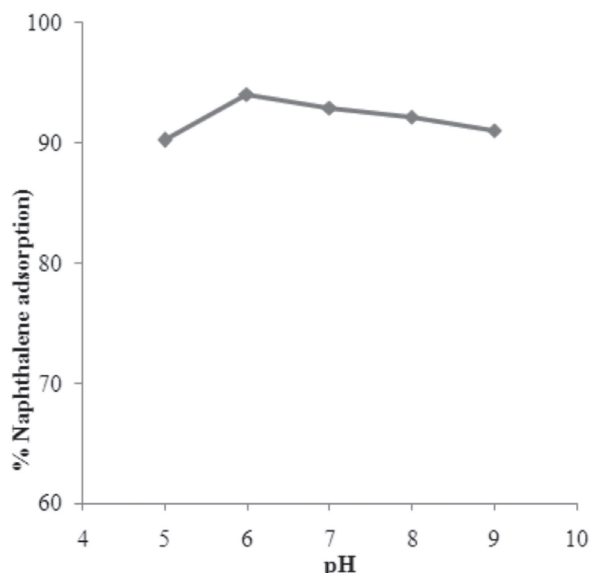

Fig. 4. Effect of pH on adsorbed quantity of naphthalene onto de-oiled rice bran charcoal. Initial naphthalene ion concentration 50 mgL^{-1} and adsorbent dose 9.0 g L^{-1}

Effect of naphthalene concentration and contact time

The naphthalene concentration ranging from 50 mg L^{-1} to 150 mg L^{-1} was investigated to determine the effect of initial concentration of naphthalene and contact time on adsorption by utilizing de-oiled rice bran charcoal (DRBC) at 40^{0}C and the results are shown in Figures 5 and 6. It was found that with the increase in naphthalene concentration from 50 mg L^{-}

^{1} to 150 mg L^{-1}, equilibrium adsorption, Q$_e$ increased from 5.22 mg g^{-1} to 13.68 mg g^{-1} in 75 minutes when solution pH was 6.0 and adsorbent dose was 9.0 g L^{-1}. Initially, the rate of removal was fast and it slowly decreased to attain the equilibrium state, after which no significant increase in the removal rate was observed. Equilibrium was achieved for five different initial naphthalene concentrations equilibrium after 75 min (Figure 5). Hence, 75 min was chosen as equilibrium time in the present study. Initially, the more number of active binding sites are available, which is the major cause of faster biosorption at the start of adsorption. Therefore, the adsorption occurred at a very fast rate and is generally influenced by the diffusion phenomenon from the bulk to the surface. In the later phases adsorption is generally an attachment controlled phenomenon because of decrease in the available binding sites. Similar results have been reported for adsorption of naphthalene onto various biosorbents (Agarry and Aremu, 2012). As the initial concentration of naphthalene is increased, the removal percentage of naphthalene decreases (Figure 6). This trend is because of the reason that all the adsorbents have some fixed number of active binding sites and above a specific concentration these binding sites get saturated (Tsai and Chen, 2010), although the adsorption efficiency at equilibrium was observed to rise with increased initial concentration of naphthalene (Figure 5). This observation was because of an increased concentration gradient which provides an increased driving effort to surpass the resistance to the mass
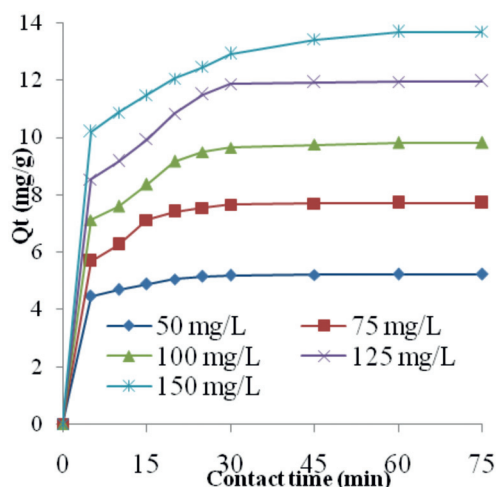

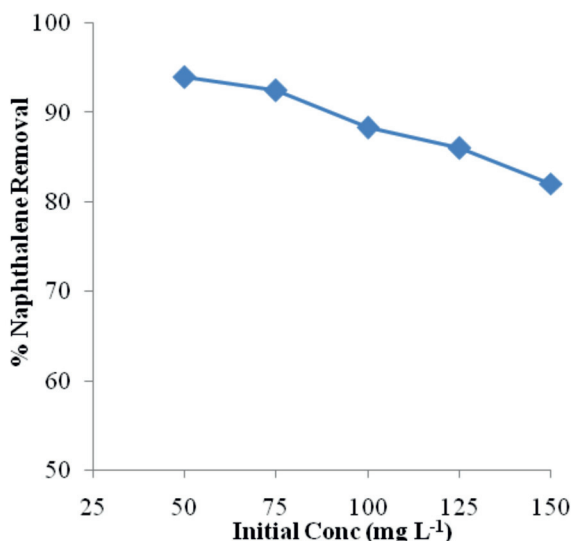**Fig. 6.** Effect of initial naphthalene concentration on %age naphthalene removal. Interval of initial naphthalene concentration (50-150 mg L^{-1}), adsorbent dose 9.0 g L^{-1}, pH 6.0, temp. 40 °C and contact time 75 minutes

transfer of naphthalene between solid and aqueous phase (Baek et al., 2010).

Effect of adsorbent dose

As the adsorption is directly influenced by the surface area available for naphthalene, so to study the effect of adsorbent dose it was varied from 5.0 g L^{-1} to 11.0 g L^{-1} to investigate its effect for 1.0 hour contact time, 50 mgL^{-1} initial naphthalene concentration, pH 6.0 at a temperature of 40 °C. The influence of adsorbent dosage on the adsorbed quantity of naphthalene with time is represented in Figure 7. Higher percentage removal of naphthalene was observed on increasing the dose of biosorbent. This was probably because of presence of more binding sites on the adsorbent surface and increased adsorptive surface area (Das and Mondal, 2011; Nasuha et al., 2010). However, reverse trend was shown by the equilibrium adsorption capacity. With the increase in adsorbent dose, the adsorption capacity started decreasing (Figure 8). This is mainly because of reduction in total adsorption surface area available to the naphthalene due to aggregation or overlapping of binding sites (Crini et al., 2007, Akar et al., 2009). Hence, on increasing the adsorbent mass, the quantity of adsorbed naphthalene per unit mass of adsorbent was decreased, resulting in a decline in adsorption capacity with increase in adsorbent mass concentration. Further, the highest removal of naphthalene was observed by using 9.0 g
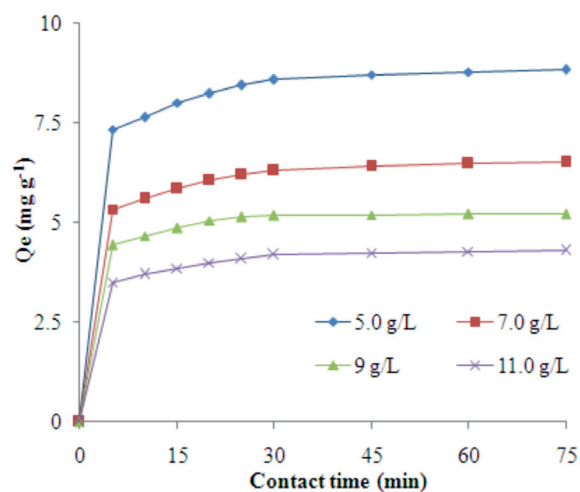

Fig. 5. Effect of contact time on adsorption of naphthalene. Interval of initial naphthalene conc. (50-150 mg L^{-1}), adsorbent dose 9.0 g L^{-1}, pH 6.0 and temp. 40 °C

Fig. 7. Effect of adsorbent dose on adsorption quantity. Initial naphthalene concentration 50 mg L⁻¹, pH 6.0 and temp. 40 °C

of de-oiled rice bran charcoal and further increase in adsorbent dosage did not have any significant effect on the biosorption yield. This is because of the non-availability of binding sites on the adsorbent and the formation of equilibrium state between the naphthalene in solution and on the biosorbent.

Effect of solution temperature

It is vital to consider the effect of temperature during the adsorption of naphthalene. In this investigation, the effect of temperature on the naphthalene adsorption in the range of 30 °C-60 °C was studied.
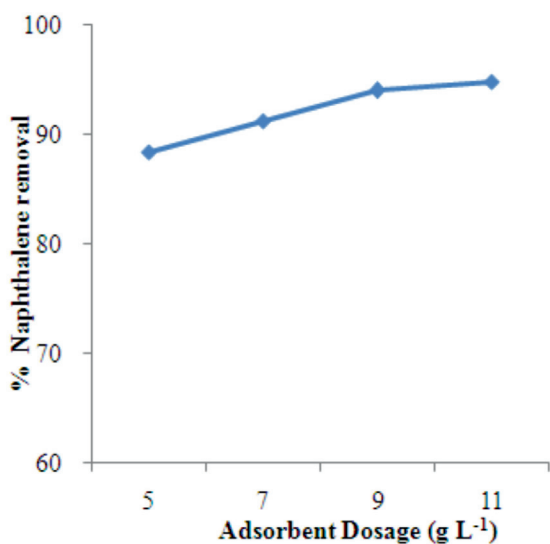

Fig. 8. Effect of adsorbent dose on %age adsorption. Initial naphthalene concentration 50 mg L⁻¹, pH 6.0, temp. 40 °C and contact time 75 minutes

The mobility of naphthalene increases with an increase in the temperature and hence an increase in absorption on the biosorption surface is observed. As shown in Figure 9, the absorption (%) increases up to 40 °C and thereafter it starts decreasing. This was exclusively because of the increase in surface activity indicating that naphthalene adsorption on de-oiled rice bran was an endothermic process. Similar results have been given for the naphthalene biosorption onto organo-sepiolite (Gok *et al.,* 2008).

Adsorption kinetics

Various models are able to convey the controlling process of adsorption procedure for example mass transfer as well as chemical reaction. The intra-particle dispersion, pseudo-first order and pseudo-second order prototypes were highly frequently utilized to review the match of investigational data of lead ions adsorption on the kinetics equations recommended by numerous authors (Weber and Morris, 1963).

The kinetic adsorption of naphthalene onto De-oiled Rice Bran Charcoal was studied at a temperature of 40 °C with an initial concentration of 50 mgL⁻¹. The kinetics prototype of pseudo-first order is largely designed for the low dilutions of aqueous solution. This model is submitted by the relative of Lagergren founded on the adsorbed quantity. The pseudo-first order considers the adsorption rate of occupation sites to be proportional to the number of unoccupied sites. This model of pseudo-first order is characterized by the resulting relation (Ru-Ling *et al.*, 2014):
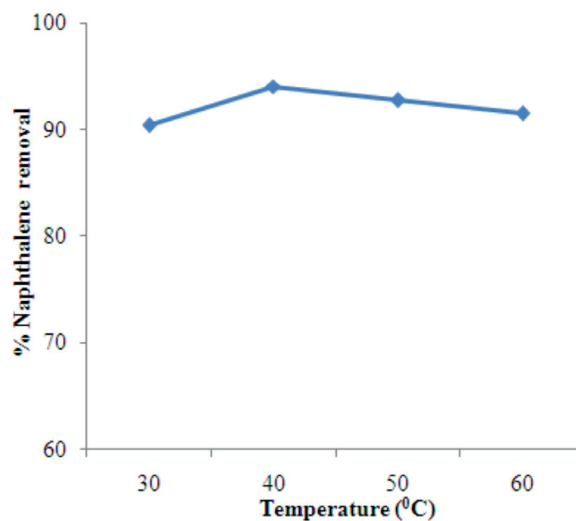

Fig. 9. Effect of temperature on adsorption of naphthalene onto de-oiled rice bran charcoal

$$\ln (Q_e - Q_t) = \ln Q_e - K_1 t \qquad .. (3)$$

where K_1 is the steady speed of adsorption of the pseudo-first order prototype (min^{-1}), a straight-talking line of $\ln (Q_e - Q_t)$ vs.t suggests the application of pseudo-first order kinetics prototype.

Another equation, pseudo-second order (Talal, 2014) can be utilized for kinetics analysis and is founded on the adsorption equilibrium capability that might be conveyed in the following form:

$$\frac{t}{Q_t} = \frac{1}{K_2 Q_e^2} + \frac{t}{Q_e} \qquad .. (4)$$

where K_2 is the steady speed of adsorption model of pseudo-second order (g/mg min^{-1}); if this equation is verified, by tracking t/Q_t according to t, we should acquire a line of slope $1/Q_e$ and ordinate in the starting equal to $\frac{1}{K_2 Q_e^2}$.

The adsorption kinetics modelling of naphthalene onto De-oiled Rice Bran Charcoal adsorbent by pseudo first order kinetic and pseudo second order kinetic model is presented in Figures 10 and 11 respectively. The parameters calculated by the two models are presented in Table 1, which also mentions the adsorbed quantity of the naphthalene and correlation coefficients.
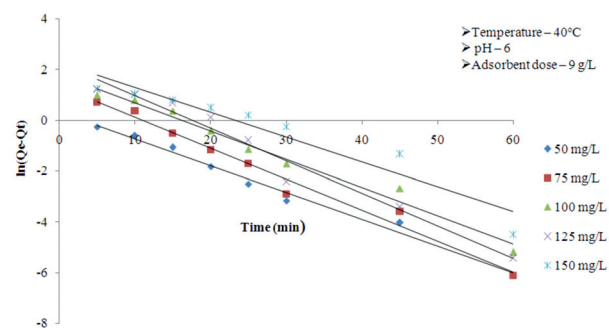

Fig. 10. Pseudo first order model of adsorption kinetics of naphthalene onto de-oiled rice bran charcoal

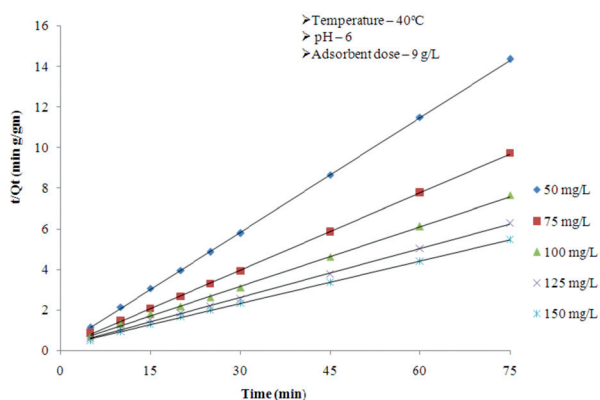From these results, it is clear that in case of pseudo-first order, the actual quantity of

Fig. 11. Pseudo second order model of adsorption kinetics of naphthalene onto de-oiled rice bran charcoal

naphthalene adsorbed is different from that calculated using pseudo-first order kinetics. On the other hand, the actual adsorbed quantity is closer to the calculated value using the kinetics model of the pseudo-second order. This model is utilized to systems in issue of adsorbing/adsorbed analyzed studying the obtained values of R^2 coefficients, which are extremely close together to the unity. Hence it is concluded that the pseudo-second order model correlates the kinetic data better ($R^2 \geq 0.998$) than pseudo-first order.

Adsorption isotherms

The Langmuir prototype is centered on chemical exchanges among solute molecules and adsorbent. According to this prototype, the adsorption of molecules arises in a single layer (establishing a molecular monolayer). This concentrated adsorption on specific sites can cover only one molecule per site. The mathematical expression is:

$$Q_e = \frac{Q_L K_L C_e}{1 + K_L C_e} \qquad .. (5)$$

where Q_L (mg/g) is the maximum adsorption capability (monolayer coverage capability), K_L (L/

Table 1. Comparison between pseudo-first order and pseudo-second order adsorption constant rate, calculated and experimental Qe values for different initial naphthalene concentrations

Initial Naphthalene Conc. (mg/L)	$(Q_e)_{exp}$	Pseudo-first order			Pseudo-second order		
		$Q_{e (cal.)}$	K_1	R_f^2	$Q_{e (cal.)}$	K_2	R_s^2
10	5.222	1.290	0.101	0.971	5.319	0.181	0.999
20	7.711	3.762	0.121	0.979	7.937	0.096	0.999
30	9.811	6.056	0.111	0.981	10.204	0.039	0.999
40	11.944	9.440	0.128	0.970	12.500	0.028	0.998
50	13.678	9.718	0.097	0.913	14.286	0.022	0.999

mg) is the equilibrium constant linked to the affinity among adsorbent and adsorbate. The vital feature of Langmuir isotherm can be conveyed by the dimensionless constant called equilibrium parameter, R_L, defined by:

$$R_L = \frac{1}{1 + K_L C_o} \qquad .. (6)$$

where R_L values indicate the type of isotherm to be irreversible ($R_L = 0$), favorable ($0 < R_L < 1$), and unfavorable ($R_L > 1$) (Miyah et al., 2016; Mahmoodi and Arami, 2008).

The Freundlich isotherm believes that adsorption happens across a heterogeneous surface with a multilayer adsorption mechanism, and that adsorbed sum increases with adsorbate concentration according to the following equation:

$$Q_e = K_F C_e^{\frac{1}{n_F}} \qquad .. (7)$$

where K_F is the Freundlich constant and n_F is a constant related to adsorption intensity.

The plots of experimental adsorption data at 60 °C with Langmuir and Freundlich equations are given in Figures 12 and 13 respectively. The results obtained at different temperatures using Langmuir and Freundlich equations are tabulated in Table 2.
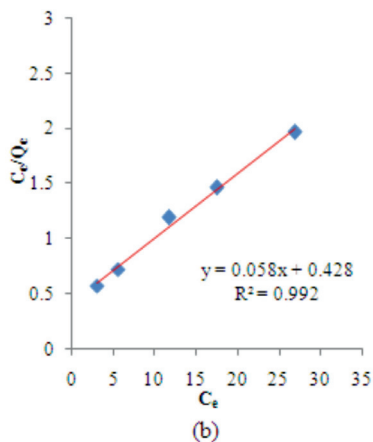
Adsorption isotherms of Freundlich and Langmuir were utilized to fit the values of experimental data. The results obtained by using Langmuir and Freundlich equations at different temperatures are tabulated in Table 2. The values of the linear regression coefficients show that Freundlich model gave the best fit in the investigated concentrations range as given in the Figures 13.
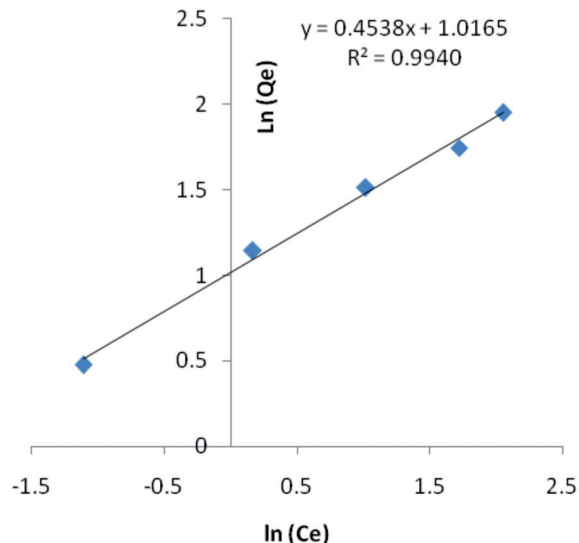

Fig.13. Freundlich isotherms for adsorption of naphthalene ions onto de-oiled rice bran charcoal at 40 °C

CONCLUSION

The present study concluded that de-oiled rice bran charcoal (DRBC) carbonized at a temperature of 500 °C for 2.5 hrs can be used as an effective adsorbent for removal of naphthalene from aqueous solution as it adsorbs 94.00% of naphthalene at initial naphthalene concentration of 50 mg L^{-1}, pH 6.0, adsorbent dose 9.0 g L^{-1}, temperature 40 °C and contact time 75 minutes. Pseudo-second order model correlates the kinetic data better ($R^2 \geq 0.998$) than pseudo-first order. Freundlich isotherm model could represent the adsorption data with reasonable and consistent parameters.

Fig.12. Langmuir isotherms for adsorption of naphthalene onto de-oiled rice bran charcoal at 40 °C

Table 2. Isotherm constants for naphthalene adsorption at different temperatures onto De-oiled rice bran charcoal

Temperature (°C)	Langmuir isotherm model			Freundlich isotherm model		
	Q_L	K_L	R_L^{2}	K_F	n_F	R_F^{2}
30	18.182	0.068	0.972	2.307	2.049	0.998
40	17.241	0.136	0.992	3.428	2.331	0.984
50	17.036	0.106	0.987	2.989	2.262	0.991
60	17.422	0.083	0.977	2.598	2.153	0.997

REFERENCES

Agarry, S.E. and Aremu, M.O. 2012. Batch Equilibrium and Kinetic Studies of Simultaneous Adsorption and Biodegradation of Naphthalene by Orange Peels Immobilized *Pseudomonas aeruginosa* NCIB 950. *J. Biorem. Biodegrad.* 3 (2) : 138-150.

Agency for Toxic Substances and Disease Registry (ATSDR), 1990. Toxicological Profile for Naphthalene and 2-Methylnaphthalene. US Public Health Service, US Department of Health and Human Service, Atlanta, GA, USA.

Akar, S. T., Ozcan, A. S., Akar, T., Ozcan, A. and Kaynak, Z. 2009. Biosorption of a Reactive Textile Dye from Aqueous Solutions Utilizing an Agro-waste. *Desalination.* 249 : 757-761.

Amoore, J.E. and Hautala, E. 1983. Odor as an Aid to Chemical Safety: Odor Thresholds Compared with Threshold Limit Values and Volatilities for 214 Industrial Chemicals in Air and Water Dilution. *J. Appl. Toxicol.* 3 : 272-290.

Baek, M.H., Ijagbemi, C.O., Se-Jin, O. and Kim, D.S. 2010. Removal of Malachite Green from Aqueous Solution using Degreased Coffee Bean. *J. Hazard. Mater.* 176 : 820-828.

Barakat, M.A. 2011. New Trends in Removing Heavy Metals from Industrial Wastewater. *Arabian Journal of Chemistry.* 4 : 361-377.

Barr, D.P. and Aust, S.D. 1994. Mechanisms White Rot Fungi use to Degrade Pollutants. *Environ Sci Technol.* 28 : 78-87.

Boffetta, P., Jourenkova, N. and Gustavsson, P. 1997. Cancer Risk from Occupational and Environmental Exposure to Polycyclic Aromatic Hydrocarbons. *Cancer Causes Control.* 8 : 444-472.

Cabal, B., Budinovaa, T., Aniab, C.O., Tsyntsarski, B., Parra, J.B. and Petrovaa, B. 2009. Adsorption of Naphthalene from Aqueous Solution on Activated Carbons Obtained from Bean Pods. *Journal of Hazardous Materials.* 161 : 1150-1156.

Crini, G., Peindy, H. N., Gimbert, F. and Robert, C. 2007. Removal of C.I. Basic Green 4 (Malachite Green) from Aqueous Solutions by Adsorption using Cyclodextrin Based Adsorbent: Kinetic and Equilibrium Studies. *Sep. Purif. Technol.* 53 : 97-110.

Das, B. and Mondal, N.K. 2011. Calcareous Soil as a New Adsorbent to Remove Lead from Aqueous Solution: Equilibrium, Kinetic and Thermodynamic Study. *Univer. J. Environ. Res. Technol.* 1 : 515-530.

Douben, P.E.T. 2003. *PAHs: An Ecotoxicological Perspective (Ecological & Environmental Toxicology Series.* Wiley, Chichester, West Sussex.

Gok, A., Ozcan, S. and Ozcan, A. 2008. Adsorption Kinetics of Naphthalene on to Organo-sepiolite from Aqueous Solutions. *Desalination.* 220 : 96-107.

Gu, L., Guo, H., Zhou, P., Zhu, N., Zhang, D., Yuan, H. and Lou, Z. 2014. Enhanced Adsorptive Removal of Naphthalene Intermediates from Aqueous Solution by Introducing Reed Straw into Sewage Sludge Based Activated Carbon. *Environ Sci Pollut Res.* 21: 2043-2053.

Guyo, U., Mhonyera, J. and Moyo, M. 2015. Pb(II) adsorption from aqueous solutions by raw and treated biomass of maize stover-a comparative study. *Process Saf. Environ. Prot.* 93: 192-200.

Ke, L., Luo, L., Wang, P., Luan, T. and Tam, N.F. 2010. Effects of Metals on Biosorption and Biodegradation of Mixed Polycyclic Aromatic Hydrocarbons by a Freshwater Green Alga *Selenastrum capricornutum. Bioresour Technol.* 101 : 6961-6972.

Kong, Z., Li, X., Tian, J., Yang, J. and Sun, S. 2014. Comparative study on the adsorption capacity of raw and modified litchi pericarp for removing Cu(II) from solutions. *J. Environ. Manage.* 134 : 109-116.

Mahmoodi N. M. and Arami, M. 2008. Modelling and Sensitivity Analysis of Dyes Adsorption onto Natural Adsorbent from Colored Textile Wastewater. *J. Appl. Polym. Sci.* 109 : 4043-4048.

Marti-Cid, R., Llobet, J. M., Castell, V. and Domingo, J. L. 2008. Evolution of the Dietary Exposure to Polycyclic Aromatic Hydrocarbons in Catalonia, Spain. *Food Chem Toxicol.* 46 : 3163-3171.

Matina, A., Biparvab, P. and Gheshlaghi, M. 2014. Gas Chromatographic Determination of Polycyclic Aromatic Hydrocarbons in Water and Smoked Rice Samples after Solid-Phase Microextraction using Multiwalled Carbon Nanotube Loaded Hollow Fiber. *J Chromatogr A.* 1374 : 50-57.

Miyah, Y., Lahrichi, A., Idrissi, M., Boujraf, S., Taouda, H. and Zerrouq, F. 2017. Assessment of Adsorption Kinetics for Removal Potential of Crystal Violet Dye from Aqueous Solutions using Moroccan Pyrophyllite. *Journal of the Association of Arab Universities for Basic and Applied Sciences.* 23 : 20-28.

Nasuha, N., Hameed, B. H. and Din, A.T.M. 2010. Rejected Tea as a Potential Low Cost Adsorbent for the Removal of Methylene Blue. *J. Hazard. Mater.* 175 : 126-132.

Savova, D., Apak, E., Ekinci, E., Yardim, F., Petrof, N., Budinova, T., Razvigorova, M. and Minikora, V. 2001. Biomass Conversion to Carbon Adsorbents and Gas. *Biomass Bioenerg.* 21 : 133-142.

Singh, B., Walia, B. S. and Arora, R. 2018. Parametric and kinetic study for the adsorption of Crystal Violet dye by using carbonized Eucalyptus. *International Journal of Computational Engineering Research.* 8 (9) : 1-11.

Tasar, S., Kaya, F. and Ozer, A. 2014. Biosorption of Lead (II) Ions from Aqueous Solution by Peanut Shells: Equilibrium, Thermodynamic and Kinetic Studies. *Journal of Environmental Chemical*

Engineering. 2 (2) : 1018-1026.

Tsai, W.T. and Chen, H.R. 2010. Removal of Malachite Green from Aqueous Solution using Low-cost Chlorella-based Biomass. *J. Hazard. Mater.* 175 : 844-849.

Vipulanandan, C. and Ren, X. 2000. Enhanced Solubility and Biodegradation of Naphthalene with Biosurfactant. *J Environ. Eng.* 126 (7) : 629-634.

Weber, W.J. and Morris, J.C. 1963. Kinetics of Adsorption on Carbon from Solution. *J. Sanit. Eng. Div. Am. Soc. Civil Eng.* 89 : 31-59.

WHO Guidelines for Drinking-Water Quality, First Addendum to Third Edition Vol. 1 Recommendations, World Health Organization, 2006.

Williams, P.T. 1990. Sampling and Analysis of Polycyclic Aromatic-Compounds from Combustion Systems - A Review. *J. Inst. Energy.* 63 : 22-30.