



Adsorption studies on treatment of textile wastewater using low-cost adsorbent

K. Senthilkumar*, V. Chitra Devi, S. Mothil, M. Naveen Kumar

Kongu Engineering College, Erode 638060, Tamil Nadu, India, Tel. +04294 226601; Fax: +04294 220087;
emails: uksen2003@gmail.com (K. Senthilkumar), erchitrasuresh@gmail.com (V. Chitra Devi),
smothil666@gmail.com (S. Mothil), er.naveenmanick@gmail.com (M. Naveen Kumar)

Received 12 January 2018; Accepted 5 July 2018

ABSTRACT

In this work, marine sediment (natural clay) was used as adsorbent for the treatment of textile effluent collected from a textile industry located in Tamil Nadu, India. Experiments were carried out using batch adsorption techniques to study the effect of process variables such as contact time, pH, agitation speed, adsorbent size, and temperature on the removal of organic compounds from textile effluent. The applicability of the various kinetic models and adsorption isotherms was tested. The kinetics of adsorption of effluent was found to be good fit with the pseudo-second-order equation based on the adsorption capacity on the solid phase. The equilibrium data have been analyzed using Freundlich and Langmuir isotherms. It was found that the adsorption data fits better into the Langmuir model. From the experimental results, it is concluded that the marine sediment (natural clay) used in this study was found to be a good adsorbent in the textile effluent treatment.

Keywords: Natural adsorbent; Textile effluent treatment; Adsorption isotherms; Kinetic models

1. Introduction

The textile industries generate huge amounts of colored wastewaters, which determined the expansion of water pollution and of environment, respectively. Approximately 100–3,000 m³/d of water is required for the dyeing process in the textile industries, leading to the generation of a large quantity of wastewater. The resulted wastewater is characterized by high content of dyestuff, salts, a high-chemical oxygen demand derived from additives, a high suspended-solid content and a fluctuating pH, depending on the process used [1]. These effluents often cause serious environmental problem due to a deep color present in them. The discharge water requires pretreatment for color elimination prior to its disposal into the river. In recent years, increasing awareness of water pollution and its far-reaching effects has prompted concerted efforts toward pollution abatement [2]. Excessive concentration of dyes in environment negatively affects many living species. Excessive ingestion of dyes by humans

can cause accumulative poisoning, cancer, nervous system damage, etc. [3]. The treatments of textile effluent create several problems as they have complex structures [4]. Organic compounds from wastewater have chemicals, biological resistance and therefore it is very difficult to treat the textiles effluents by conventional methods [5–7].

It has been reported in the literature that various methods for the treatment of effluent from textile industries include adsorption, flotation, ion exchange, coagulation, biosorption, filtration, and precipitation are the conventional methods and the advantages and disadvantages of each method have extensively reviewed [8]. Adsorption methods in solution systems play a vital role in many areas of practical environmental technology, mainly in wastewater treatment, because of several advantages such as high efficiency, flexibility, simple operation, and does not form harmful products [9]. Activated carbon has been successfully used in treating textile wastewater, being the most widely used adsorbent due its high capacity for the adsorption of organic material [6]. Treatment of textile effluent using an adsorption process by various adsorbents has become one of the major treatments for such wastewater because this process is simple, inexpensive, and

* Corresponding author.

easy to design [10]. Different authors have used several low-cost natural adsorbents for the treatment of different adsorbates such as natural clay for Nickel and Lead metals [11,12], activated clay for dyes [13], saw dust walnut, wood sawdust for dyestuffs [14], and Fuller's earth for dyestuffs [15] and the adsorption capacities for these adsorbents were found to be 12.5, 585, 36.98, 31.98, 27.8, and 26.2 mg/g, respectively.

The conventional process used to treat textile industry wastewater is based upon chemical precipitation, but the drawbacks of such methods are production of huge volumes of environmentally toxic sludge thereby increasing disposal problems, contamination in the treated wastewater, etc. Unfortunately, conventional treatment techniques are not always effective toward textile effluents, one of the most difficult-to-treat wastewaters on account of their considerable amount of suspended solids, high chemical demand and the massive presence of weakly biodegradable and often toxic substances. Therefore an efficient, an eco-friendly and cost-effective remedies for wastewater treatment are needed [10,16,17]. Hence to overcome these drawbacks, a search for cheap, effective adsorbent such as marine sediment (natural clay) is used in this study. The marine sediment (natural clay) has received particular attention as an economical adsorbent for removing organic compounds from textile effluent due to its ease of availability [16,18]. In this work, an attempt has been made to use natural clay to study the removal of organic compounds from textile effluent collected from a textile industry located in Perundurai, Tamil Nadu, India.

2. Materials and methods

Samples of textile effluent collected from a textile industry were analyzed and characterized for the same conditions and it has been found that the average value for the parameters has been reported in Table 1 and error was found to be less than $\pm 3\%$. Table 2 represents the composition of the adsorbent marine sediment (natural clay) used in the study.

2.1. Adsorbent preparation

The marine sediment (natural clay) was found in the river coasts of Kerala state, India. It was collected, purified, and sieved according to the required sizes using standard sieves. All the experiments were carried out in a 250 mL glass beaker. 100 g of adsorbent was dissolved in 1,000 mL of distilled water and stirred for 5 h. After stirring, the solution was allowed to settle and then it was filtered by using Whatman filter paper. After filtration, the adsorbent was dried in a hot air oven and then the purified adsorbent was crushed. Different sizes of adsorbent were separated using sieve shaker and activated by using 17% solution of sulfuric acid. Treatment of clay minerals with concentrated inorganic acids usually at high temperature is normally referred to as acid activation. Acid treatment often replaces exchangeable cations with hydrogen ions and releases aluminum and other cations from both tetrahedral and octahedral sites, but leaves the silicon groups largely intact [17]. The various equipment such as pH meter (Elico Pvt. Ltd, Hyderabad), TDS meter (Elico Pvt. Ltd, Hyderabad), and spectrophotometer (Systronics India Ltd, Chennai) were used to determine the various parameters during the experimental study. All the

Table 1
Characteristics of the textile effluent used in the present study

Parameters	Values ^a
pH	9.27
Total dissolved solids (ppm)	5,910
Turbidity (ppm)	97.4
Total suspended solids (ppm)	184.09
True color	653 Hazen
Appearance color	1,915.5 Hazen
Chemical oxygen demand (ppm)	942
Biological oxygen demand (ppm)	351
Total alkalinity (ppm)	1,600
Total hardness (ppm)	520
Calcium hardness (ppm)	320
Magnesium hardness (ppm)	200
Chloride (ppm)	2,807
Nitrogen (ppm)	14.19
Ammoniacal nitrogen (ppm)	5.8
Total phosphate (ppm)	5.71
Oil and grease (ppm)	13.19
Total iron (ppm)	1.26
Reactive silica (ppm)	33.15
Fluoride (ppm)	3.97
Sulfate (ppm)	598
Surfactants (ppm)	1.28

^aNote: Average values and the error margin was less than $\pm 3\%$.

Table 2
The composition of the adsorbent marine sediment (natural clay)

Characteristics	Values
Color	Black
Appearance of desiccant	Solid granular
Particle size of desiccant (mm)	0.08–1.6
pH	9.05
Density (kg/m ³)	913
Silicon dioxide (%)	62.80
Aluminum oxide (%)	17.80
Calcium oxide (%)	3.40
Sodium oxide (%)	0.3
Potassium oxide (%)	0.2
Titanium dioxide (%)	1
Magnesium oxide (%)	5.3
Calcium carbonate (%)	0.5
Iron oxide (Fe ₂ O ₃) (%)	7.70
Others (%)	0.9

chemicals used in the study were AR grade and procured from Loba Chemie (P) Ltd, India.

2.2. Adsorption process and experimental conditions

In the work, all the adsorption experiments were carried out by batch adsorption method. Adsorption study

was performed by agitating a dried sample of natural clay composite with the known size being added to each 1,000 mL of effluent solution having an initial amount of organic compounds 942 mg/L. Various experiments have been conducted to study the effect of various parameters in different ranges such as pH (2–12), adsorbent dosage (10–25 g/L), size of adsorbent (0.08–1.6 mm), agitator speed (0–1,900 rpm), and temperature (30°C, 40°C, 50°C, and 60°C) on the removal of organic compounds present in the textile effluent. Samples were taken at regular time intervals and amount of organic compounds present in effluent was measured using standard methods [18]. The pH of effluent was adjusted using 0.01 N sodium hydroxide and/or 0.01 N hydrochloric acid solutions. The amount of adsorption at time (t), q_t (mg/g) was calculated by the following equation:

$$q_t = \frac{(C_0 - C_t)v}{m} \quad (1)$$

where C_0 (mg/L) is the initial amount of organic compounds present in the effluent, C_t (mg/L) is the amount of organic compounds present in the effluent at any time, v is the volume of the effluent (L), and m (g) is the mass of dry adsorbent used. Similarly, the adsorption capacity at equilibrium q_e (mg/g) can be calculated by using equilibrium value of amount of organic compounds present in the sample C_e (mg/L).

The removal percentage of organic compounds present in the effluent (R) can be calculated using the following formula,

$$R(\%) = \frac{(C_0 - C_t)}{C_0} \times 100 \quad (2)$$

Due to the inherent bias resulting from linearization of the isotherm model and kinetic model, the nonlinear regression root mean square error (RMSE) test was employed as criterion for the quality of fitting [19]. The RMSE of a model is evaluated by using the following formula,

$$RMSE = \sqrt{\left(\frac{1}{N} - 2 \sum_{i=1}^N (q_i - q_{ie})^2 \right)} \quad (3)$$

where q_i (mg/g) is the experimental value of adsorption capacity, q_{ie} is the calculated value of adsorption capacity using the model (mg/g), and N is the number of observations in the experiment. The smaller RMSE value indicates the better curve fitting [20].

3. Results and discussion

3.1. Effect of pH on removal of organic compounds

The pH of aqueous solution is one of the most important factors controlling the adsorption process and pH is a function of hydrogen and hydroxyl ions concentration [21]. In this work, an attempt has been made to study the effect of pH on adsorption process was studied in the range of 2–12. From the experimental results it was observed that the increase of pH values enhances the removal percentage of organic compounds present in the effluent as shown in Fig. 1. This may be due to the fact that the number of negative

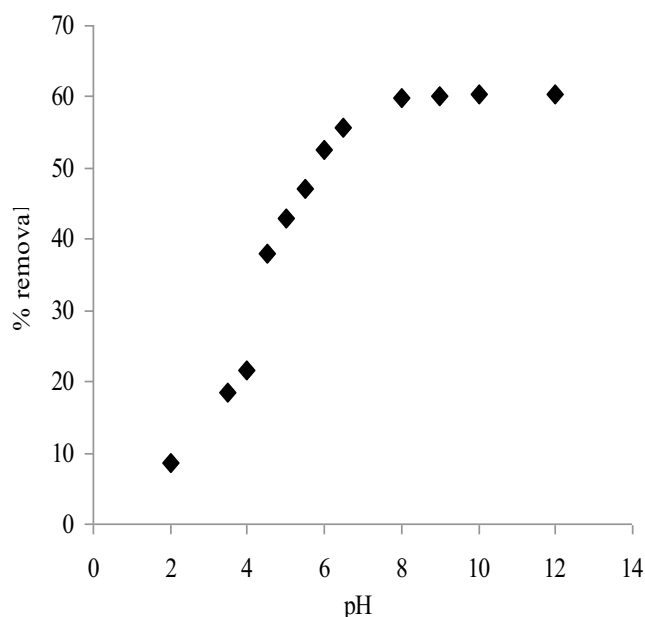


Fig. 1. Effect of pH on removal of organic compounds in the effluent.

charges on the adsorbent surface increases the attraction of positively charged dye molecule and thereby increasing the rate of adsorption [22,23]. The change of pH affects the adsorptive process through dissociation of functional groups on the adsorbent surface active sites. This subsequently leads to a shift in reaction kinetics and equilibrium characteristics of adsorption process. All amino groups of the natural clay are anionized and the dye effluent anion is pulled in strongly by electrostatic attraction. From the experimental results, the optimum pH was found to be 9.05.

3.2. Effect of contact time and adsorbent dosage on removal of organic compounds

From the experimental results, it was observed that when the time of contact between adsorbent and effluent was increased, then the percentage removal of organic compounds present in the effluent was increased rapidly during the initial stages until the equilibrium was reached, as shown in Fig. 2. A similar trend was observed in literature also [4]. The rapid adsorption at the initial contact time can be attributed to the availability of the positively charged surface of the adsorbent. The experimental results reveal that there was no change in percentage removal of organic compounds after 7 h, therefore the optimum contact time for the adsorption was found to be 7 h. In order to study the effect of adsorbent dosage on the percentage removal of organic compounds, the adsorbent dose has been varied from 10 to 25 g/L. It was also observed from Fig. 2 that percentage removal of organic compounds increases with increasing adsorbent amount for a given contact time. This may be due to the fact that the increase in adsorbent dosage may enhance the surface area and availability of more adsorption sites. From the experimental results, the optimum amount of adsorbent was found to be 25 g/L which was used for the further studies.

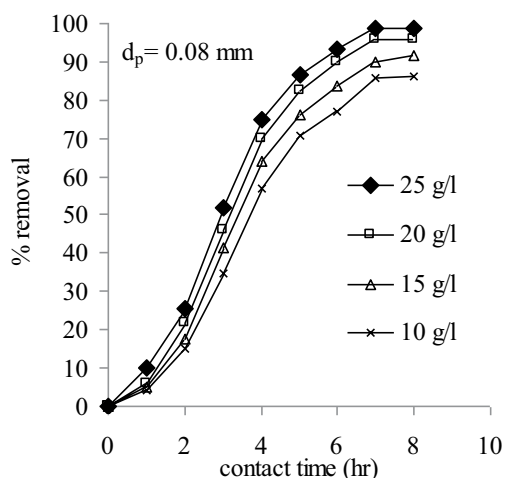


Fig. 2. Effect of adsorbent dosage and contact time on removal of organic compounds.

3.3. Effect of agitation speed on organic compounds removal

Agitation is an important parameter in adsorption processes, which is used to increase the distribution of the solute in the bulk solution and the formation of the external boundary layer [24,25]. The experiments were performed to investigate the effect of agitation speed on percentage removal of organic compounds in the effluent at various stirring rate (0–1,900 rpm). The experiments were carried out for a constant adsorption time and with the effluent pH of 9.05 in the batch reactor. From the results, it was observed that removal percentage of organic compounds increased with the increase in agitator speed as shown in Fig. 3 and found that the optimum agitation speed was 1,650 rpm.

3.4. Effect of temperature on removal of organic compounds

Temperature of the adsorption process is another important factor that can influence the efficiency of adsorption process. The influence of temperature on removal of organic

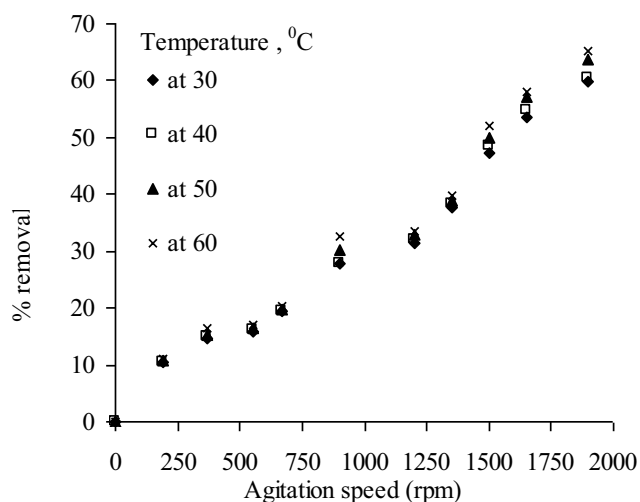


Fig. 3. Effect of agitation speed on removal of organic compounds.

compounds in the effluent was studied at different temperatures such as 30°C, 40°C, 50°C, and 60°C. The experimental results of variation of percentage removal of organic compounds at different temperatures are shown in Fig. 4. The removal of organic compounds present in the effluent at high temperature was found to be slightly greater compared with that of at a lower temperature. This may be due to the fact that increase of temperature enhances the interaction between adsorbate and adsorbent, and creation of active centers at high temperatures. This phenomenon revealed that increase of solution temperature increases the molecules mobility and number of molecules that acquires sufficient energy to undergo an interaction with surface of the adsorbent from the marine sediment [25,26]. The same trend was reported in the literature [21,27].

3.5. Effect of particle size on removal of organic compounds

Fig. 5 is a typical result of the variation of percentage removal of organic compounds with time for different particle sizes 0.08–1.6 mm. From this plot, it was observed that as the particle size decreases, the removal percentage of organic compounds in the effluent was increased. This may be due to the fact that when the particle size decreased, surface area increased and also may be due to the inability of the large dye molecule to penetrate all the internal pore structure of the marine sediment and similar observance was reported in literature for the adsorption of certain dyes on peat and wood particles [14,28].

4. Kinetics of adsorption

Most minerals like clays are rich in hydroxyl- and oxy-moieties on their external surfaces. As a result, water molecules easily form hydrogen bonds with these mineral groups. For hydrophobic compounds to adsorb directly onto oxyhydroxide mineral surfaces, they have to replace water molecules, which is energetically unfavorable. Hence it is observed that organic matter is the dominant adsorbent for hydrophobic compounds in sediments [29–32]. From the literature [10], it is observed that the adsorption capacity

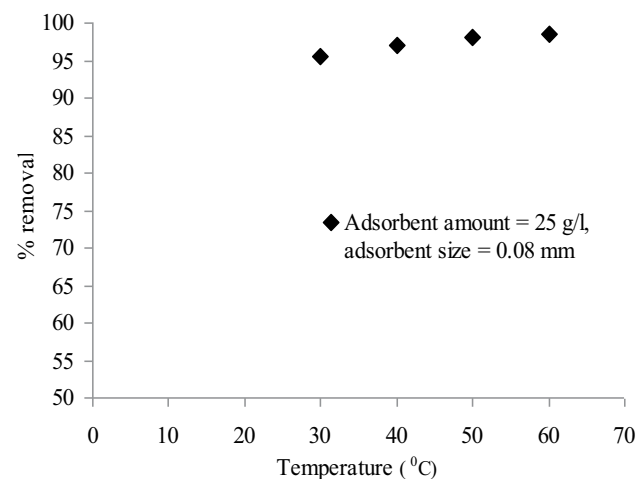


Fig. 4. Effect of temperature on removal of organic compounds.

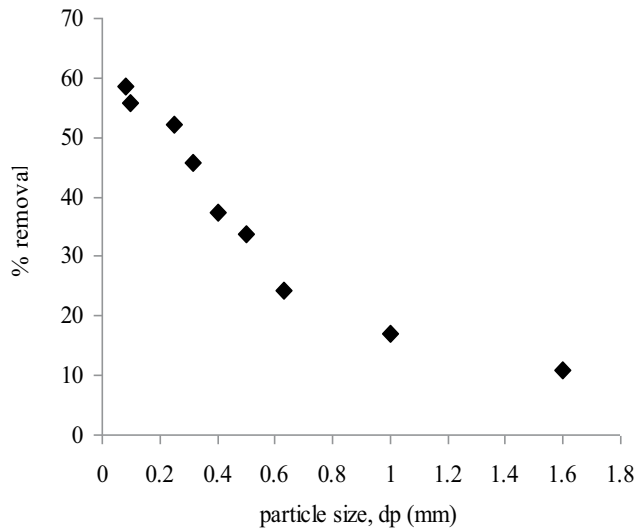


Fig. 5. Effect of particle size on removal of organic compounds.

of clays generally result from a net negative charge on the structure of minerals. This negative charge gives clay the capability to adsorb positively charged species. It was also observed that the adsorption capabilities of natural clay are suggested to be due to a net negative charge on the structure of fine grain silicate minerals. This negative charge is neutralized by the adsorption of positively charged cations, such as heavy metals, dyes, and organic matters [14]. To investigate the mechanism of adsorption process including chemical reaction and mass transfer, an appropriate kinetic model is needed to evaluate the rate data. Pore diffusion model, homogeneous surface diffusion model, and heterogeneous diffusion model (also known as pore and diffusion model)

have been used in the literature to explain the kinetics of adsorption process [4,33–36]. Table 3 represents the consolidated values of various parameters of the different models at various temperatures.

4.1. Pseudo-first-order equation

The adsorption kinetics may be described by a pseudo-first-order equation [20]. The linear pseudo-first-order equation is as follows:

$$\log(q_e - q_t) = \log q_e - \left(\frac{k_1 t}{2.303} \right) \quad (4)$$

where q_e and q_t are adsorption capacity (mg/g) at equilibrium and at time t , respectively, and k_1 is the equilibrium rate constant of pseudo-first-order adsorption (min^{-1}). The slopes and intercepts of plots of $\log(q_e - q_t)$ versus t were used to determine the first-order rate constant k_1 and the adsorption capacity (mg/g) at equilibrium q_e . However, the experimental data deviated considerably from the theoretical data, as shown in Fig. 6. The RMSE for the first-order kinetic model obtained for all the studies was high. Also the theoretical q_e values found from the first-order kinetic model did not give reasonable values. This indicates that the kinetics of adsorption of organic compounds present in the effluent is not a first-order reaction.

4.2. Pseudo-second-order equation

The adsorption kinetics may also be described by a pseudo-second-order equation [20]. The linear pseudo-second-order equation is given as follows:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (5)$$

Table 3
Details of calculated constants and parameters for various models

Models	Parameters	At 30°C	At 40°C	At 50°C	At 60°C
Pseudo first order	R^2	0.8948	0.9060	0.9177	0.918
	k_1 (g/mg min)	0.02	0.027	0.036	0.045
	q_e (mg/g)	15.6	12.85	9.73	7.05
	RMSE	9.2	8.57	6.12	5.18
Pseudo second order	R^2	0.9298	0.9708	0.9601	0.9514
	k_2 (g/mg min)	6.7×10^{-3}	4.82×10^{-3}	4.29×10^{-3}	3.9×10^{-3}
	q_e (mg/g)	11.78	11.15	12.5	9.76
	RMSE	3.44	3.16	2.98	1.18
Fractional power	R^2	0.8621	0.8818	0.88	0.85
	k	1.03×10^{-3}	1.2×10^{-3}	1.08×10^{-3}	1.23×10^{-3}
	v	0.2	0.27	0.3	0.17
	RMSE	3.76	4.59	5.98	4.6
Elovich	R^2	0.781	0.8226	0.8315	0.8345
	α	2.9×10^{-3}	5.4×10^{-3}	5.8×10^{-3}	3.9×10^{-3}
	β	571.4	250	222	438
	RMSE	6.89	3.45	5.95	7.12

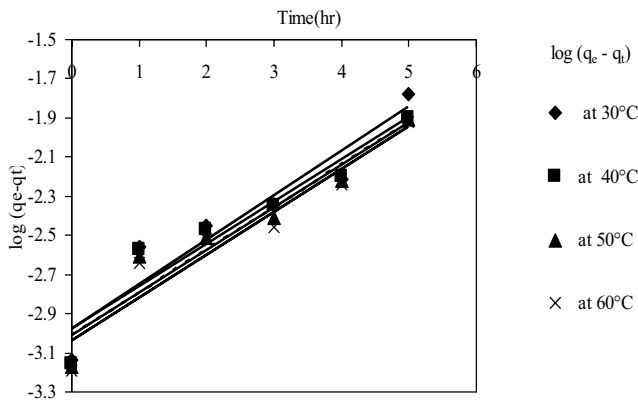


Fig. 6. Determination of constants in pseudo-first-order equation.

where k_2 is the equilibrium rate constant of pseudo-second-order adsorption (g/mg min). The slopes and intercepts of plots t/q_t versus t were used to calculate the second-order rate constants k_2 and q_e . The straight lines in plot of t/q_t versus t show good agreement of experimental data with the second-order kinetic model for all the experimental studies. The correlation coefficients (R^2) for the second-order kinetic model obtained were found to be greater than 0.9298 for all readings. The calculated q_e values also agree very well with the experimental data, as shown in Fig. 7. These results indicate that the kinetics of adsorption of effluent was found to be good fit for the second-order kinetic model.

4.3. Fractional power model

The adsorption kinetics can also be described by power function equation [19]. The linear power function equation is given as:

$$\ln q_t = \ln k + v \ln t \tag{6}$$

The plot $\ln q_t$ and $\ln t$ should give linear relationship from which v and k can be determined from the slope and intercept

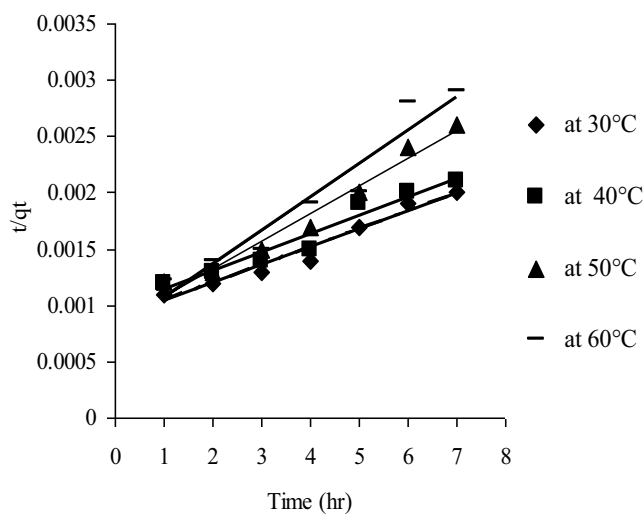


Fig. 7. Determination of constants in pseudo-second-order equation.

of the plot, respectively, as shown in Fig. 8. The experimental results revealed that the rate constant of power function v has been calculated as greater than 0.17 and indicated that this model described the time-dependent [4]. Power model describes rates of adsorption (as in the common Freundlich model) and chemical reaction (for estimation of reaction orders). However, the regression coefficient R^2 is not very high (0.85–0.88) which pointed out that power function is not the best model to correlate kinetic data.

4.4. The Elovich equation

The linear Elovich equation is given as follows [37,38].

$$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln t \tag{7}$$

where α is the initial adsorption rate (mg/g min) and the parameter β is related to the extent of surface coverage and activation energy for chemical adsorption (g/mg). Here, a linear relationship has been obtained between amount adsorbed (q_t) and $\ln t$ over the whole adsorption period, with residual RMSE between 0.78 and 0.83 for all the experiments. In case of using the Elovich equation, the RMSE are lower than those of the pseudo-second-order equation and others, hence it may not be used to explain the kinetics of adsorption of textile effluent, as shown in Fig. 9.

When the evaluated parameters for various models were compared (Table 3), it was observed that the pseudo-second-order equation proved the best correlation for all of the adsorption experiments, whereas the pseudo-first-order, fractional power model, and Elovich equation does not give a best fit to correlate kinetic data, as shown in Fig. 10. The adsorbent–adsorbate systems studied here has been found to be a best fit into second-order kinetic model, based on the assumption that the rate-limiting step may

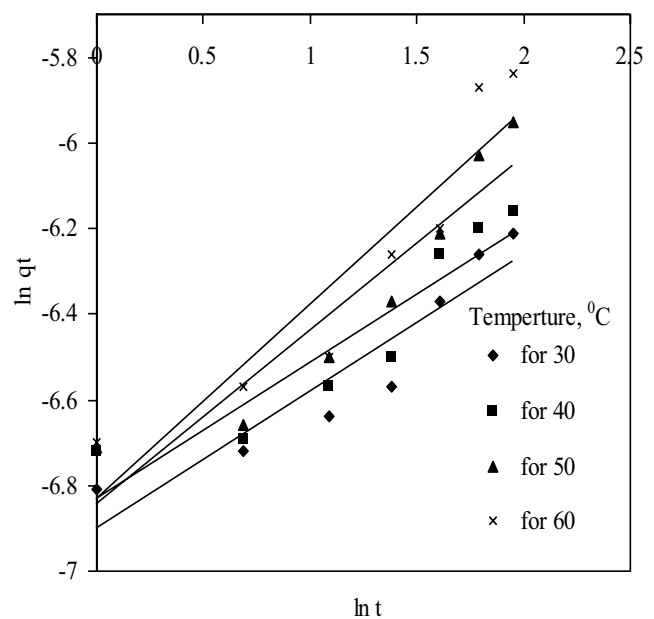


Fig. 8. Determination of constants using fractional power model.

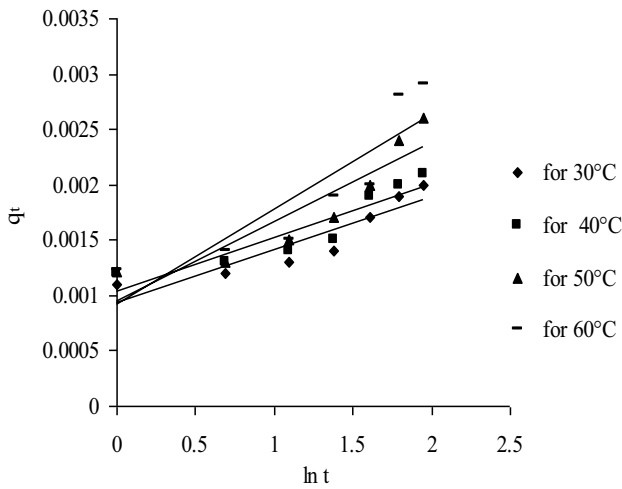


Fig. 9. Determination of constants using the Elovich equation model.

be chemical sorption or chemisorption involving valency forces through exchange of electrons between adsorbent and adsorbate [4].

5. Adsorption isotherms

The analysis and design of the adsorption process require equilibrium data for better understanding of the process. Sorption equilibria provide fundamental physicochemical data for evaluating the applicability of the sorption process as a unit operation [4]. In the investigation, the equilibrium data were analyzed at different temperatures using Freundlich and Langmuir isotherms [38–40].

5.1. Freundlich isotherms

$$q_e = K_f C_e^{1/n} \tag{8}$$

where K_f and n are the Freundlich constants characteristic of the system. Eq. (8) can be linearized in a logarithmic form and the Freundlich constants were determined and tabulated in Table 4. In Freundlich isotherm K_f and $1/n$ are Freundlich constants. The Freundlich isotherm plots are found to be linear. The K_f parameter is a measure of adsorption capacity that was found to increase with increase of temperature (Table 4). The values of $1/n$ (adsorption intensity) are found to be less than 1 that indicates a favorable adsorption [38].

5.2. Langmuir isotherms

$$\frac{C_e}{q_e} = \frac{1}{b q_{max}} + \frac{C_e}{q_{max}} \tag{9}$$

where q_e is the adsorption capacity (mg/g) at equilibrium, C_e is the amount of organic compounds at equilibrium, q_{max} represents the maximum adsorption capacity (mg/g), and b (L/mg) is Langmuir adsorption isotherm constant. The Langmuir isotherm was found to be the best fitting isotherm compared with the other isotherms. The statistical significance of the correlation coefficient (R^2) and RMSE were the criteria by which the fitting of the data to the various isotherms was tested and tabulated in Table 4. The values of q_{max} and “ b ” increased with temperature, suggesting that adsorption capacity and intensity of adsorption are increased at the high temperatures. From the literature it was observed that some low-cost natural adsorbents such as natural clay [11], saw dust walnut, saw dust cherry, sawdust pitch pine [13], Fuller’s earth [14], activated bamboo charcoal [39], coir pith carbon [40], and palm pith carbon [41] were used for the treatment of textile effluent and the maximum adsorption capacities for these adsorbents were found as 12.5, 36.98, 31.98, 27.8, 26.2, 45.25, 19.12, and 19.16 mg/g, respectively, whereas maximum adsorption capacity for marine sediment used in the study has been found to be 79.36 mg/g. Besides, from the literature, it is

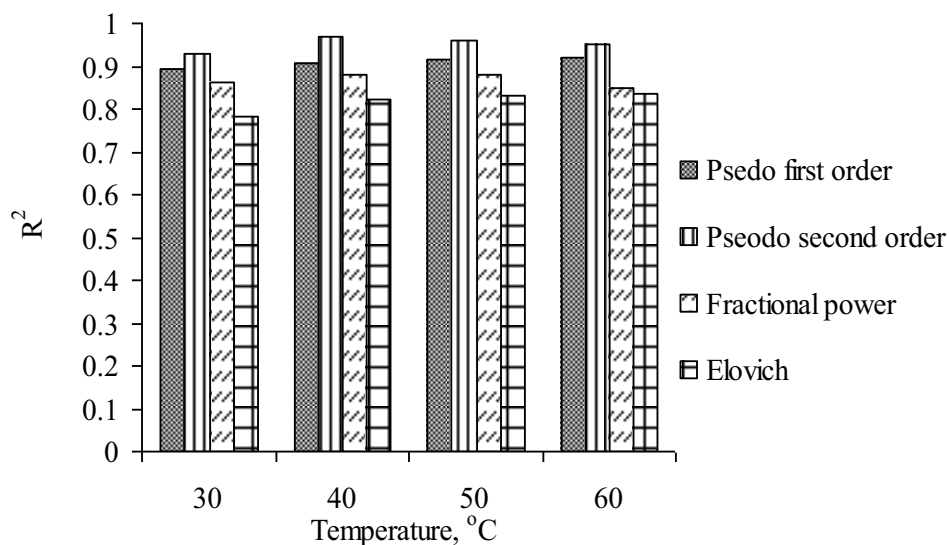


Fig. 10. Comparison of various kinetic models.

Table 4
Details of calculated isotherm parameters and corresponding RMSE values

Parameters	Models							
	Langmuir				Freundlich			
	30°C	40°C	50°C	60°C	30°C	40°C	50°C	60°C
RMSE	4.142	4.146	4.144	4.145	6.160	6.168	6.240	6.210
R^2	0.992	0.990	0.991	0.989	0.9825	0.9818	0.9820	0.9819
q_{\max} (mg/g)	79.328	79.342	79.359	79.364	–	–	–	–
b (L/mg)	0.032	0.047	0.052	0.069	–	–	–	–
K_f (mg/g)	–	–	–	–	40.4	41.8	42.5	44.1
$1/n$	–	–	–	–	0.10	0.17	0.21	0.25
Equilibrium parameter R_L	0.032	0.022	0.02	0.015	–	–	–	–

noted that the percentage adsorption has been reported by using various low-cost adsorbents such as activated clay [42] for the removal of cationic dyestuffs (61%–90%), wollastonite and kaolinite [42] for treatment of carpet effluents (73% and 84.23%), sunflower stalk [43] for treating dye effluent (67.50%), and sugarcane dust [44] for textile wastewater treatment (80%).

The essential features of a Langmuir isotherm can be expressed in terms of a dimensionless constant, separation factor or equilibrium parameter, R_L which is defined [45] as follows:

$$R_L = \frac{1}{(1 + bC_0)} \quad (10)$$

where b is the Langmuir constant and C_0 is the initial amount of organic compounds present in the effluent. The values of R_L indicate the type of isotherm to be irreversible ($R_L = 0$), favorable ($0 < R_L < 1$), linear ($R_L = 1$), or unfavorable ($R_L > 1$). The dimensionless separation factors calculated for natural clay (marine sediment) is between 0.015 and 0.032. The R_L values are found to be less than 1 and greater than 0, indicating favorable adsorption.

6. Characterization of adsorbent

The surface morphology of the clay was observed under scanning electron microscope (SEM) analysis (Fig. 11). The SEM image of magnifications 500× (a) and 5,000× (b) confirms that clumpy crystal and some flake-like structures on the surface with cavities with consistent distribution of micropores were observed. X-ray diffraction (XRD) is the basic technique to determine the crystalline structure, composition, and physical properties of materials. The XRD spectrum (Figs. 12(a) and (b)) shown that the majority of mineral clay is composed of kaolinite which is $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ and reported as the crystal phase with more than 80.6% of the total weight. Similarly free sand SiO_2 crystalline content is also present. The peaks shown that small amount of illite ($(\text{Al},\text{Mg},\text{Fe})_2(\text{Si},\text{Al})_4\text{O}_{10}[(\text{OH})_2(\text{H}_2\text{O})]$) is present in the mineral clay. The structural analysis of clay was further studied using FTIR. The spectra in Figs. 13(a) and (b) represent the degree of crystallinity and regularity of the structure of the clay minerals. IR spectra show the prominent peak of kaolinite: 3,600–3,720 cm^{-1} (–OH stretching), 1,050–1,100 cm^{-1} (–Si–O stretching), 950 cm^{-1} (–OH bending), 400–650 cm^{-1} (–Si–O bending) vibrations, and 490 cm^{-1} shows the halide deposits on the

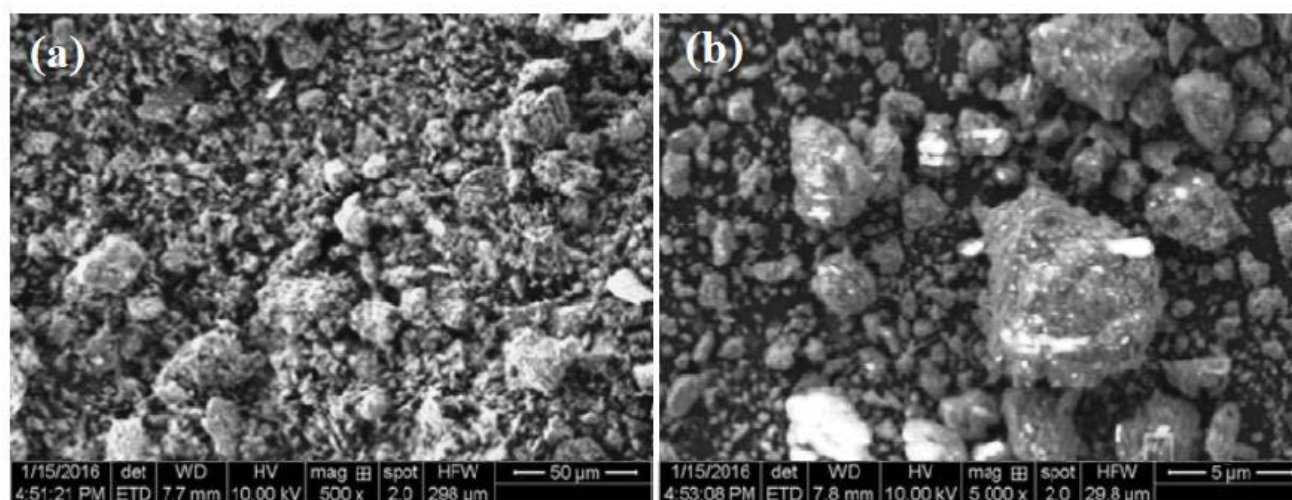


Fig. 11. Scanning electron microscope images: (a) natural clay 500× and (b) natural clay 5,000×.

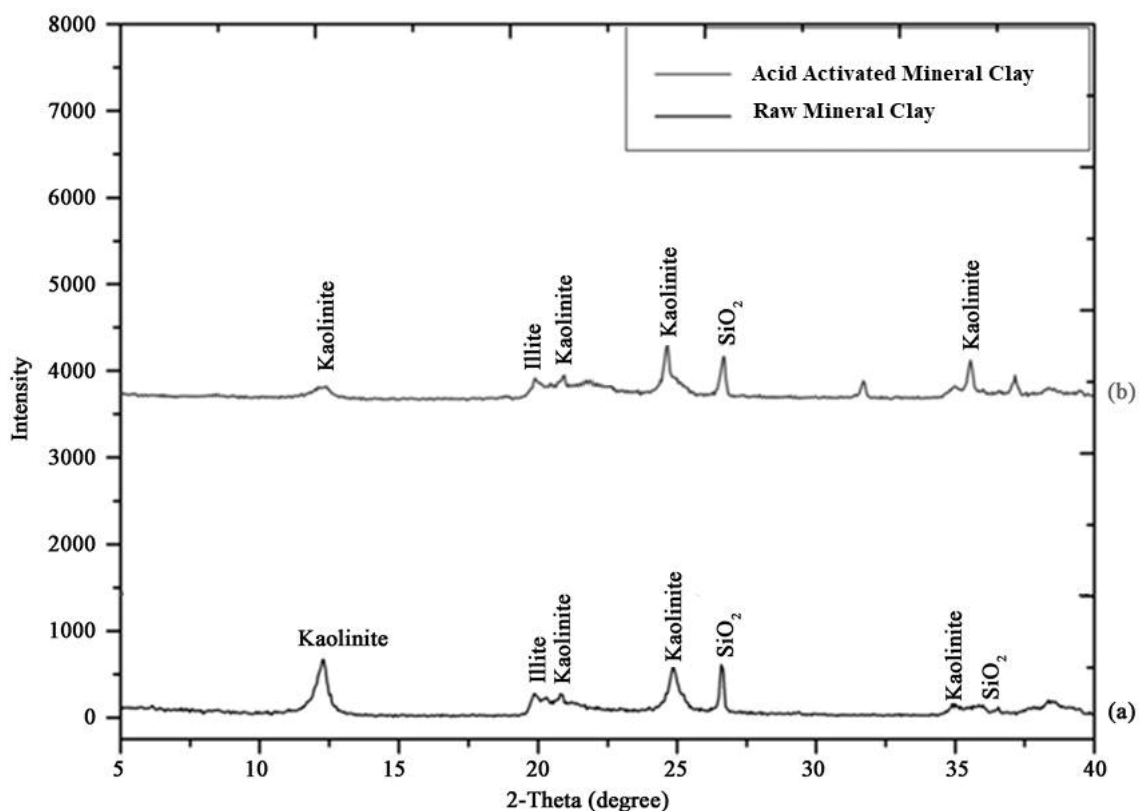


Fig. 12. XRD spectra of marine sediment: (a) raw mineral clay and (b) acid activated mineral clay.

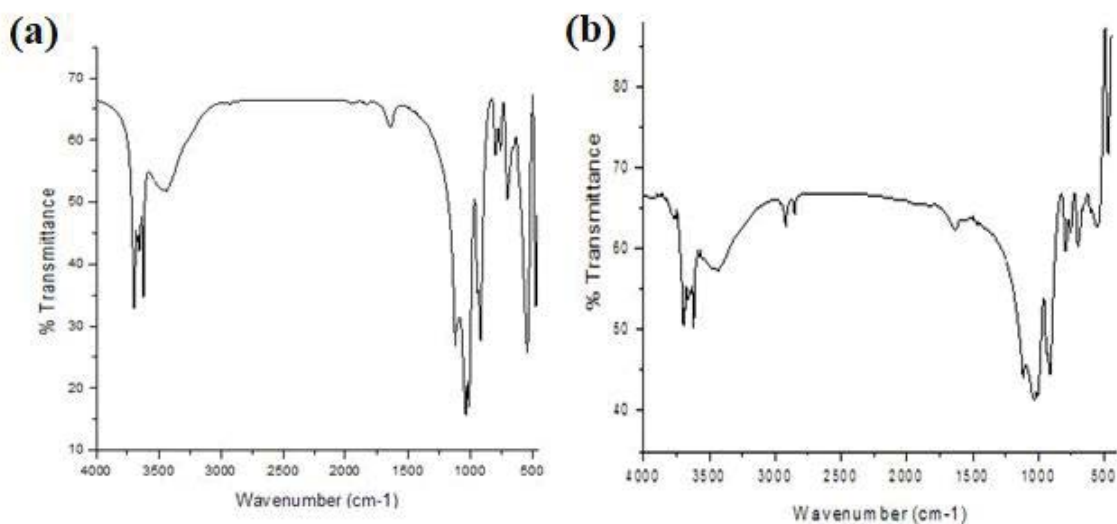


Fig. 13. FTIR spectra: (a) natural clay and (b) acid treated clay.

clay. Similarly, amine and amino groups are confirmed by the $3,300\text{ cm}^{-1}$ (N–H stretch) and $1,550\text{--}1,620\text{ cm}^{-1}$ (N–H bend).

7. Conclusion

Adsorption experiments were carried out using marine sediment (natural clay) as an adsorbent for the treatment of textile effluent. The influence of various important variables

such as pH, particle size, contact time, and temperature on adsorption process was studied. The experimental results show that percentage reduction of organic compounds present in the textile effluent increased with increase in contact time and it was found that the optimum contact time for the adsorption experiment was 7 h. The percentage reduction of organic compounds increases with increasing adsorbent amount for a given contact time and the optimum amount

of adsorbent was found to be 25 g/L. From the studies of effect of agitator speed on organic compounds removal, it was observed that organic compounds removal percentage increased with increase in agitator speed and found that optimum agitation speed was 1,650 rpm. The percentage removal capacity of organic compounds was studied with the increase of pH in the range of 2–12. From these results, it was observed that optimum pH was found to be 9.05. The removal of organic compounds from the effluent at high temperature (60°C) was found to be slightly greater compared with that of at a lower temperature (30°C). Based on the experimental results, it can be concluded that marine sediment (natural clay) was found to be a very good adsorbent for treating the textile industry effluent. The kinetics of adsorption of dyes present in the effluent was studied by using pseudo-first-order and second-order equations, fractional power model, and Elovich equation. From the experimental results it was observed that the kinetics of adsorption of effluent was found to be good fit with the pseudo-second-order equation based on the adsorption capacity on the solid phase. The equilibrium data have been analyzed using Freundlich and Langmuir isotherms. It was observed that the adsorption data fitted better to Langmuir model than Freundlich isotherm model.

Symbols

B	—	Langmuir adsorption isotherm constant
C_0	—	Initial amount of organic compounds present in the effluent, mg/L
C_t	—	Amount of organic compounds present in the sample at any time, mg/L
q_t	—	Adsorption capacity at time t , mg/g
q_e	—	Adsorption capacity at equilibrium, mg/g
v	—	Volume of the effluent, L
m	—	Mass of dry adsorbent used, g
C_e	—	Amount of organic compounds present in the sample at equilibrium, mg/L
R	—	Removal percentage of organic compounds present in the effluent, %
q_i	—	Experimental value of adsorption capacity, mg/g
q_{ie}	—	Calculated value of adsorption capacity using the model, mg/g
q_{max}	—	Maximum adsorption capacity, mg/g
N	—	Number of observations in the experiment
k_1	—	Equilibrium rate constant of pseudo-first-order adsorption, 1/min
R^2	—	Regression coefficient
α	—	Initial adsorption rate, mg/g min
β	—	Parameter is related to the extent of surface coverage and activation energy for chemical adsorption, g/mg
K_f and n	—	Freundlich constants
R_L	—	Separation factor or equilibrium parameter
v	—	Power function constant in linear power function equation

Abbreviations

RMSE	—	Root mean square error
rpm	—	Revolution per minute

References

- [1] K. Vijayaraghavan, M.W. Lee, Y.S. Yun, A new approach to study the decolorization of complex reactive dye bath effluent by biosorption technique, *Bioresour. Technol.*, 99 (2008) 5778–5785.
- [2] E.O. Igbinosa, A.I. Okoh, Impact of discharge wastewater effluents on the physicochemical qualities of a receiving watershed in a typical rural community, *Int. J. Environ. Sci. Technol.*, 6 (2009) 175–182.
- [3] G. Issabayeva, M.K. Aroua, N.M. Sulaiman, Continuous adsorption of lead ions in a column packed with palm shell activated carbon, *J. Hazard. Mater.*, 155 (2007) 109–113.
- [4] N. Ouazene, M.N. Sahmoune, Equilibrium and kinetic modelling of astrazon yellow adsorption by sawdust: effect of important parameters, *Int. J. Chem. React. Eng.*, 8 (2010) 1–28.
- [5] M. Dogan, Y. Ozdemir, M. Alkan, Adsorption kinetics and mechanism of cationic methyl violet and methylene blue dyes onto sepiolite, *Dyes Pigm.*, 75 (2007) 701–713.
- [6] N. Kannan, M.M. Sundaram, Kinetics and mechanism of removal of methylene blue by adsorption on various carbons – a comparative study, *Dyes. Pigm.*, 51 (2001) 25–40.
- [7] F. Kargi, S. Ozmihci, Biosorption performance of powdered activated sludge for removal of different dyestuffs, *Enzyme Microbial Technol.*, 35 (2004) 267–271.
- [8] V.K. Gupta, N. Suhas, Application of low-cost adsorbents for dye removal – a review, *J. Environ. Manage.*, 90 (2009) 2313–2342.
- [9] R. Rajeshkannan, M. Rajasimman, N. Rajamohan, Decolourization of malachite green using tamarind seed: optimization, isotherm and kinetic studies, *Chem. Ind. Chem. Eng. Q.*, 17 (2011) 67–79.
- [10] G. Crini, Non-conventional low-cost adsorbents for dye removal – a review, *Bioresour. Technol.*, 97 (2006) 1061–1085.
- [11] S. Hawash, H. El-Abd, M.S. El-Geundi, M.M. Nassar, J.Y. Farah, Useful adsorption equilibriums by means of natural clay, *Adsorpt. Sci. Technol.*, 10 (1993) 231.
- [12] J.B. Nishigandha, A.A. Suryavanshi, S.N. Tirthakar, Removal of heavy metal lead (Pb) from electrochemical industry waste water using low cost adsorbent, *Int. J. Res. Eng. Technol.*, 4 (2015) 731–733.
- [13] M.S. El-Guendi, H.M. Ismail, K.M.E. Attyia, Activated clay as an adsorbent for cationic dyestuffs, *Adsorpt. Sci. Technol.*, 12 (1995) 109.
- [14] F. Ferrero, Dye removal by low cost adsorbents: hazelnut shells in comparison with wood sawdust, *J. Hazard. Mater.*, 142 (2007) 144.
- [15] G. McKay, M.S. Otterburn, J.A. Aga, Fuller's earth and fired clay as adsorbent for dyestuffs, *Water, Air, Soil Pollut.*, 24 (1985) 307.
- [16] F. Ayari, E. Srasra, M. Trabelsi-Ayadi, Low-cost adsorbents for a dye uptake from contaminated water modeling of adsorption isotherms: the Langmuir, Freundlich and Elovich models, *Surf. Eng. Appl. Electrochem.*, 44 (2008) 489–498.
- [17] K. Senthilkumar, V. Sivakumar, P. Akilamudhan, Experimental studies on disposal of various industrial solid wastes, *Mod. Appl. Sci.*, 2 (2008) 128.
- [18] APHA, Standard Methods for Examination of Water and Wastewater, American Public Health Association, Washington, DC, 1991.
- [19] B. Benguella, A. Yacouta-Nour, Adsorption of bezanyl red and nylomine green from aqueous solutions by natural and acid-activated bentonite, *Desalination*, 235 (2009) 276–292.
- [20] K.G. Bhattacharyya, S. Sen Gupta, Adsorption of Fe (III) from water by natural and acid activated clays: studies on equilibrium isotherm, kinetics and thermodynamics of interactions, *Adsorption*, 12 (2006) 185–204.
- [21] A.A. Siti Nur, S.I. Mohd Halim, L. Kamal Md, S. Izhar, Adsorption process of heavy metals by low-cost adsorbent: a review, *World Appl. Sci. J.*, 28 (2013) 1518–1530.
- [22] M.N. Sahmoune, K. Louhab, A. Boukhiar, Studies of chromium removal from tannery effluents by dead *Streptomyces rimosus*, *Chem. Prod. Proc. Mod.*, 3 (2008) 29.
- [23] M. Parmar, T.L. Singh, Heavy metal Cu, Ni and Zn: toxicity, health hazards and their removal techniques by low cost

- adsorbents: a short overview, *Int. J. Plant Anim. Environ. Sci.*, 3 (2013) 143–147.
- [24] M.N. Sahmoune, K. Louhab, A. Boukhiar, J. Addad, S. Barr, Kinetic and equilibrium models for the biosorption of Cr(III) on *Streptomyces rimosus*, *Toxicol. Environ. Chem.*, 91 (2009) 1291–1303.
- [25] M.R. Samarghandi, S. Azizian, M. Shirzad Siboni, S.J. Jafari, S. Rahimi, Removal of divalent nickel from aqueous solutions by adsorption onto modified holly saw dust: equilibrium and kinetics, *Iran. J. Environ. Health Sci. Eng.*, 8 (2011) 181–188.
- [26] G. Crank, *The Mathematics of Diffusion*, Clarendon Press, London, NY, 1933.
- [27] M.M. Abd El-Latif, M.F. El-Kady, A.M. Ibrahim, M.E. Ossman, Alginate/polyvinyl alcohol - kaolin composite for removal of methylene blue from aqueous solution in a batch stirred tank reactor, *J. Am. Sci.*, 6 (2010) 280–291.
- [28] Y.S. Ho, G. McKay, Sorption of dye from aqueous solution by peat, *Chem. Eng. J.*, 70 (1998) 115–124.
- [29] M.H. Ehrampoush, Gh. Ghanizadeh, M.T. Ghaneian, Equilibrium and kinetics study of reactive red 123 dye removal from aqueous solution by adsorption on eggshell, *Iran. J. Environ. Health Sci. Eng.*, 8 (2011) 101–108.
- [30] S. Mann, A. Mandal, Performance of low-cost adsorbents for the removal of fluoride ions – an overview, *Int. J. Eng. Sci. Innov. Technol.*, 3 (2014) 437–443.
- [31] Y.H. Hiroyuki, O. Akihida, K. Takeshi, Adsorption of acid dye on cross-linked chitosan fibers: equilibria, *Chem. Eng. Sci.*, 48 (1993) 2267–2272.
- [32] M.T. Sulak, E. Demirbas, M. Kobya, Removal of Astrazon Yellow 7GL from aqueous solutions by adsorption onto wheat bran, *Bioresour. Technol.*, 98 (2007) 2590–2598.
- [33] C.T. Chiou, *Partition and Adsorption of Organic Contaminants in Environmental Systems*, Wiley Interscience, NJ, 2002, pp. 106–233.
- [34] F.-C. Wu, R.-L. Tseng, R.-S. Juang, Adsorption of dyes and phenols from water on activated carbons prepared from corncob wastes, *Environ. Technol.*, 22 (2001) 205–213.
- [35] A. Ornek, M. Ozacar, I.A. Sengil, Adsorption of lead onto formaldehyde or sulphuric acid treated acorn waste: equilibrium and kinetic studies, *Biochem. Eng. J.*, 37 (2007) 192–200.
- [36] D.N. Taha, I.S. Samaka, L.A. Mohammed, Adsorptive removal of dye from industrial effluents using natural Iraqi palygorskite clay as low-cost adsorbent, *J. Asian Sci. Res.*, 3 (2013) 945–955.
- [37] H.M.F. Freundlich, Uber die adsorption in losungen, *Z. Phys. Chem.*, 57 (1906) 385–470.
- [38] I. Langmuir, The constitution and fundamental properties of solids and liquids. Part I. Solids, *J. Am. Chem. Soc.*, 38 (1916) 2221–2295.
- [39] J.-W. Ma, H. Wang, F.-Y. Wang, Z.-H. Huang, Adsorption of 2,4-dichlorophenol from aqueous solution by a new low-cost adsorbent-activated bamboo charcoal, *Sep. Sci. Technol.*, 45 (2010) 2329–2336.
- [40] C. Namasivayam, D. Kavitha, Adsorptive removal of 2,4-dichlorophenol from wastewater by low-cost carbon from an agricultural solid waste: coconut coir pith, *Sep. Sci. Technol.*, 39 (2004) 1407–1425.
- [41] M. Sathishkumar, A.R. Binupriya, D. Kavitha, S.E. Yun, Kinetic and isothermal studies on liquid-phase adsorption of 2, 4-dichlorophenol by palm pith carbon, *Bioresour. Technol.*, 98 (2007) 866–873.
- [42] G.S. Gupta, S.P. Shukla, An inexpensive adsorption technique for the treatment of carpet effluents by low cost materials, *Adsorpt. Sci. Technol.*, 13 (1996) 15–26.
- [43] G. Sun, X. Xu, Sunflower stalk as adsorbents for color removal from textile wastewater, *Ind. Eng. Chem. Res.*, 36 (1997) 808–812.
- [44] S.D. Khattri, M.K. Singh, Colour removal from dye wastewater using sugar cane dust as an adsorbent, *Adsorpt. Sci. Technol.*, 17 (1999) 269–282.
- [45] K.R. Hall, T. Vermeylem, Pore-and solid-diffusion kinetics in fixed-bed adsorption under constant-pattern conditions, *Ind. Eng. Chem. Fundam.*, 5 (1966) 212–223.