Methods and objects of chemical analysis, 2018, Vol. 13, No. 2, 90–98

Waste Water Treatment with Surfactant-Modified Fuller's Earth for Removal of Acid Blue 29. A Statistical Approach

Jasmin Shah†, Muhammad Rasul Jan†, Mian Muhammad*‡, Behisht Ara†‡, Irum Hasan†

† Institute of Chemical Sciences, University of Peshawar, Khyber Pakhtunkhwa, Pakistan;
‡ Department of Chemistry, University of Malakand, Khyber Pakhtunkhwa, Pakistan; *e-mail: mianchem@uom.edu.pk.

Recieved: February 28, 2018; Accepted: May 17, 2018
DOI: 10.17721/moca.2018.90-98

In this work, Fuller's earth modified with sodium dodecyl sulphate was investigated for removal of Acid blue 29 dye from waste water samples. The effect of various parameters on batch adsorption experiments and various kinetics, isotherms and mass transfer mechanisms were studied. About 98.5% adsorption efficiency was achieved within 60 min at pH 3. The pseudo-second-order kinetics model and Dubinin-Radushkevich isotherm model were found best fit to the adsorption data with correlation value (R^2 = 0.999). In statistical evaluation, the individual as well as the interaction effect of various factors on adsorption was investigated and it was observed that concentration, pH and adsorbent dose are the significant factors with p values of 0.0001, 0.004 and 0.006 respectively. The coefficient of determination (R^2 = 0.930) shows that % adsorption is highly dependent on the studied factors and their interactions. The adsorbent shows higher adsorption capacity of 1514.3 mg g^{-1} with 3 regeneration cycles.

Keywords: sodium dodecyl sulphate, fuller's earth, acid blue 29, isotherms, adsorption kinetics

Dyes are colour-imparting, often complex chemical compounds that can fix themselves to fabrics or surfaces. Synthetic dyes are expansively used in a variety of fields of today's advanced technologies. Azo dyes are considered to be one of the important pollutants in waste water [1]. These are mostly used with certain fibre types such as wool, silk, modified acrylic, polyamide, polypropylene fibres and so on [2]. Acid blue 29 (AB 29) is an anionic azo dye used in the textile, paints, inks, plastics and leather industries [3].

The dyes when runs off into the water bodies, will influence aesthetics, transparency and CO_2 solubility of water. Being having stable chemical structure, dyes are not usually degraded or removed by conventional physical and chemical processes [2, 4-6]. Due to the present undesirable concerns regarding the dyes, specific methods and technologies have to be focused on to remove them from different kinds of waste water streams [7].

Adsorption is the key processes most effectively employed for dyes removal in advanced wastewater treatment. It has been found to be superior to other techniques for water re-use in terms of initial cost, flexibility and regeneration of the adsorbent [7, 8]. A large number of cost-effective and easily available natural, agricultural or biological materials have been employed under different physiochemical process parameters for efficient removal of dyes. These include activated carbon, banana stalk, ground nut hull, cocoa pod husks, mango peels, rice husks, Periwinkle shell, coconut shell, rubber seed coat, fly ash, coconut shell, Jerusalem artichoke, maize stem tissue [4], chitosan, orange peel, palm fruit bunch, shale oil ash, a volcanic siliceous rock and agro-industrial wastes [9].

Fuller's earth, also known as bentonite clay, is a sedimentary clay that contains high proportion of clay minerals of the smectite group. In both natural and activated form, it can be employed for adsorption of dyes form waste water because of its superior properties like small crystal size, high cation exchange capacity, large chemical active surface area, swelling characteristics, and water sealing and bonding properties [10].

Activated fuller's earth has the advantage of higher adsorption capacity. Upon activation, a modification in the textural characteristics of fuller's earth occurs which leads to improved adsorption characteristics. A variety of treatment techniques have been reported for activation of natural fuller's earth. These include acid treatment, alkali treatment and organic treatment [11, 12]. The inorganic acid treatment is not preferred because of the acid fuming and related compromise on equipment's safety [13].

Surfactant modified clay (SMC) or surfactant–clay complexes have been reported as potential sorbents for wastewater and contaminated soils [14-20]. The surface properties of a solid material are modified by surfactants by getting adsorbed onto its surfaces. The surface charge on the material may be neutralized or reversed and its surface may become hydrophobic to hydrophilic. Surfactants may be used either for transportation or for the immobilization of the toxic chemicals such as heavy metal ions and dyes [21].

The current method is presented as an addition to those devoted to remove dyes from waste water. This work describes feasibility of the adsorption of Acid Blue 29 (AB 29) dye form aqueous solution onto Fuller's earth (FE) modified with sodium dodecyl sulphate (SDS). The FE and surfactant-modified fuller's earth (SMFE) were characterized by SEM and FTIR spectroscopy. Batch adsorption experiments were carried out as a function of pH, contact time, adsorbent dosage and initial concentration of AB 29. Various kinetics, isotherms and mass transfer

mechanisms were studied for the adsorption of AB 29 from aqueous solutions and individual and interacting effect of different controlling factors on the adsorption of the analyte were statistically evaluated.

Experimental method and instrumentation

Fuller's earth was supplied by B.D.H. having an average particle diameter of 128 μm; it was used as delivered. Both Acid Blue 29 (AB 29) and Sodium dodecyl sulphate (SDS) were purchased form Sigma-Aldrich Chemie GmbH, Germany and were used without further purification. All other reagents, including acids and salts for buffering, used in this work were of A.R. grade reagents. Double distilled water was used in all experiments.

Scanning Electron Microscope Model JEOL - JSM 5910, Japan, under high–vacuum microprobe was used for morphological investigation and the FTIR spectra of FE and SMFE were obtained with FTIR Prestige-21 Spectrophotometer (Shimadzu, Japan). Spectrophotometric investigations of the concentration of the dye samples were carried out using a UV/VIS, Spectrophotometer (SP- 300 Plus, Optima Inc., Tokyo, Japan). For PH measurements pH meter (model 7020 Kent Industrial Measurement Electronic Instruments Ltd., Chertsey Survey England) was used.

Acid blue 29 solution was prepared by dissolving 0.1 g of AB 29 in 100 mL distilled water. From stock solution 100 μg mL^{-1} solution was prepared by dilution with distilled water. In order to investigate the effect of pH on the adsorption phenomena, a Britton-Robinson (BR) buffer was prepared by mixing 11.42 mL of CH_3COOH, 13.6 mL of H_3PO_4 and 12.3 g of H_3BO_3, in a 500 mL flask and diluted up to 500 mL with distilled water. Buffer of different pH in the range of 2-10 were prepared by adding NaOH solution in different proportions and pH was adjusted using pH meter.

Preparation of and characterization of the adsorbent. To make the surface of the adsorbent more active for adsorption, fuller's earth was modified with SDS. In a 250 mL beaker 50 g of fuller's earth and 2% solution of SDS were mixed well and shaken for 30 min. Then equilibrated overnight, filtered the solution, and dried completely in an oven below 80ºC. The bigger particles were separated and crushed with pestle and mortar, passed through a sieve to obtain uniform particle size of 45 μm and stored in a bottle for further use.

Fourier-transform infrared (FTIR) spectra were measured using FTIR Prestige-21 Spectrophotometer (Shimadzu, Japan) in the scanning range of 4000 to 400 cm^{-1}. The morphology of the SMFE before and after adsorption was observed by scanning electron microscopy (SEM) using a JEOL - JSM 5910, Scanning Electron Microscope under high–vacuum microprobe.

Adsorption experiments. Adsorption experiments were carried out in a batch mode using SMFE, aqueous solution of AB 29, and BR buffer (pH, 2-10). In order to investigate the effect of pH on the adsorption process, the adsorbent SMFE (0.1 g) was weighed in a series of beakers. AB 29 solution (1.0 mL of 1000 μg mL^{-1}), was added to each beaker followed by addition of 2.0 mL BR buffer in the range of 2-10 pH respectively and diluted up to 25 mL with distilled water. All solutions were equilibrated for 60 min, then filtered and the absorbance of each filtrate was measured at wavelength of maximum absorbance (λ_{max}), 600 nm. The concentration of unadsorbed dye was determined from an already constructed calibration curve. The amount of the dye adsorbed (%) was calculated by using the formula given in equation (1).

$$\%\, Adsorbed = \frac{C_i - C_e}{C_i} \times 100 \quad , \qquad (1)$$

where, C_i = initial dye concentration (μg mL^{-1} added) and C_e = concentration of dye at equilibrium (μg mL^{-1} unadsorbed).

The effect of adsorbent dose was studied by carrying out the adsorption experiment at room temperature with mass of SMFE in the range of 0.05-0.3 g, 1.0 mL of AB 29 (1000 μg mL^{-1}), 2.0 mL of BR buffer of pH 3, equilibration time 60 min and dilution with distilled water up to 25 mL.

The effect of adsorption time (contact time) on removal of AB 29 was studied by carrying out the experiment, with all the conditions and concentrations the same except the contact time which was varied in the range of from 30-90 min. The effect of the initial dye concentration on dye removal was studied by shaking various concentrations of AB 29 solution ranging from 500-20000 ug with SMFE for 60 min, keeping all the remaining variables constant.

Kinetic experiments were carried out by batch adsorption method, at room temperature (Average 30 ºC) on a shaker using 250 mL capped Pyrex glass bottles containing 1.0 mL of 1000 μg mL^{-1} of AB 29 solution and 0.1 g of the adsorbent, with solutions buffered at different pH, without shaking and with shaking, and time ranging from 30-90 min. Different kinetic models were applied to the kinetic data obtained at pH 2, 3, and 7, and different contact time for equilibration.

The adsorption isotherms of AB 29 on the SMFE were determined in the concentration range of 500-20000 μg mL^{-1}, with all other parameters (pH, mass of SMFE, and equilibration time) kept at optimized conditions.

The amount of dye adsorbed per unit mass of adsorbent was calculated using equation (2):

$$q_e = \frac{(C_i - C_e)V}{m} \quad , \qquad (2)$$

where, q_e (μg g^{-1}) is the amount of dye adsorbed per unit mass of adsorbent at equilibrium, C_i and C_e are the initial and equilibrium dye concentrations (μg mL^{-1}), V is the volume of the solution (L) and m is the mass of adsorbent (g).

Statistical Analysis. For statistical analysis, the software package IBM SPSS Statistics V18.0.0 was used. Data was collected form the adsorption experiments performed having five different variables: (1) the dependent variable, % adsorption; (2) the independent variable, adsorbent dose having two categories "0.15 g" and "0.25 g"; (3) the independent variable, pH which has two categories: "pH 4" and "pH 10"; (4) the independent variable, the initial concentration of adsorbate which has two categories: "100 µg mL-1", "200 µg mL-1" and (5) the independent variable, the contact time which has two categories: "30 min" and "60 min".

Results and discussion

The FTIR spectra were used for investigation of fullers' earth modification with SDS (Figure 1).

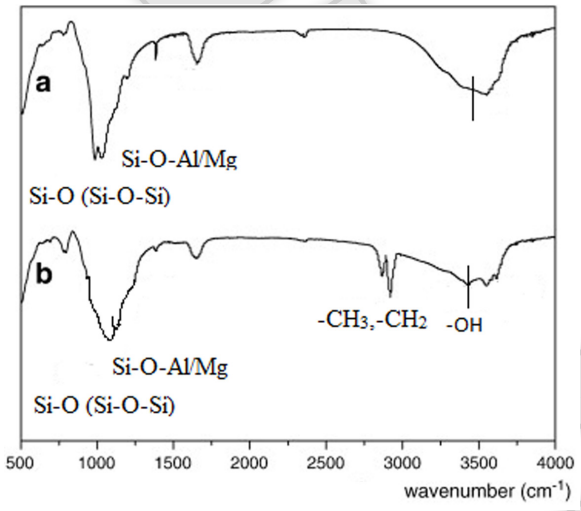

Fig. 1. FTIR spectra of the fuller's earth (a) and SMFE (b).

Compared to the spectrum of fuller's earth (a), the spectrum of SMFE (b) exhibited additional peaks at 2850 cm^{-1} and 2940 cm^{-1} that could be due to the symmetric and asymmetric stretching vibration mode of methyl and methylene groups. The absorption bands at 3450 cm^{-1} of the modified SMFE samples, corresponding to the -OH stretching vibration and bending vibration of H_2O in FE, weaken and flatten. This fact indicates that the H_2O content is reduced with the replacement of the hydrated cation of surfactant ions, as a result, the surface properties of FE change from hydrophilic to hydrophobic. The broad band at about 3400 cm^{-1} due to H-O-H stretching in fuller's earth was observed to reduce, indicating that the content of water adsorbed in SMFE was less than the fuller's earth. The peaks related to Si-O-Al/Mg and Si-O (Si-O-Si) at around 600 cm^{-1} to 1200 cm^{-1} in the fuller's earth were not changed in the SMFE spectra, revealed that the crystal structure in the fuller's earth was not changed upon modification with SDS.

The morphologies of SMFE before and after adsorption of the dye is shown in Figure 2 at same magnification power (30.000 X). From the SEM micrographs, it is evident that before adsorption, the SMFE layers are separated, forming small tactoids of larger spacing. So, the adsorbent possesses a higher surface area and a more porous nature. Also, the surface seems typically wrinkled network with irregular pores, which after adsorption of the dye became slightly flat and pores were not visible. This reveals that thin layer of the dye has covered the whole external surface of the beads. Similarly, after adsorption the surface texture becomes coarse and uneven because of the penetration of AB 29 molecules into the porous packets of the SMFE.

The effect of the mass of adsorbent on adsorption of AB 29 (1000 µg) was investigated. As shown in Figure 3, the adsorption capacity of SMFE increases with increasing its mass from 0.05 g to 0.1 g. The observation can be attributed to the fact that the amount of surfactant which intercalated into the surface galleries and interlamellar packets increases with an increase of SMFE, resulting in an increase in the absorption of the dye. However, beyond this limit the adsorption capacity remains almost constant because when the amount of SMFE exceeds 0.1 g, the solution becomes short of adsorbate though the number of active sites increases. Thus, under the present experimental conditions, 0.1 g of SMFE possesses maximum adsorption capacity for 1000 µg of AB 29.

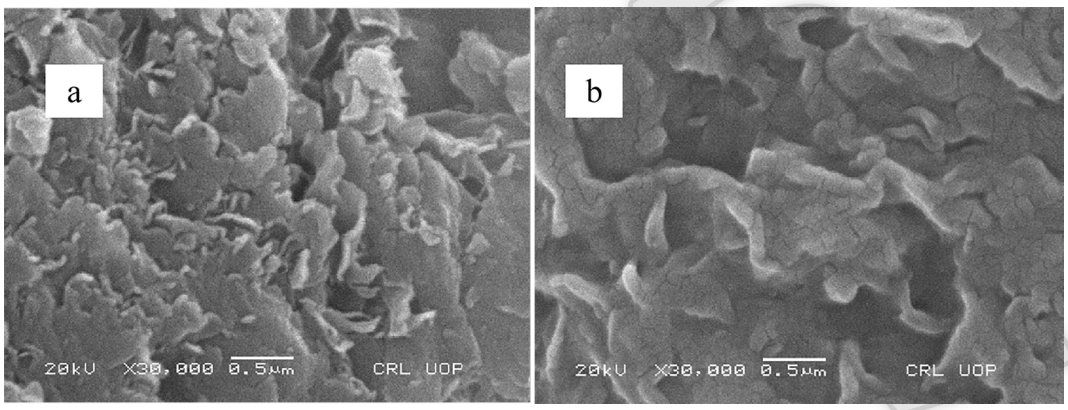

Fig. 2. SEM micrographs of SMFE (a) AB 29 unadsorbed; (b) AB 29 adsorbed.

The effect of concentration of AB 29 on removal efficiency was investigated at a variable concentration ranging from 500–20000 μg per 0.1 g of the adsorbent. As shown in Figure 3, the percent adsorption increases up to 5000 μg, beyond which it goes on decreasing. This can be explained based on the fact that more molecules were in solution competing for the available binding sites of the adsorbent at higher concentrations. Thus, maximum adsorption capacity of 0.1 g of SMFE is 500 μg.

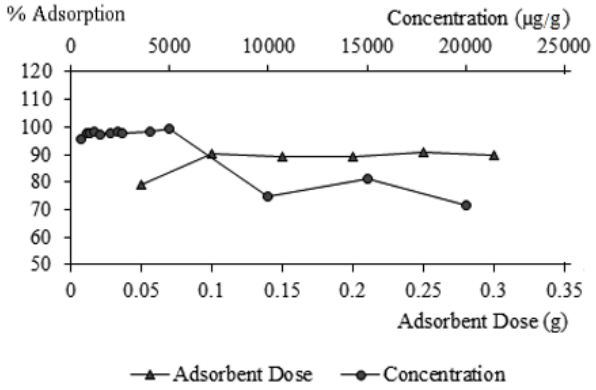

Fig. 3. Effect of adsorbent dose and concentration of adsorbate on adsorption of AB 29.

The pH of the solution not only influences the functional groups on the active sites of the adsorbent, the surface charge of the adsorbent and the structure of the dye molecule. Figure 4 shows the effect of pH of the solution on the adsorption of AB 29 under equilibrium conditions in the range of pH (2.0–10.0), where % adsorption of AB 29 was plotted against pH. It is evident that pH values affect the adsorption considerably. Initially, at pH 2.0, the adsorption seems lesser with a sudden increase, as the pH is raised to pH 3.0. AB 29 shows optimum adsorption in acidic solution of pH 3.0. Beyond the optimum point, as the pH rises, the adsorption decreases with small deviations from a constant imaginary horizontal curve. The slim decrease in adsorption may be due to the fact that repulsion exists between anionic dye molecules and the excessive hydroxyl ions at higher pH values. Yet, reasonably high adsorption capacity of the anionic dye on the adsorbent still occurred at pH 9.0 and even pH 10.0 due to the fact that Cation Exchange Capacity (CEC) of clay is not a dominant factor in adsorption onto the surfactant modified surface and physical interactions between the dye and SMFE has taken place. The findings may also be attributed to the fact that in the molecule of Acid Blue 29, there is a primary amine ($–NH_2$) attached to the naphthalene ring which will be positively charged at the initial pH of 3.0, which would be expected to bind with negatively charged functional groups on the SMFE surface. Thus, the tertiary amine groups would still be available as binding sites in the AB 29 molecule.

The rate of uptake of AB 29 by the SMFE was investigated by following the change in % adsorption with time at constant shaking rate. As depicted in figure 4, it is clear that the curve is linear before the equilibrium point (60 min) at which maximum dye uptake occurs and is linear beyond the equilibrium point. The sudden increase in adsorption may probably be attributed to boost in the mass transport driving force developed from a higher ratio of AB 29 molecules to reactive vacant adsorbent sites. The increase in adsorption (about 7%), when contact time is increased from 30-40 min is not a significant one and the statistical analysis of the adsorption process also indicates that contact time is not a significant factor.

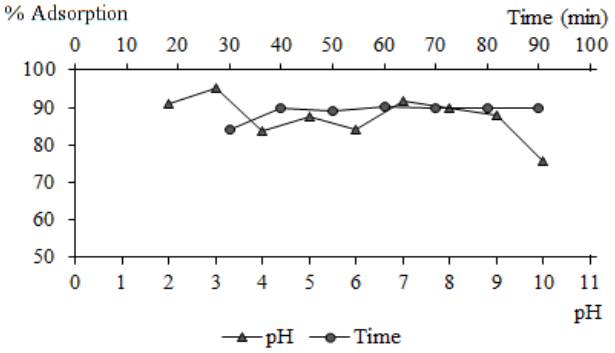

Fig. 4. Effect of pH and contact time on the adsorption of AB 29 onto SMFE.

Several kinetic models, employed to elucidate the adsorption mechanism, have been currently reported. In the present study, kinetics of adsorption was described by pseudo first order model [22], pseudo second order model [23], intraparticle diffusion model [24] and Elovich model [25]. The linear form of the equations for pseudo-first-order model, the pseudo-second-order model and the intra-particle diffusion model [8], and the Elovich model [13] are given in table 1 along with the experimental values of the kinetic parameters.

In Table 1, q_e and q_t (mg g^{-1}) are the amounts of AB 29 adsorbed at equilibrium and at time t (min), respectively, and k_1 (min^{-1}) is the rate constant of the pseudo-first-order model. The values of q_e and k_1 can be obtained from the intercept and slope of a plot of log ($q_e - q_t$) versus t. Similarly, k_2 (g (mg min)$^{-1}$) is the pseudo-second-order rate constant. The parameters qe and k_2 here can be calculated from the slope and the intercept of the plot (t/q_t) versus t. The K_{int} (mg (g $min^{1/2}$)$^{-1}$) is the intra-particle diffusion rate constant and C (mg g^{-1}) is the intercept, which represents the thickness of the boundary layer. A larger C value indicates a greater effect of the boundary layer. The α and β are known as Elovich coefficients. α represents the initial adsorption rate (mg (g min)$^{-1}$) and β is related to the extent of surface coverage (g mg^{-1}). The Elovich coefficients are calculated from linear plot of q_t versus ln (t) with a slope of (1/β) and an intercept of ln (αβ)/β.

Table 1. Kinetic parameters for the adsorption of AB 29 onto SMFE.

Model	Equation	Parameters	Values
Pseudo-first-order kinetic	$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t$	K_1 (min^{-1})	0.0599
		q_e (calc) (mg g^{-1})	6 776.415
		R^2	0.0279
Pseudo-second order kinetic	$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}$	k_2 (mg (g min)$^{-1}$)	0.02
		q_e (calc) (mg g^{-1})	250
		R^2	0.9999
Intraparticle diffusion	$q_t = k_{int} t^{1/2} + c$	K_{int} (mg g^{-1} $min^{1/2}$)	0.067
		C (mg g^{-1})	243.9
		R^2	0.0073
Elovich	$q_t = \frac{ln\,\alpha\beta}{\beta} + \frac{1}{\beta} lnt$	lnα (mg (g min)$^{-1}$)	2 256.970
		β (g mg^{-1})	9.295
		R^2	0.0024
		q_e (exp) (mg g^{-1})	246.161

As evident from the data in Table 1 and Figure 5(a), the large difference of experimental and theoretical values of (q_e) and very high deviation of R^2 value from unity means that the adsorption mechanism does not follow the pseudo-first order model. However, in case of pseudo-second order model (Table 1, Fig. 5(b)), a very close agreement of q_e (exp) with q_e (calc) and R^2 value very close to unity suggest that the model is best fit for interpretation of adsorption data. Figure 5c) shows that the plot of qt versus t½ is not passing through the origin and is multilinear indicating that intraparticle diffusion is not the controlling step during sorption of Acid blue 29 onto SMFE. Also, the difference of R^2 value of the curve form unity confirm the inapplicability of intraparticle diffusion model to the absorption data. The Elovich constants as shown in Table 1 and curve as shown in Figure 5(d) suggest that the low R^2 values of this model make it inapplicable for interpretation of experimental data. This suggests that in the adsorption process, chemisorption; such as chemical bonds between the dye and SMFE with heterogeneous surface, is not a rate controlling factor.

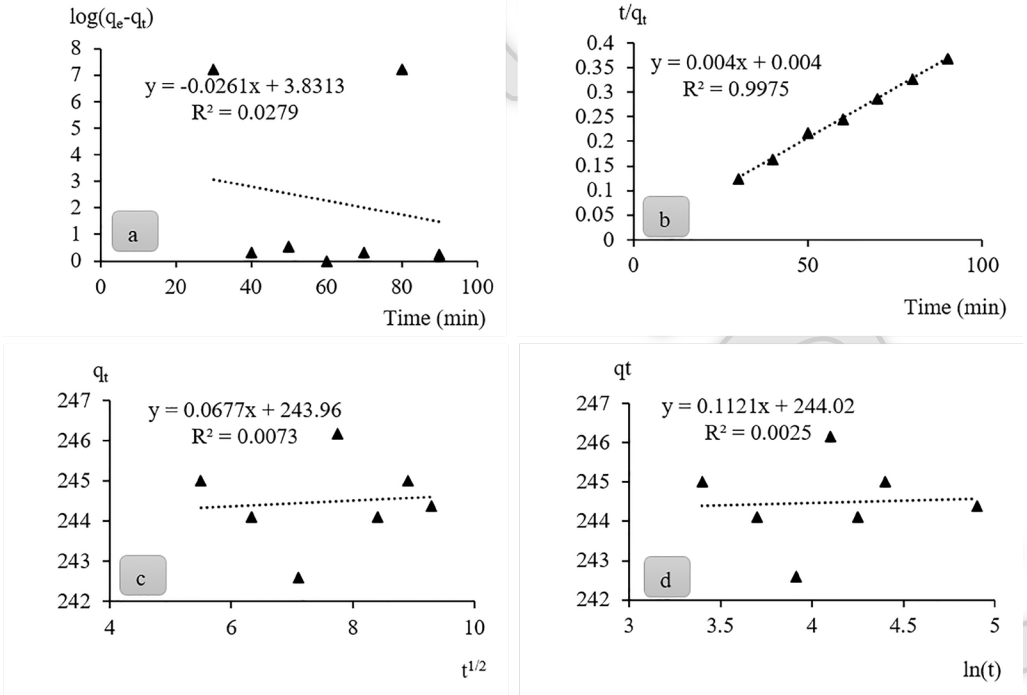

Fig. 5. Pseudo-first order kinetics plot (a), Pseudo-second order kinetics plot (b), Intraparticle diffusion (c) and Elovich model plot (d) for the adsorption of AB 29 (C_i=1000 mg L^{-1}, pH 3.0) dye on SMFE (T=303K).

A number of isotherms model are reported in literature to find the relationship between the amount of solute adsorbed per gram of adsorbent 'q_e' and the equilibrium concentration (mg L^{-1}) 'C_e'. The experimental data were treated by using four isotherm models i.e. Langmuir, Freundlich, Temkin and Dubinin-Radushkevich (D-R) model. The linear forms of these equations are given in Table 2. The values of regression coefficients (R^2) obtained from the studied models were used as the fitting criteria for comparing these isotherms.

The linear form of Langmuir adsorption isotherm is given by the equation as depicted in Table 2 and is efficient for evaluating the Langmuir parameters. Here q_e is the calculated dye adsorption (mg g^{-1} sorbent); C_e is the equilibrium concentration (mg L^{-1}); b (L mg^{-1}) is the constant of equilibrium, whose value depends on affinity between sorbate and sorbent, Q_{max} (L mol^{-1}) is the maximum amount of adsorption of AB 29 at complete monolayer coverage related to maximum capacity, taken from slope of the curve when C_e is plotted versus C_e/q_e as shown in Figure 6(a).

Table 2. Summary of equilibrium isotherm parameters.

Model	Linear Equation	Parameter	Value
Langmuir	$\frac{C_e}{q_e} = \frac{1}{bQ_{\max}} + \frac{C_e}{Q_{\max}}$	b (L mg^{-1})	36.49
		L mol^{-1}	0.0036
		Q°(mg g^{-1})	10136.11
		R^2	0.7714
Freundlich	$\log q_e = \log K_F + (1/n)\log C_e$	K_F	239.5
		1/n	0.350
		R^2	0.6878
Temkin	$q_e = B_T ln A_T + B_T ln C_e$	A_T	1.581
		B_T	14.30
		R^2	0.9293
Dubinin-Radushkevich (D-R)	$lnq_e = lnQ_{\max} - K_{DR}\varepsilon^2$	Q_m(mg g^{-1})	1514.28
		E (KJ mol^{-1})	0.01365
		R^2	0.9651

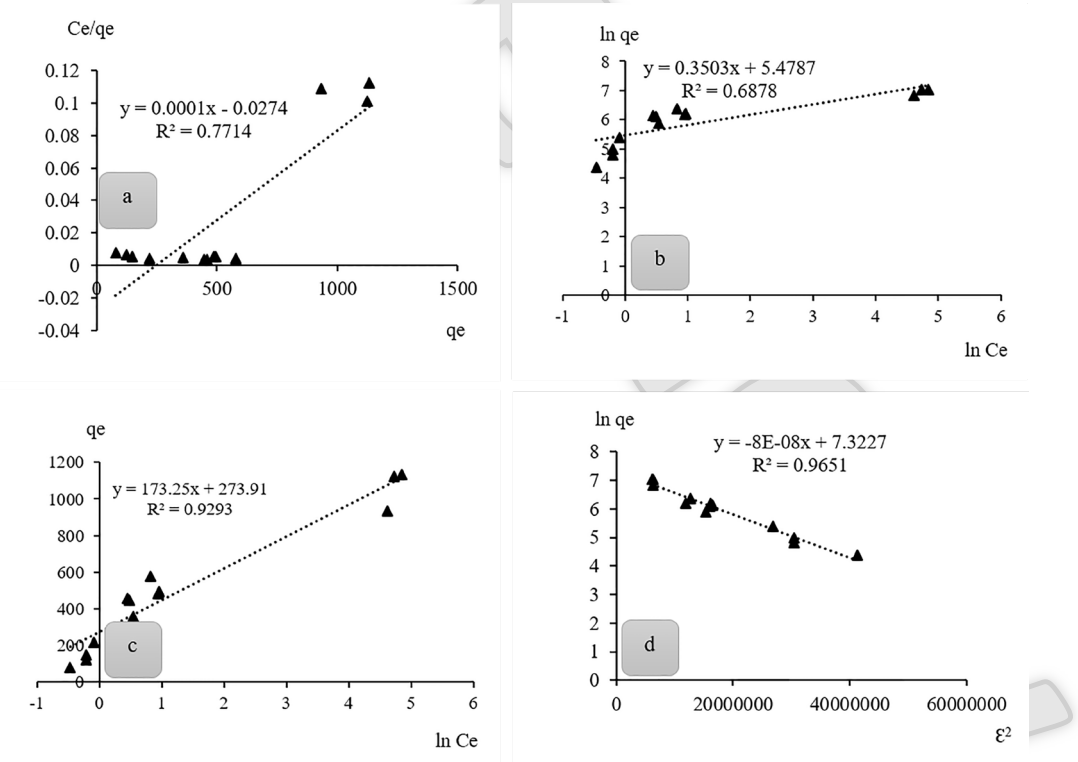

Fig. 6. Linear fitting plots of (a) Langmuir, (b) Freundlich, (c) Temkin and (d) Dubinin-Radushkevich isotherm models for the adsorption of AB 29 onto SMFE.

The value of Langmuir parameter, Q^o (maximum monolayer adsorption capacity, mg g^{-1}) obtained for the adsorption of AB 29 onto SMFE was 10136.11 mg g^{-1} at 30 ˚C which represents a very high practical limiting adsorption capacity when the surface is fully covered with dye molecules. Though the rest of the parameters support applicability of Langmuir adsorption isotherm to the data but the R^2 value, far away from unity, indicates that our data does not fit well to Langmuir adsorption isotherm. The inapplicability of Langmuir model to the data suggests that, in this case we cannot assume chemisorption or chemical adsorption which is a strong chemical bond between molecules of adsorbate and the surface of adsorbent. Also, it reflects that the adsorption sites on the surface of SMFE are not evenly distributed.

As given in Table 2, the linear form of Freundlich adsorption isotherm can be obtained by plotting log q_e versus log C_e, where qe is the calculated dye adsorption (mg g^{-1} sorbent) and Ce is the equilibrium concentration (mg L^{-1}). The K_F is the Freundlich constants related to sorption capacity and 1/n, known as heterogeneity factor, is the Freundlich constants related to sorption intensity and its value less than 1 shows stronger sorption though here it indicates more heterogeneity as the value (0.0.350) is closer to zero. The plot of log qe versus log Ce gives poor fitted curves (Fig. 6 (b)) and the value of R^2 for the Freundlich model was too low to be considered reasonable, indicating that the Freundlich model does not represent these equilibrium data. The inapplicability of Freundlich isotherm indicates that the adsorption is based on surface interaction rather than a partitioning one.

The effects of some indirect adsorbate/adsorbate interactions on adsorption isotherms is explained by Temkin isotherm model. It suggests that the heat of adsorption of all the molecules in the layer would decrease linearly with coverage due to indirect interactions. The experimental equilibrium data of adsorption of AB 29 onto SMFE was assessed according to Temkin isotherm model equation (Table 2). In the Temkin model, AT (L g^{-1}) is the binding constant that represents the maximum binding energy, BT = (RT)/b is the Temkin constant, R is the universal gas constant, 8.314 J mol K^{-1}, and T is the absolute temperature in Kelvin. The constant b is related to the heat of adsorption. For the analysis of data with the Temkin model, the parameters of the equation have been determined with a plot of qe vs. ln Ce (Figure 6 (c)). As shown in Table 2, the low R^2 value of this model shows its unsuitability for explanation of the experimental data.

In order to interpret whether the sorption mechanism is physiosorption or chemisorption, Dubinin–Radushkevich isotherm model (D–R) is used. It is generally applied to express the adsorption mechanism with a Gaussian energy distribution onto a heterogeneous surface. As given in Table 2 in the D-R model, K_{DR} is a constant related to adsorption energy, Ɛ (Polanyi potential) is RT ln(1 + 1/Ce), Q_{max} is the adsorption capacity(mg g^{-1}), and R and T are the gas constant and temperature (K), respectively [26]. The value of K_{DR} (mol^2 $(kJ^2)^{-1}$) can be calculated from the slope of the plot of ln qe vs. ε^2 (Figure 6(d)) and Q_{max} (mg g^{-1}) is determined from the intercept. The mean free adsorption energy E (kJ mol^{-1}), is the energy of adsorption per molecule of adsorbate, when it is transferred to the surface of the solid from infinity in the solution ($E = (2K)^{-1/2}$). It was calculated to be 0.01365 kJ mol^{-1} at 30°C. These results showed that AB 29 adsorption on SMFE follows a physiosorption phenomenon due to the free adsorption energies lower than 8.0 kJ mol^{-1}. If the E (kJ mol^{-1}) value lies between 8 and 16 kJ mol^{-1}, the adsorption process is controlled by a chemical mechanism, while for E < 8 kJ mol^{-1}, the adsorption process proceeds through a physical mechanism [27].

A plot of ln qe versus $Ɛ^2$ should yield a straight line. This plot for the present experimental data is shown in Fig. 6(d). The regression coefficients (R^2) obtained from the D-R isotherm model are better than those of the other studied isotherm models as seen from Table 2. As a result, the Dubinin-Radushkevich (D-R) isotherm model is an appropriate description of the data for adsorption of AB 29 on SMFE.

To statistically determine the impact of different factors on the % adsorption, three-way between-subjects ANOVA technique (Univariate analysis) was employed and p value of 0.05 was considered statistically significant. The individual effect of different factors such as adsorbent dose, Initial concentration, pH and contact time was initially investigated followed by checking the interactive effect of all the factors concerned.

Table 3 shows that concentration, pH and adsorbent dose are the significant factors with p values of 0.0001, 0.004 and 0.006 respectively. On the other hand, contact time was found statistically insignificant because here the P value is greater than 0.05. Furthermore, to investigate the interactive effect, the interaction of concentration, pH and adsorbent dose were highly significant ($p < 0.05$) while the rest of the interactions were found to show low significance. The coefficient of determination ($R^2 = 0.930$) shows that % adsorption is highly dependent on the studied factors and their interactions.

Table 3. Tests of Between-Subjects Effects.

Dependent Variable: Response					
Source	**Type III Sum of Squares**	**df**	**Mean Square**	**F**	**Sig.**
Corrected Model	2244.495[a]	15	149.633	14.219	.000
Intercept	214199.852	1	214199.852	20355.041	.000
Concentration	775.885	1	775.885	73.731	.000
pH	116.625	1	116.625	11.083	.004
Contact Time	23.171	1	23.171	2.202	.157
Adsorbent dose	3.245	1	3.245	.308	.006
Concentration * pH	516.088	1	516.088	49.043	.000
Concentration * Contact time	277.125	1	277.125	26.335	.000
Concentration * Adsorbent dose	19.609	1	19.609	1.863	.001
pH * Contact time	28.671	1	28.671	2.725	.118
pH * Adsorbent dose	28.445	1	28.445	2.703	.003
Contact time * Adsorbent dose	33.764	1	33.764	3.209	.092
Concentration * pH * Contact time	45.577	1	45.577	4.331	.054
Concentration * pH * Adsorbent dose	152.033	1	152.033	14.447	.002
Concentration * Contact time * Adsorbent dose	176.485	1	176.485	16.771	.045
pH * Contact time * Adsorbent dose	4.922	1	4.922	.468	. 040
Concentration * pH * Contact time * Adsorbent dose	42.851	1	42.851	4.072	.061
Error	168.371	16	10.523	-	-
Total	216612.718	32	-	-	-
Corrected Total	2412.866	31	-	-	-

[a] R Squared = .930 (Adjusted R Squared = .865)

Conclusions

The present study shows that waste Fuller's earth modified with SDS can be used as a potential adsorbent for the removal of Acid blue 29 (AB 29) with a higher adsorption capacity (1514.3 mg g^{-1}). The results showed that adsorption of Acid blue 29 is pH dependent and maximum adsorption was achieved at pH 3 with shaking. The adsorption of Acid blue 29 increases with contact time and equilibrium was established within 60 minutes with shaking. The equilibrium data well fitted into Dubinin-Radushkevich isotherm indicating that physiosorption is the major sorption phenomena. It was observed that kinetic data of Acid blue 29 using fuller's earth followed pseudo-second-order kinetic model. The plot of intraparticle diffusion model was not passing through the origin which indicates that the adsorption process is affected by more than one parameter. Fuller's earth is readily available in different parts of the world and can be readily used for the removal of metal ions, pesticides and dyes.

References

1. Salem I.A., El-Ghamry H.A., El-Ghobashy M.A. Catalytic decolorization of Acid blue 29 dye by H_2O_2 and a heterogeneous catalyst. *Beni-Suef Univ. J. Basic Appl. Sci.* 201, 3, 186-192.

2. Öztürk A., Malkoc, E. Adsorptive potential of cationic Basic Yellow 2 (BY2) dye onto natural untreated clay (NUC) from aqueous phase: Mass transfer analysis, kinetic and equilibrium profile. *Appl. Surf. Sci.* 2014, 299, 105-115.

3. Uzunoğlu D., Özer A. Adsorption of Acid Blue 121 dye on fish (Dicentrarchus labrax) scales, the extracted from fish scales and commercial hydroxyapatite: equilibrium, kinetic, thermodynamic, and characterization studies. *Desalin. Water Treat.* 2015, 1-23.

4. Fat'hi M.R., Asfaram A., Hadipour A., Roosta M. Kinetics and thermodynamic studies for removal of acid blue 129 from aqueous solution by almond shell. *J. Environ. Health Sci. Eng.* 2014, 12, 62.

5. Ahmad M.A., Puad N.A.A., Bello. O.S. Ki-

netic, equilibrium and thermodynamic studies of synthetic dye removal using pomegranate peel activated carbon prepared by microwave-induced KOH activation. *Water Resour. Ind.* 2014, 6, 18-35.

6. Shirzad-Siboni M., Jafari S.J., Giahi O., Kim I., Lee S.M., Yang J.K. Removal of acid blue 113 and reactive black 5 dye from aqueous solutions by activated red mud. *J. Ind. Eng. Chem.* 2014, 20, 1432-1437.

7. Sabhi S., Kiwi J. Degradation of 2, 4-dichlorophenol by immobilized iron catalysts. *Water Res.* 2001, 35, 1994-2002.

8. Morais L., Freitas O., Goncalves E., Vasconcelos L., Beca C.G. Reactive dyes removal from wastewaters by adsorption on eucalyptus bark: variables that define the process. *Water Res.* 1999, 33, 979-988.

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

10. Yagub M.T., Sen T.K., Afroze S., Ang H.M. Dye and its removal from aqueous solution by adsorption: a review. *Adv. Colloid Interface Sci.* 2014, 209, 172-184.

11. Konicki W., Pełech I., Mijowska E., Jasińska, I. Adsorption Kinetics of Acid Dye Acid Red 88 onto Magnetic Multi□Walled Carbon Nanotubes□Fe_3C Nanocomposite. *CLEAN–Soil Air Water*, 2014, 42, 284-294.

12. Usman M., Ekwueme V., Alaje T., Mohammed, A. Characterization, acid activation, and bleaching performance of Ibeshe clay, Lagos, Nigeria. *ISRN Ceramics* 2012, 2012, 1-5.

13. Kulkarni B., Jatkar, S. Activation and clarifying properties of Fuller's Earth Part VII-Activation of Fuller's Earth. *J. Indian Inst. Sci.* 2013, 23, 227.

14. Khan A., Naqvi J., Kazmi M.A., Ashraf, Z. Surface activation of fuller's earth (bentonite clay) using organic acids. *Sci. Int.* 2015, 27, 329.

15. Mulligan C.N., Yong R.N., Gibbs, B.F. On the use of biosurfactants for the removal of heavy metals from oil□contaminated soil. *Environ. Prog.* 1999, 18, 50-54.

16. Mulligan C., Yong R., Gibbs B. Surfactant-enhanced remediation of contaminated soil: a review. *Eng. Geol.* 2001, 60, 371-380.

17. Al-Asheh S., Banat F., Abu-Aitah, L. Adsorption of phenol using different types of activated bentonites. *Sep. Purif. Technol.* 2003, 33, 1-10.

18. Li Z., Willms C.A., Kniola, K. Removal of anionic contaminants using surfactant-modified palygorskite and sepiolite. *Clay. Clay Miner.* 2003, 51, 445-451.

19. Wibulswas R. Batch and fixed bed sorption of methylene blue on precursor and QACs modified montmorillonite. *Sep. Purif. Technol.* 2004, 39, 3-12.

20. Ghiaci M., Abbaspur A., Kia, R., Seyedeyn-Azad, F. Equilibrium isotherm studies for the sorption of benzene, toluene, and phenol onto organo-zeolites and as-synthesized MCM-41. *Sep. Purif. Technol.* 2004, 40, 217-229.

21. Yang J.W., Lee Y.J., Park J.Y., Kim S.J., Lee, J.Y. Application of APG and Calfax 16L-35 on surfactant-enhanced electrokinetic removal of phenanthrene from kaolinite. *Eng. Geol.* 2005, 77, 243-251.

22. Parekh P., Parmar A., Chavda S., Bahadur, P. Modified Calcium Alginate Beads with Sodium Dodecyl Sulfate and Clay as Adsorbent for Removal of Methylene Blue. *J. Dispers. Sci. Technol.* 2011, 32, 1377-1387.

23. Shukla N.B., Madras G. Kinetics of adsorption of methylene blue and rhodamine 6G on acrylic acid□based superabsorbents. *J. Appl. Polym. Sci.* 2012, 126, 463-472.

24. Daneshvar E., Kousha M., Jokar M., Koutahzadeh N., Guibal, E. Acidic dye biosorption onto marine brown macroalgae: isotherms, kinetic and thermodynamic studies. *Chem. Eng. J.* 2012, 204, 225-234.

25. Neumann M.G., Schmitt C.C., Gessner, F. Adsorption of dyes on clay surfaces' pp. 307-321 in: *Encyclopedia of Surface and Colloid Science* 2006 (Marcel Dekker Editor), New York.

26. Lagergren S., Svenska, B.K. On the theory of so-called adsorption of dissolved substances. *The Royal Swedish Academy of Sciences Document*, Band 1898, 24, pp. 1.

27. Ho Y.S., McKay, G. Pseudo-second order model for sorption processes. *Process Biochem.* 1999, 34, 451-465.