International Journal of ChemTech Research
CODEN (USA): IJCRGG, ISSN: 0974-4290, ISSN(Online):2455-9555
Vol.10 No.9, pp 346-355, 2017

Removal of Toxic Dyes by Acid Activated Clay from Dye Effluents through Adsorption: A Sustainable Approach

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Abstract : Treatment of waste water containing dyes drags everyone attention as it is a serious environmental issue. For the betterment of society, sustainable method like adsorption using adsorbent like clay is suggested for removing these dyes from effluents. Now clay treated with acid offers greater efficiency for dye removal than untreated one. So in the present work, acid activated clay is used for the adsorption of anionic dye Acid Violet 49 from aqueous solution. Affective adsorption parameters of dye including contact time, initial dye concentration, adsorbent dosage, solution pH and ionic strength was investigated by carrying out batch experiments. To know the rate of dye removal kinetic models were applied which indicated that mechanism of adsorption is governed by pseudo second order model. FTIR and SEM techniques were used to know the structural modification occurred on the surface of adsorbent after adsorption.

Keywords : AV49, acid activated clay, kinetics, adsorption, adsorbent.

Introduction

The discharge of dye effluents from various textile and other industries has detrimental effect on environment. So removal of dyes from these effluents before their release to the nature is very much required as investigated in several studies [1], [2], [3], [4], [5]. Dyes are the organic compounds that are used mainly for coloring purpose. Chemically these compounds contain chromophores (colour bearing groups), conjugated system and auxochromes (colour enhancing groups). Chromophoric groups present in the skeleton of dye can be, for example, phthalocyanine, triarylmethane, nitro, azo, anthraquinone, methane etc. Conjugated system is generally a structure containing alternate double and single bonds. The color helpers called auxochromes are carboxylic acid, sulfonic acid, amino, halogens and hydroxyl groups[6]. The combination of these above mentioned groups (chromophore, conjugated system and auxochrome) gives dye a complex structure which makes them difficult to remove from their source.

Now various chemical [7], biological [8] and electrochemical [9] methods have been employed for the removal of dyes from waste water through degradation. These methods breaks complex dye structure into simple ones. Dyes and their degradation products, both resists complete degradation as they are thermally and photochemically stable[10]. They persists in the environment causing toxicity and mutagenicity to life. So among all available methods, physical [11] methods are generally preferred as they completely remove dyes from their respective source. Adsorption is one of the most effective physical method and has lead over other methods especially when low cost, cheap adsorbent is used. In our present work, acid activated clay is used as adsorbent. Natural clay is abundant and readily available. Efficiency of clay can be improved by treating it with acid, resulting in acid activated clay with greater efficiency as adsorbent.

Acid Violet 49 (AV49) is a water soluble anionic dye which is used mainly for dyeing silk, wool and polyamide fibre. AV49 is among those dyes which are released in industrial effluents. It is chosen as representative in an attempt to solve the issue of waste water treatment. Molecular structure of this dye is shown in Figure 1.

The aim of this work is to test efficiency of acid activated clay as adsorbent in removing AV49 dye from its aqueous solution and study the effect of various parameters which affect adsorption like solution pH, initial dye concentration, dose of adsorbent, contact time and ionic strength.

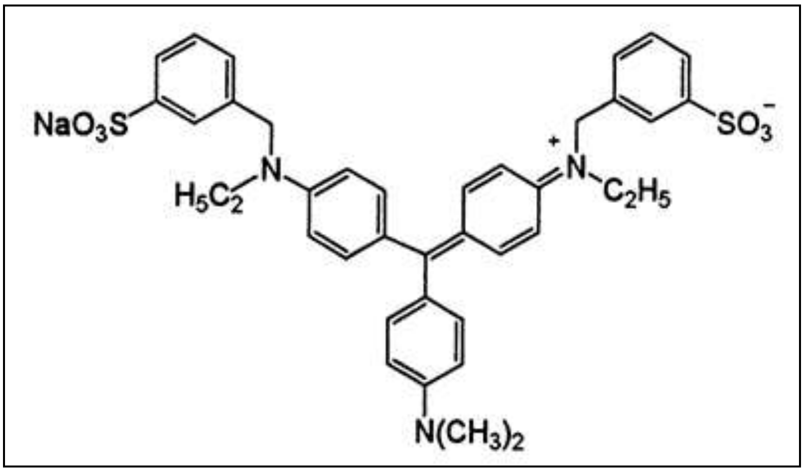


Figure 1: Molecular structure of AV49

Materials and Methods

Acid Violet 49 (Adsorbate):

AV49 (C.I.42640, molecular formula = $C_{39}H_{40}N_3NaO_6S_2$, molecular weight = 733.87 g mol^{-1}) belongs to triarylmethane class and was procured from a dye manufacturing company in Indore, Madhya Pradesh, India. A stock solution of AV49 having concentration 10^{-3} M was prepared. To obtain solutions of desired concentration, stock solution was diluted accordingly. For each experiment freshly prepared solutions were used. Absorbance of dye solution having different concentration was measured using Systronics UV-Visible Spectrophotometer Type 118 at λ_{max} 550 nm.

Acid activated clay (adsorbent) and its characterization:

Acid activated clay was obtained from a local firm of Indore, Madhya Pradesh, India and is used without any further purification. Chemical analysis of clay was done using JEOL JSM 5600 Scanning Electron Microscope (SEM) attached with Energy Dispersive X-Ray spectrometer (EDS). Surface modification of adsorbent before and after adsorption was done by Fourier Transformation Infra-Red (FTIR) technique using Bruker Vertex 70 FTIR spectrometer and Scanning Electron Microscope (SEM).

Batch Kinetics Experiments

Adsorption experiments were carried out batch wise. Specified amount of adsorbent was added to 50 ml aqueous solution of AV49 having desired concentrations (5–50 mg L^{-1}) which were taken in Erlenmeyer flask of 150 ml capacity. The system was closed with a stopper and flask was kept on magnetic stirrer (REMI Elektrotechnik Ltd., MS 500, rpm 1200) at constant speed. After definite time interval, 15 ml dye solution was withdrawn, centrifuged on centrifugation machine (centrifuge type C852/4, rpm 3500) for 5 minutes. The supernatant solution was taken in cuvette and absorbance was noted. This procedure was continued till system achieved equilibrium. The same method was used for different concentration of dye.

% Removal of the system, was determined by equation (1) –

$$\% \, Removal = \left(\frac{C_i - C_o}{C_i}\right) * 100 \qquad (1)$$

The amount of dye adsorbed at any time, q_t (mg g^{-1}) was calculated using Eq. (2) -

$$q_t = \frac{(C_i - C_o) * V}{m} \qquad (2)$$

where C_i and C_o are the initial and final concentration of dye (mg L^{-1}) at any time t, respectively, V is the volume (L) of dye solution and m is the mass (g) of clay used.

Kinetic models

In order to determine the rate constant of adsorption process, pseudo first order and pseudo second order models are used. The Linear form of Lagergren pseudo-first order kinetics [12] is given by equation (3)-

$$log(\, q_e - q_t) = \, log(q_e) - \frac{K_1}{2.303} t \qquad (3)$$

By plotting a graph between log (q_e - q_t) versus t, one can obtain the value of K_1 from slope.

Ho and Mckay's pseudo-second order model [13] is expressed as-

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t \qquad (4)$$

Equation (4) gives linear form of pseudo-second order model. Now $K_2 q_e^2$ is substituted as h and value of h and K_2 can be calculated by plotting a relation between t/q_t versus t.

For the above expressions (equation 3 & 4), q_t (mg g^{-1}) is amount of dye adsorbed at any time t, q_e (mg g^{-1}) is amount of dye adsorbed at equilibrium, t (min) is time, K_1 and K_2 are the pseudo-first order and pseudo-second order rate constants, respectively.

Results and Discussion

Characterization of Acid activated clay using EDS, FTIR and SEM:

Chemical composition of acid treated clay was determined using EDS. The results shows that it contains SiO_2 (59.83 %), Al_2O_3 (9.77 %) and Fe_2O_3 (8.48 %) as major components. Other components like CaO (2.59 %), TiO_2 (1.83 %), SO_3 (2.90 %) and Cl (0.58 %) are present in minor proportion. The reduction in weight was taken as loss on ignition which is 14.02 %.

FTIR studies also confirmed the presence of above components in the clay. Figure 12 a.) Shows the FTIR spectra of acid activated clay (SA). The observed bands are the characteristic bands of montmorillonite clay as reported in literature[14], [15], [16], [17], [18] . Shift in position of some bands from the reported literature is due to distortion of structure due to acid attack. The band particularly at 916 cm^{-1}, 875 cm^{-1}, 790 cm^{-1}, 523 $cm^{-1}$and 497 cm^{-1} confirms the presence of SiO_2, Al_2O_3 and Fe_2O_3 in adsorbent as evident by EDS analysis.

The right panel of SEM image (Figure 11 (SA)) shows the surface morphology of acid activated clay. It is observed that the surface of the adsorbent consist of irregular shapes which contains pores which are available for adsorption.

Adsorption Studies:

Effect of contact time

Effect of contact time was studied by taking 20 mg L^{-1} initial concentration of AV49. Experiment was carried out at natural pH with temperature 30 °C, volume of dye solution taken was 50 ml and mass of adsorbent was 0.02 gm. Contact time varied from 5-120 minutes. Figure 2 indicates the effect of contact time on the rate of dye uptake by activated clay. It is observed that in the beginning removal of dye from solution was very fast and then becomes constant after 50 minutes. This can be explained as initially there were more no. of vacant adsorption sites available, so adsorption process was very fast. After certain time, when adsorption has occurred, no. of vacant sites reduced. So the process becomes slow [19], [20], [21]. Equilibrium was achieved in 50 minutes for 20 mg L^{-1} concentration of dye.

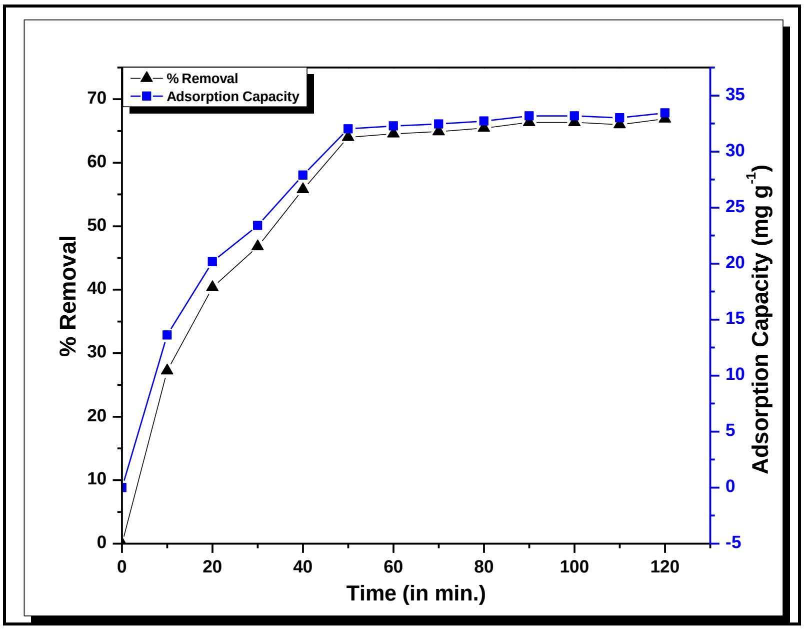


Figure 2: Effect of contact time on % Removal and Adsorption capacity using acid activated clay.

Effect of adsorbent Dose

Effect of adsorbent dosage was studied using 20 mg L^{-1} concentration of AV49 having volume 50 ml. Mass of adsorbent was varied between range 0.01-0.5 gm. Other parameters were kept constant by keeping dye in contact with adsorbent for 90 minutes. It is clear from Figure 3 that as the mass of clay increases rate of dye uptake also increases. The % Removal from 35.67 % to 104.75 % has occurred and it became insignificant after 0.125 gm mass of acid activated clay. This can be explained as the mass of clay increases, surface area for adsorption increases. As a result rate of dye removal increases [22], [19]. For convenience of study, the mass of adsorbent was selected 0.02 gm for further experiment.

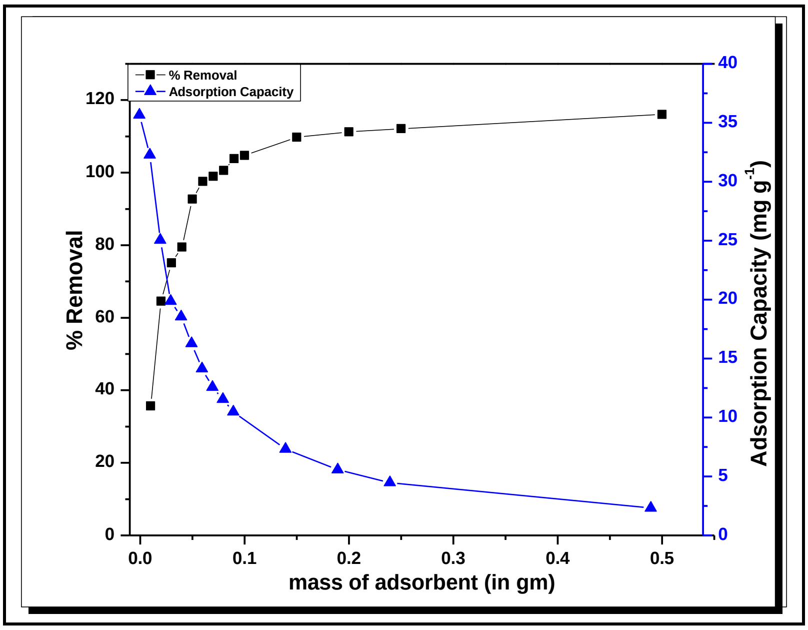


Figure 3: Effect of adsorbent dosage on % Removal and Adsorption capacity.

Effect of initial dye concentration

Study of variation in dye concentration is important as the removal of dye from effluent is affected by it. Definite amount of clay can adsorb particular amount of dye. The experiment was performed by varying initial dye concentration between 5- 50 mg L^{-1} by maintaining other parameters unaltered. As the concentration of dye increase, rate of dye removal will be less for given amount of activated clay. Results showed that initially the removal of dye increases as the time increases as indicated by Figure 4. At the start, adsorption was very fast in first 50 minutes, it then decreases as the time increases and equilibrium is achieved. This may be due to in starting concentration driving force was more, adsorption sites were more. As the time increases, this driving force decreases indicating adsorbent is saturated [23]. It also shows that as concentration increases removal of dye decreases. % Removal at equilibrium was found to decrease from 114.69 to 18.14 % for concentration 5 to 50 mg L^{-1} of dye solution, respectively.

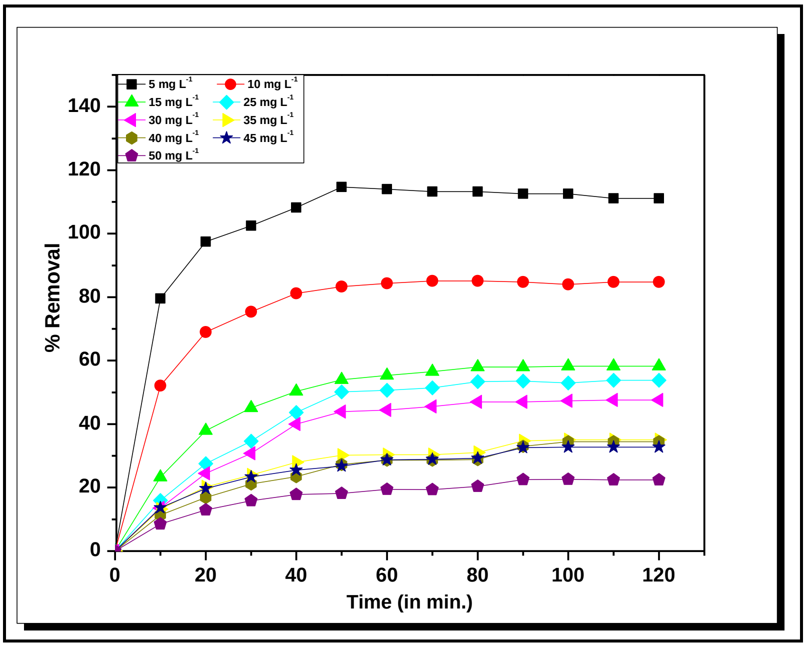


Figure 4: Effect of different initial concentration for definite amount of adsorbent.

Effect of Ionic Strength

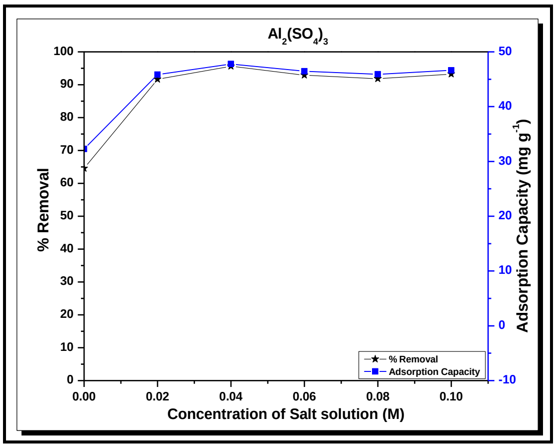


Figure 5

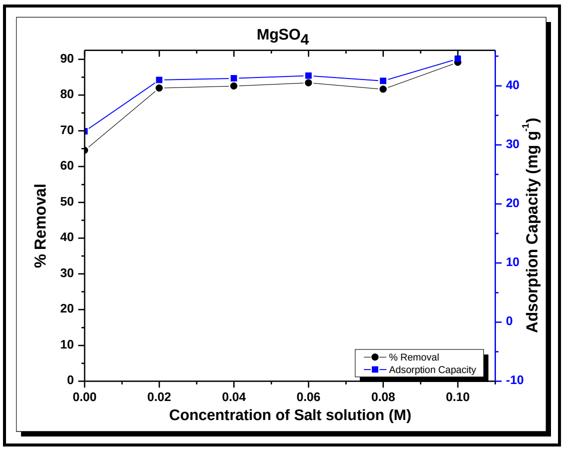


Figure 6

Figure 5 and 6: Effect of addition of $MgSO_4$ and $Al_2(SO_4)_3$, respectively on adsorption

Effect of ionic strength was studied taking different concentrations (0.02 to 0.10 M) of $MgSO_4$, and $Al_2(SO_4)_3$ by using 20 mg L^{-1} dye concentration with contact time 90 minutes. The results showed that adsorption process is affected by salt addition in dye solution. Figure 5 and 6 shows that adsorption is increased in presence of Na_2SO_4 and $MgSO_4$, respectively. Moreover, adsorption is slightly affected changing concentration of salt. Figure 7 depicts comparative effect on % Removal of dye in presence of both the salt. It is found that as the charge on cation (Mg^{2+}, Al^{3+}) increases, removal efficiency increases from 64.56 to 89.14 and 93.27 for Mg^{2+} and Al^{3+}, respectively. The increase in % Removal can be explained as on addition of salt, positive charge on the surface of adsorbent increases. Now as adsorbent surface becomes more positive, electrostatic force of attraction between adsorbent and anionic AV49 dye also increases. Thus adsorption increases [24], [25].

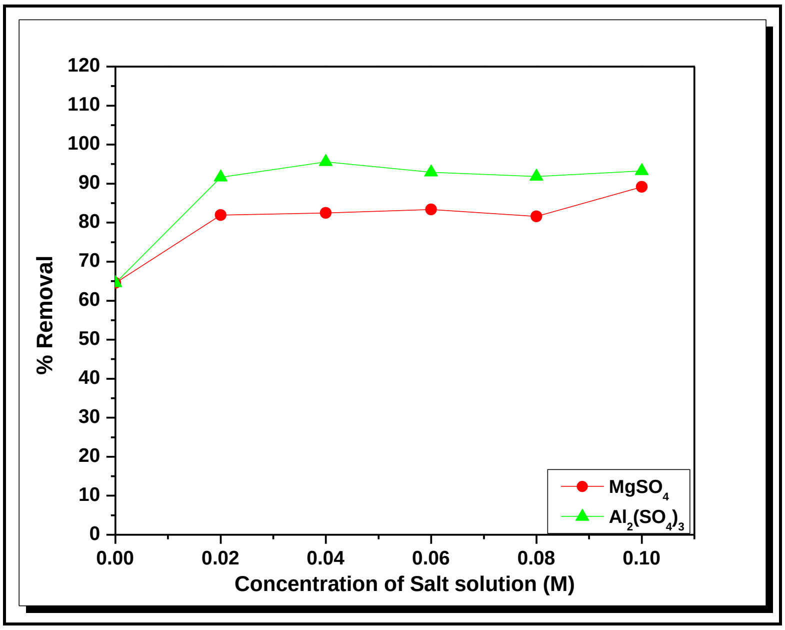


Figure 7: Comparative effect of addition of both the salts ($MgSO_4$ and $Al_2(SO_4)_3$) on adsorption.

Effect of pH

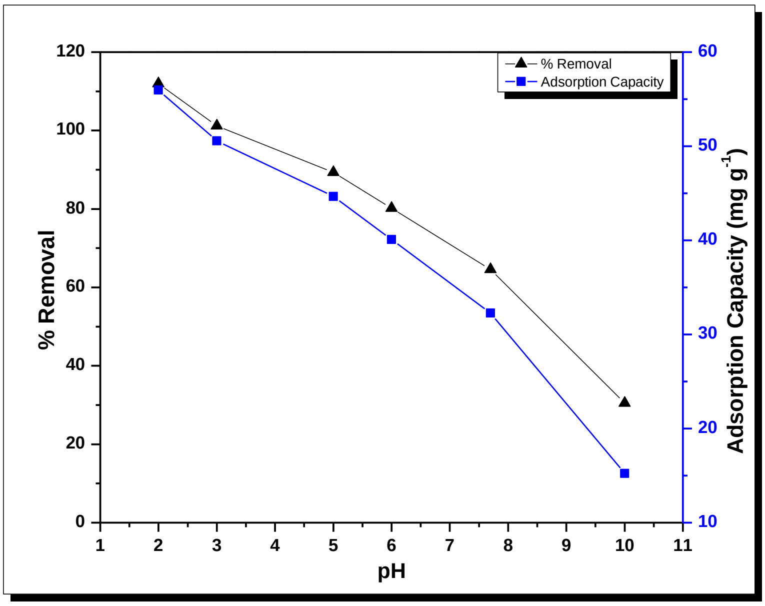


Figure 8: Effect of pH on % Removal and Adsorption capacity.

Variation of pH is also significant as it affects the rate of dye uptake from solution. In the present work, pH is varied from 2 to 10 using 0.1 M NaOH and HCl (dye concentration = 20 mg L^{-1}, volume = 50 ml, temperature =30°C, mass of adsorbent = 0.02 gm, contact time = 90 min.). The pH of the solutions were measured using Digital pHmeter Type MK-VI. As shown in Figure 8 acidic pH was favorable for adsorption than alkaline. This can be explained as AV49 dye exists in the form of anions in aqueous solution. If D represents the dye AV49, the following equation (5) can used to explain its existence in water.

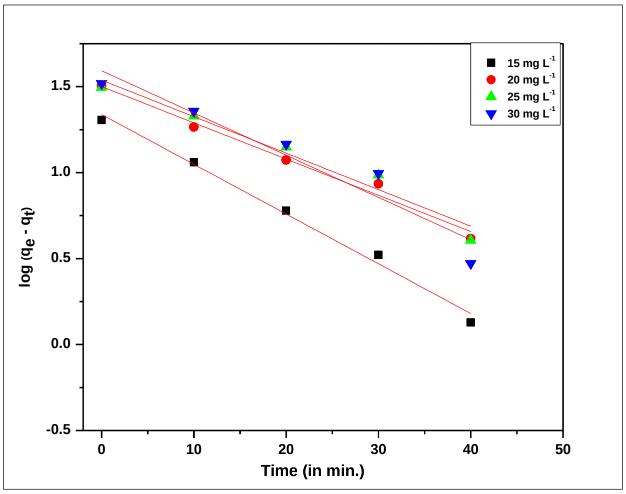
$$D - SO_3Na\ (aq) \rightarrow D - SO_3^-\ (aq) +\ Na^+(aq) \tag{5}$$

It was found that at low pH, as H^+ ions were more, so adsorption of AV49 onto acid activated clay was more. This is because of electrostatic force of attraction between positive adsorbent sites and negative group of dye molecule. As the pH increases and become alkaline, adsorption decreases. This may be due to increase in negative charge on clay surface by deprotonation of surface hydroxyl sites (A-OH e.g. Si-OH and Al-OH) as illustrated by equation (6).

$$-A - OH + OH^- \rightarrow -AO^- + H_2O \tag{6}$$

As the AV49 is anionic dye, repulsion with negative surface occurs, which inhibits the adsorption process. Similar results are obtained by [26], [27], [28].

Kinetic Studies:



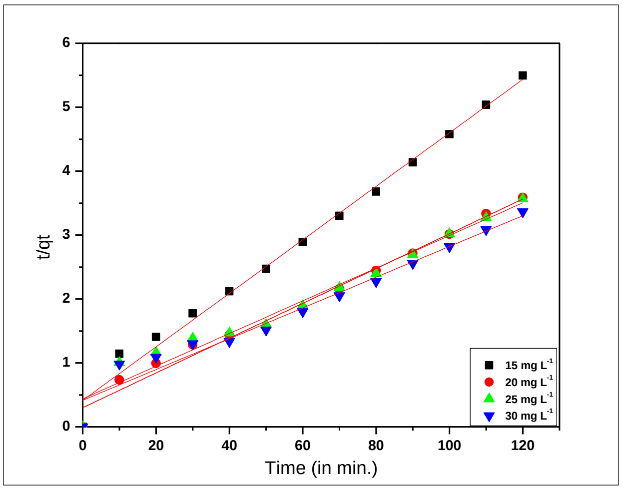


Figure 9 **Figure 10**

Figure 9 and 10: Pseudo first and second order adsorption kinetics of dye onto acid activated clay, respectively.

Table 1: Kinetic data of pseudo first and second order models.

	Pseudo-first order equation		**Pseudo-second order equation**		
C_o (mg L^{-1})	**R_1^2**	**K_1 (min^{-1})**	**R_2^2**	**K_2 (g mg^{-1} min^{-1})**	**$h = K_2q_e^2$ (g mg^{-1} min^{-1})**
15	0.9892	0.0666	0.9891	0.0042	2.4106
20	0.9795	0.0486	0.9849	0.0025	3.3419
25	0.9511	0.0489	0.9643	0.0015	2.2839
30	0.9015	0.0566	0.963	0.0014	2.4086

Table 1 shows the values of rate constants (K_1 (min^{-1}) & K_2 (g mg^{-1} min^{-1})) and correlation coefficients (R_1^2 & R_2^2) of pseudo first and second order, respectively. When the values of R_1^2 and R_2^2 are compared, it is found that R_2^2 has a good fit with all values greater than 0.963. Moreover, the validity of pseudo-second order model is evident from the linearity of the plot (Figure 10). It is clear that there is good correlation between experimental data and pseudo second order model. Therefore, there is possibility that the adsorption process follows the chemisorption mechanism[29], [30].

Study of surface morphological changes after adsorption

SEM Results:

The left side of Figure 11 shows SEM image of acid activated clay (SA) before adsorption and right side shows SEM image after adsorption of AV49 dye onto acid treated clay. The SEM image of SA before adsorption shows that the adsorbent consist of large surface area due to presence of vacant sites on the surface. After adsorption, the surface is getting smooth due to occupation of these sites and is getting saturated to maximum extent as evident from right side of Figure 11 (AV49A).

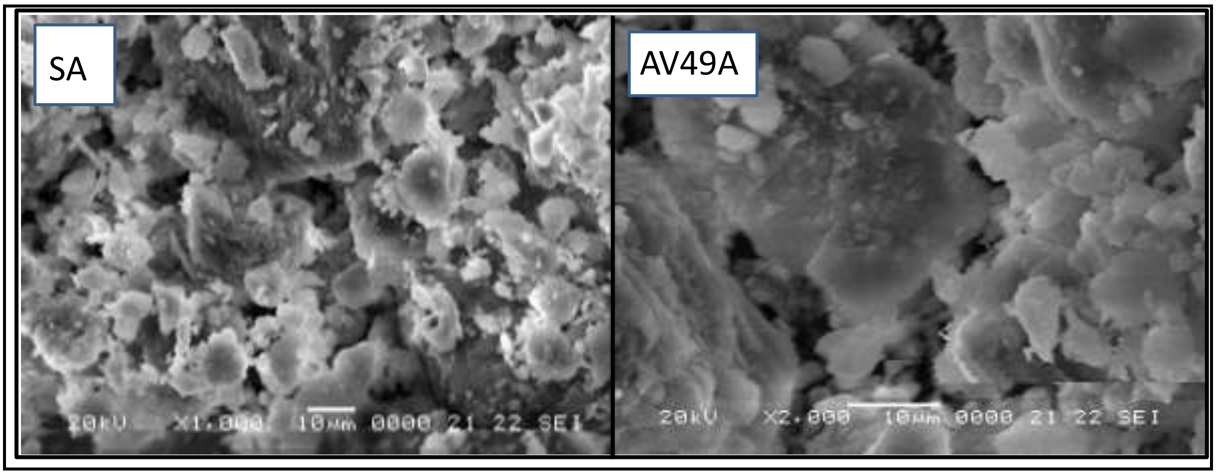


Figure 11 shows the SEM images of acid activated clay before (SA) and after (AV49A) adsorption.

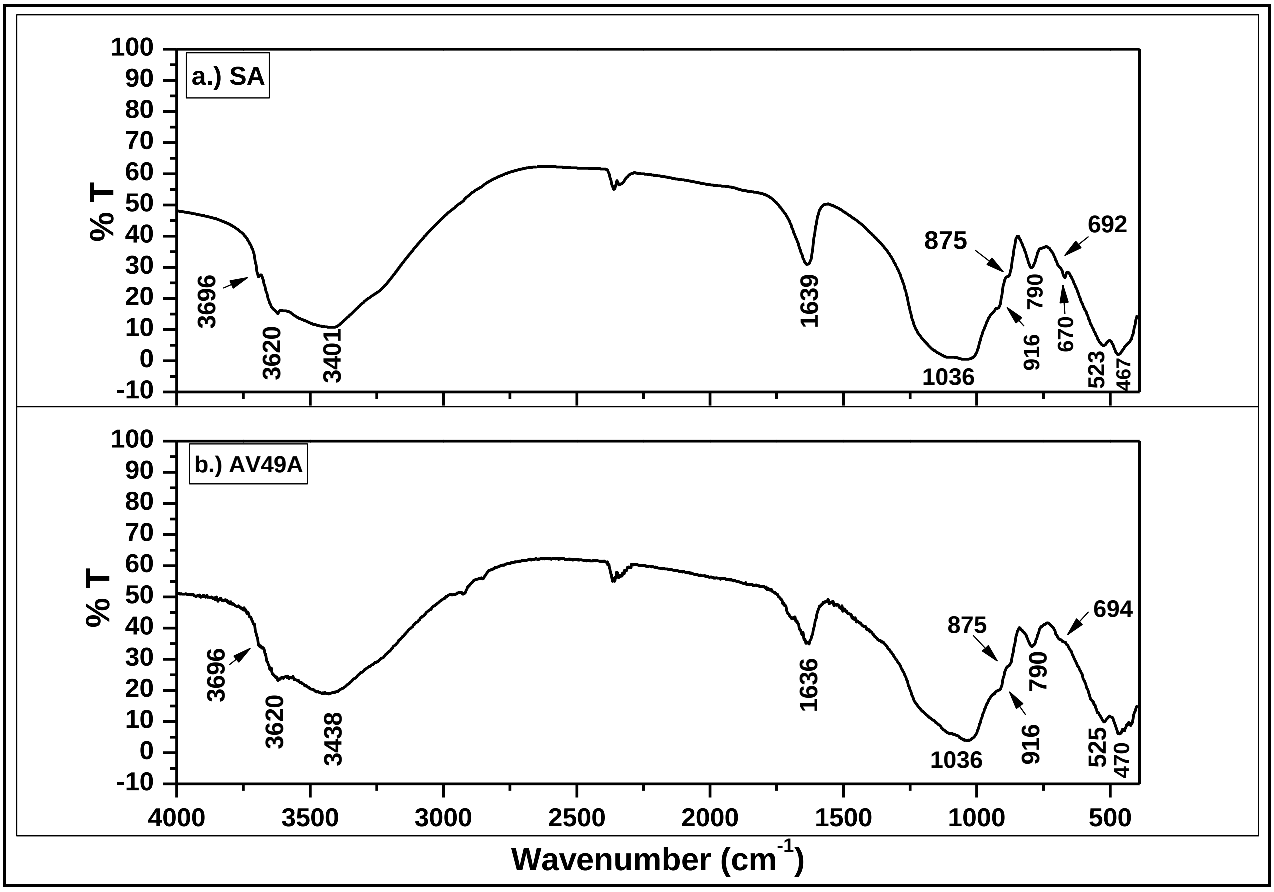


Figure 12 a.) FTIR spectra of acid activated clay (SA). Figure 12 b.) FTIR spectra of dye adsorbed acid activated clay (AV49A).

The FTIR spectra of dye adsorbed acid activated clay (Figure 12 b.) shows that interaction between dye and adsorbent causes slight shift in the position of peaks which are due to surface active groups of clay (694 cm^{-1}, 525 cm^{-1} and 470 cm^{-1}) towards higher side. This may be due to formation of chemical bond between surface moieties of the adsorbent and dye molecule [31]. The peak due to presence of free hydroxyl of water at 3401 cm^{-1} was shifted to 3438 cm^{-1}. Change in intensity of peaks (1636 cm^{-1} and 790 cm^{-1}) was also observed. Peak at 790 cm^{-1} completely disappeared. These results indicates that adsorption is taking place particularly by involvement of surface groups on the adsorbent[32]. Thus it is clear from the FTIR analysis that adsorption of AV49 has occurred on the surface of acid activated clay. The above results are also confirmed by SEM analysis.

Conclusion:

A low cost adsorbent acid activated clay has been used for the removal of AV49 dye from aqueous solution. The present study attempted to show that acid activated clay can be a good alternative to costly adsorbents like activated carbon. With the objective to test the removal efficiency of this adsorbent, different parameters have been varied. It was observed that adsorption process is dependent on initial dye concentration, mass of adsorbent, solution pH and ionic strength. Adsorption kinetics of AV49 onto acid activated clay was found to follow pseudo-second order model with good correlation. SEM results indicates that the surface of adsorbent is getting saturated after adsorption. Interpretation of FTIR results showed that adsorption of dye has occurred on the adsorbent. In conclusion, Acid activated clay has great potential as adsorbent. Thus adsorption process using clay treated with acid can be a sustainable approach for dye removal from effluents.

Acknowledgement:

The authors are grateful to UGC-DAE Consortium for Scientific Research, Indore for conducting SEM-EDS and FTIR measurements of our samples.

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