

ADSORPTIVE REMOVAL OF CATIONIC AND ANIONIC DYES FROM WATER: A CASE STUDY WITH KAOLINITE AND ACID-TREATED KAOLINITE

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Abstract: One of the most common clay mineral, kaolinite was tested in this work as adsorbents for both a cationic dye, Methylene Blue and an anionic dye, Congo red. The clay mineral was further modified by treatment with 0.25 and 0.50 M H₂SO₄. The influences of pH, interaction time, clay mineral amount and dye concentration on the adsorption process were monitored and explained on the basis of physico-chemical characteristics of the clay mineral and the behavior of the dye molecules. The optimum pH for both Methylene Blue and Congo red adsorption were 10.0 and 6.0 respectively. Adsorption was very rapid initially for ~ 30 min and then slowly attained equilibrium. The adsorption rate processes followed a second order kinetic model. The Langmuir monolayer capacity of kaolinite increased after acid treatment. The results suggest that kaolinite and its acid-treated forms would be suitable for removing both Methylene Blue and Congo red from aqueous solution through adsorption-mediated surface immobilization.

Keywords: Kaolinite; acid-treatment; Methylene Blue; Congo red

1. Introduction:

Color inducing chemicals are the first group of contaminants to be recognized in wastewater with naked eyes even at very low concentration such as < 1.0 mg/L [1, 2]. More than 100,000 commercial dyes are in use with an estimated production of $8 \times 10^5 - 1 \times 10^6$ tons per year with expected growth at 3% per annum [2–5]. The big consumers of dyes are textile, dyeing, paper and pulp, tannery and paint industries, and hence the effluents of these industries require prior treatment before discharge into natural water bodies like a river.

Dyes are considered an objectionable type of pollutant because they are generally toxic when inhaled or ingested orally. Dyes also induce skin and eye irritation. The main concerns involve the adverse effects of azo dyes to the environment, including their inhibitory effect on aquatic photosynthesis, ability to deplete dissolved oxygen, and toxicity to flora, fauna and humans. The self-purification ability of streams and conventional biological treatment systems are hindered by the presence of dyes and if the dyes are broken down anaerobically, aromatic amines are generated, which are very toxic, carcinogenic and mutagenic. Azo dyes are the most widely used dyes and represent over 60% of the total dyes. They are complex aromatic compounds with significant structural diversity. Further, the dyes have a tendency to sequester metals and may cause microtoxicity to fish and other organisms[2–7].

Various treatment technologies exist for the removal of dyes from water and they include filtration, chemical precipitation, ion exchange, adsorption and electrode deposition. In recent years, adsorption has emerged as a superior technique to other techniques for water re-use in terms of initial cost and flexibility[8].

In this study kaolinite and its acid treated forms were used to remove two dyes separately, namely, Methylene blue and Congo red. Methylene blue is a cationic thiazine dye with the chemical name tetramethylthionine chloride. It is widely used in various fields of biology and chemistry. Even though this dye is not classified as strongly hazardous, it can cause harmful effects in humans such as heartbeat increase, vomiting, shock, cyanosis, jaundice, quadriplegia, and tissue necrosis[9]. Congo red, however, is a direct benzidine-based anionic diazo dye and is a popular choice for coloring paper in paper industry. It is toxic to many organisms and is a suspected carcinogen due to the presence of aromatic amine group [10]. Hence it is important to remove these two dyes before they can harm the environment.

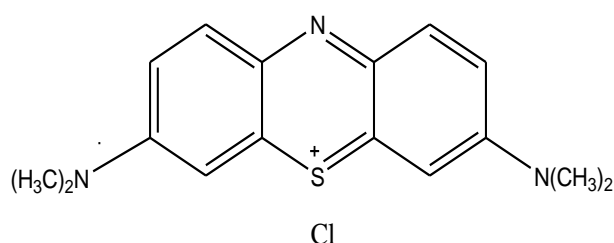
2. Materials and methods:

2.1. Clay mineral adsorbents:

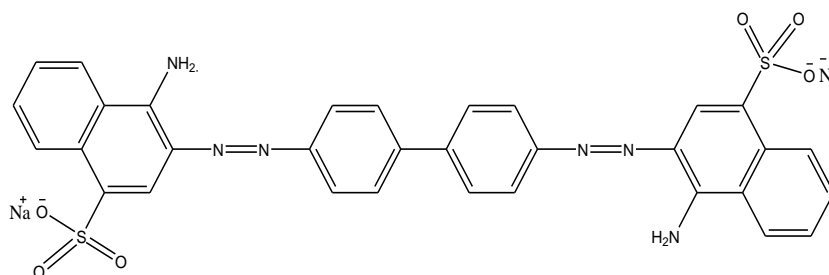
Kaolinite, KGa-1b (K) was obtained from the University of Missouri-Columbia, Source Clay Minerals Repository, USA. Kaolinite, K1 (treated with 0.25 M H₂SO₄) and K2 (treated with 0.50 M H₂SO₄) were prepared with a procedure similar to the one used by Espantaleon et al., 2003 [11]. 20 g of clay mineral was refluxed with 200 ml of 0.25 M and 0.50 M H₂SO₄ for 3 h. The resulting material was centrifuged and washed with water several times till it was free of SO₄²⁻ and then dried at 383 K in an air oven until constant weight to get rid of absorbed water.

2.2. Preparation of dye solution:

Methylene Blue, C₁₆H₁₈Cl N₃S (CI Classification Number 52015; Fisher Scientific, India) was used without further purification. The basic dye has the following structure:



Congo red, C₃₂H₂₂N₆Na₂O₆S₂ (CI Classification number: 22120; CAS number: 573-58-0) used in this work was obtained from Loba Chemie, India and was used without further purification. The dye has the following structure



A stock solution of the dye containing 1000 mg L⁻¹ was first prepared by dissolving the required amount of Methylene Blue or Congo red separately in double distilled water. Solutions for adsorption experiments were made from the stock solution in different concentrations as and when required.

2.3. Adsorption experiments:

Before the actual adsorption experiments, blank runs were carried out by taking dye solutions in the same concentration range (as used in the adsorption experiments) in Erlenmeyer flasks without the clay adsorbents and shaking the same as in the actual experiments. The walls of the flask did not show any measurable adsorption of the dye. The adsorption experiments were carried out in the same flasks by mixing a fixed amount of clay with 50 ml of aqueous dye solution. The mixture was agitated in a thermostatic water bath (NSW, Mumbai, India) for a pre-determined time interval. The mixture was centrifuged (Remi R 24, ~8000 rpm) and dye remaining unadsorbed in the supernatant liquid was determined with a spectrophotometer (Elico SL 177, India) at λ_{max} 665 and 499 nm for methylene Blue and Congo red, respectively.

The batch adsorption experiments were done with the variables in the following ranges:

- (i) Ph : 2.0 – 10.0 for Methylene blue and 6.0 – 9.5 for Congo red
- (ii) Interaction time (min) : 5, 10, 20, 30, 45, 60, 90, 120, 150, 180, 240, 300, 360
- (iii) Dye (mg L^{-1}) : 50, 70, 100, 120, 150, 170, 200, 240, 300, 350
- (iv) Amount of clay (g L^{-1}) : 1, 2, 4, 5, 6

3. Result and discussions:

3.1. Influence of pH:

The pH is an important factor that often influences the mechanism of adsorption. Variations in amount of Methylene Blue and Congo Red adsorbed in the respective pH range are shown in Fig. 1. For Methylene blue the amount adsorbed per unit mass (q_e) decreases up to pH 4.0, after which it increased almost continuously till pH 10.0. This was true for all the three clay adsorbents. However, lower pH favored adsorption of Congo Red and a significant amount was adsorbed in the pH range of 7.0 – 9.5, as was also found by other workers [12]. Kaolinite and its acid-treated forms showed highest adsorption at pH 6.0.

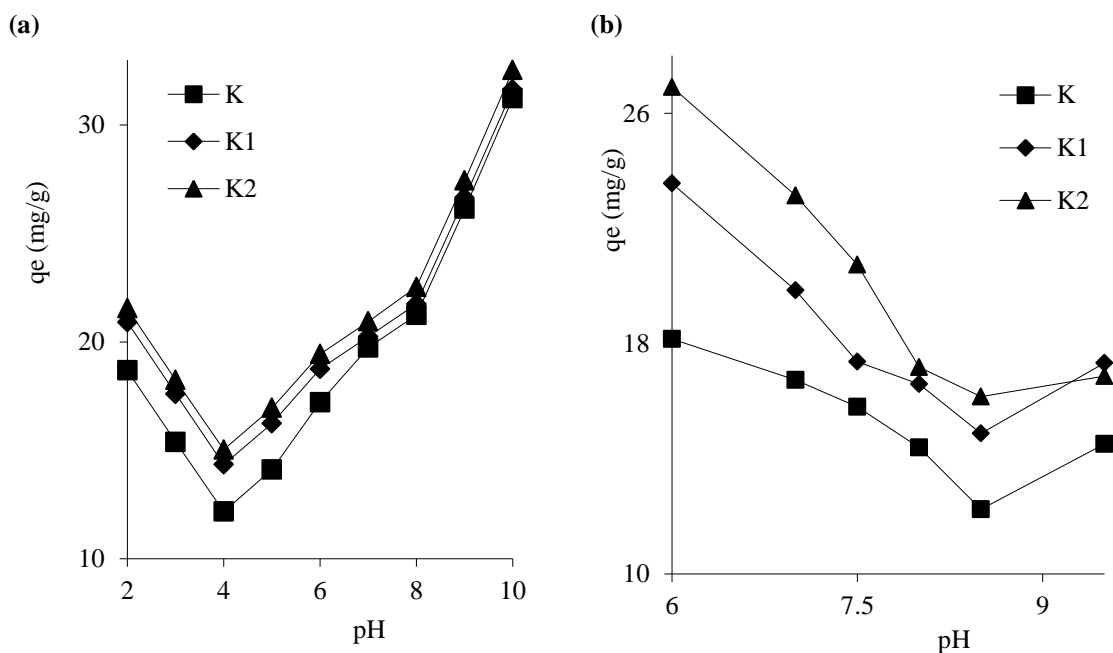


Figure 1: Effects of pH on (a) Methylene Blue (100 mg L^{-1}) and (b) Congo Red (100 mg L^{-1}) adsorption on raw and acid-treated kaolinite (2.0 g L^{-1}) at 303 K.

At low pH, kaolinite and its acid-treated forms would had a positive charge in their surface while as the pH increase, the positive charge would decrease and at very high pH the surface would be negatively charged [13]. Hence Methylene Blue being a cationic dye would be adsorbed at low pH while the anionic dye Congo Red would prefer higher pH for maximum adsorption.

3.2. Influence of Interaction Time and Kinetics of Adsorption:

The interactions of the dye with the adsorbents behaved uniformly with time. The adsorption was rapid in the first 45 minutes for both the cases after which it slowly attained equilibrium at ~180 and ~120 min respectively (Fig. 2). At any given time, kaolinite and its modified forms showed higher adsorption capacity for Methylene Blue than Congo Red. The pH did not show any measurable change even after the equilibrium was attained.

With an initial bare surface, the available surface area as well as the number of adsorption sites was very large, resulting higher rate of adsorption. This subsequently came down as the fraction of the bare surface rapidly diminishes and dye molecules were competing among themselves for the adsorption sites. The rate now was predominantly influenced by the rate at which the dye molecules are transported from the bulk to the adsorbent-adsorbate interface. The kinetics of the interactions was thus likely to be dependent on different rate processes as the interaction time increased[14].

Different models had been used to test the kinetics of both clay-dye interactions. The pseudo first-order Lagergren plots were obtained by plotting $\ln (q_e - q_t)$ vs. time according to the equation [15]:

$$\ln (q_e - q_t) = \ln q_e - k_1 t \tag{1}$$

where q_e and q_t were the amounts adsorbed per unit mass at equilibrium and at any time t , and k_1 was the first order adsorption rate constant. These curves were linear ($r \sim -0.98$ to -0.99) for both Methylene Blue and Congo Red adsorption on raw and acid-treated kaolinite.

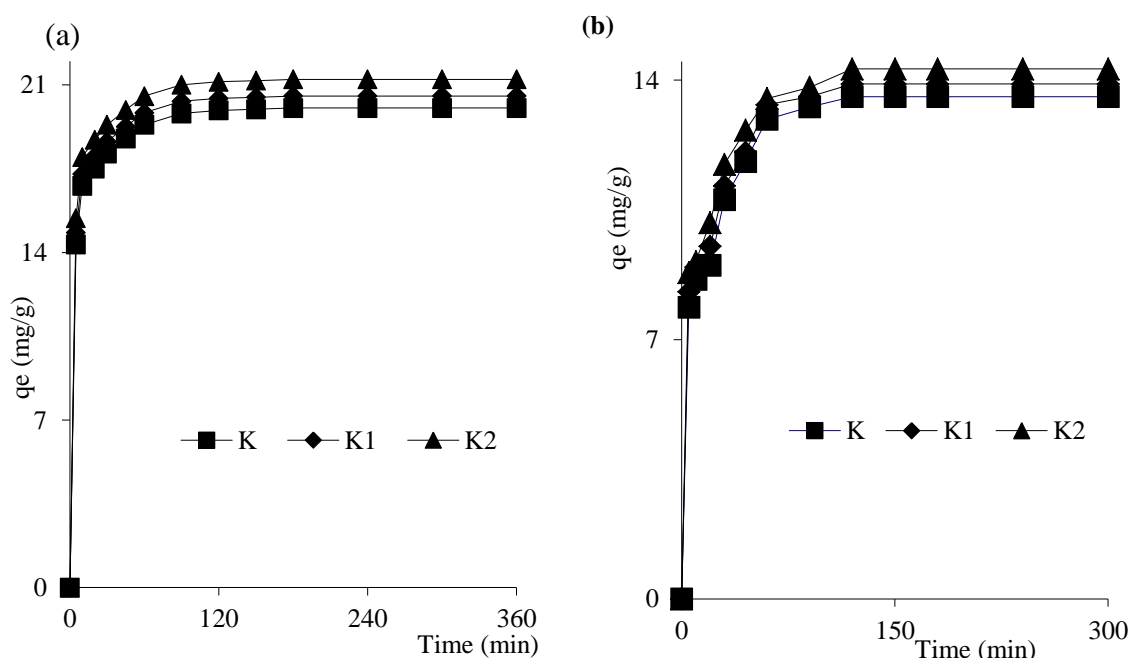


Figure 2: Influence of interaction time on (a) Methylene Blue (100 mg L^{-1}) and (b) Congo Red (100 mg L^{-1}) adsorption on raw and acid-treated kaolinite (2 g L^{-1}) at 303 K.

At 303 K, the first order rate coefficient (obtained from the slopes) showed same value of 3.2×10^{-2} for Methylene Blue. Congo Red also showed similar rate coefficient and varied in the range 3.1×10^{-2} to 3.8×10^{-2} for all the three adsorbents (Table 1). However, linearity of the Lagergren plots does not necessarily assure a first order mechanism[16] due mainly to the inherent disadvantage of correctly estimating the equilibrium adsorption capacity, q_e . The q_e values obtained from the Lagergren plots differed from the experimental q_e values by 74.86 % to 76.22 % (for Methylene Blue) and 41.69 % to 53.35 % (for Congo Red) at 303 K (Table 2). The large deviations did not support first order kinetics.

Table 1: Lagergren pseudo first order and second order rate coefficients for adsorption of Methylene Blue and Congo Red on clay minerals (kaolinites 2 g L^{-1} , initial dye concentration 100 mg L^{-1} ; temperature 303 K, k_1 in min^{-1} and k_2 in $\text{g mg}^{-1} \text{min}^{-1}$)

Temp. (K)		Rate coefficient	Clay Adsorbent		
			K	K1	K2
Methylene Blue					
303	First order	$k_1 \times 10^2$	3.2	3.2	3.2
		r	- 0.99	- 0.99	- 0.99
	Second Order	$k_2 \times 10^3$	16.9	16.9	17.1

		r	+ 0.99	+ 0.99	+ 0.99
Congo Red					
303	First order	$k_1 \times 10^2$	3.8	3.6	3.1
		r	- 0.98	- 0.98	- 0.98
	Second Order	$k_2 \times 10^3$	8.9	9.5	10.8
		r	+ 0.99	+ 0.99	+ 0.99

Table 2: Experimental and computed q_e values from Lagergren and second order plots for adsorption of Methylene Blue and Congo Red on clays (kaolinites 2 g L^{-1} , initial dye concentration 100 mg L^{-1} ; temperature 303 K).

Clay adsorbents	$q_e \text{ (mg g}^{-1}\text{)}$				
	Experimental	Lagergren plots	Second order plots	Deviation (%)	
				Lagergren plots	Second order plots
Methylene Blue					
K	20.04	5.04	20.36	74.86	- 1.6
K1	20.54	5.07	20.87	75.31	- 1.6
K2	21.24	5.05	21.55	76.22	- 1.5
Congo Red					
K	13.55	7.90	14.29	41.69	- 5.46
K1	13.89	7.48	14.53	46.14	- 4.61
K2	14.30	6.67	14.68	53.35	- 2.66

The second order kinetics governed by the equation [17]:

$$t/q_t = 1/(k_2q_e^2) + (1/q_e) t \tag{2}$$

where $k_2q_e^2$ is described as the initial adsorption rate as $t \rightarrow 0$, also yielded linear plots ($r \sim + 0.99$) of t/q_t vs. t (Fig. 3), allowing computation of q_e and k_2 . The rate coefficient, k_2 , showed almost similar values for Methylene Blue and varied from 16.9×10^{-3} to $17.1 \times 10^{-3} \text{ g mg}^{-1} \text{ min}^{-1}$ at 303 K (Table 1) indicating a greater affinity for all the kaolinites. In comparison, Congo Red showed much lower rate coefficient and varied in the range 8.9×10^{-3} to 10.8×10^{-3} suggesting a lower affinity compared to Methylene Blue for the kaolinite surface. A comparison of q_e values (experimental and those obtained from the slopes of the second order plots) showed a better agreement (Table 2) and the maximum deviation between the two sets of values are in the range of $- 1.5$ to $- 5.46 \%$ (303 K). The closeness of the two sets of values indicated a probable second order mechanism for clay-Methylene Blue and clay-Congo Red interactions.

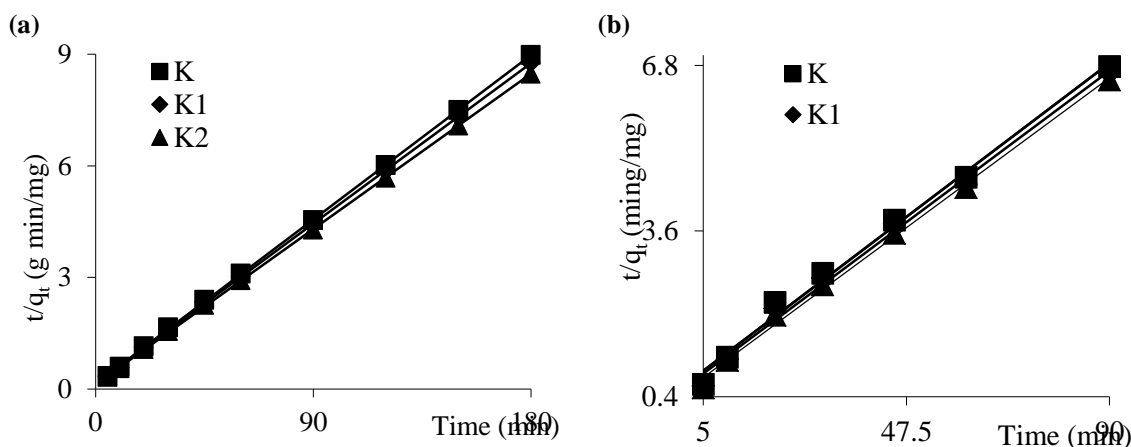


Figure 3: Second order plot for (a) Methylene Blue (100 mg L^{-1}) and (b) Congo Red (100 mg L^{-1}) adsorption on raw and acid-treated kaolinite (2 g L^{-1}) at 303 K.

3.3. Influence of adsorbent amount

For Methylene Blue concentration of 100 mg L^{-1} , the extent of adsorption increased from 36.8 to 52.0 % for K, 37.8 to 52.6 % for K1 and 29.3 to 54.3 % for K2 (clay 1 to 6 g L^{-1}). In case of Congo Red, the extent of adsorption increased from 17.34 to 56.40 %, 18.55 to 57.30 % and 19.23 to 58.32 % for K, K1 and K2 respectively (dye 100 mg L^{-1} ; clay 1.0 to 6.0 g L^{-1}).

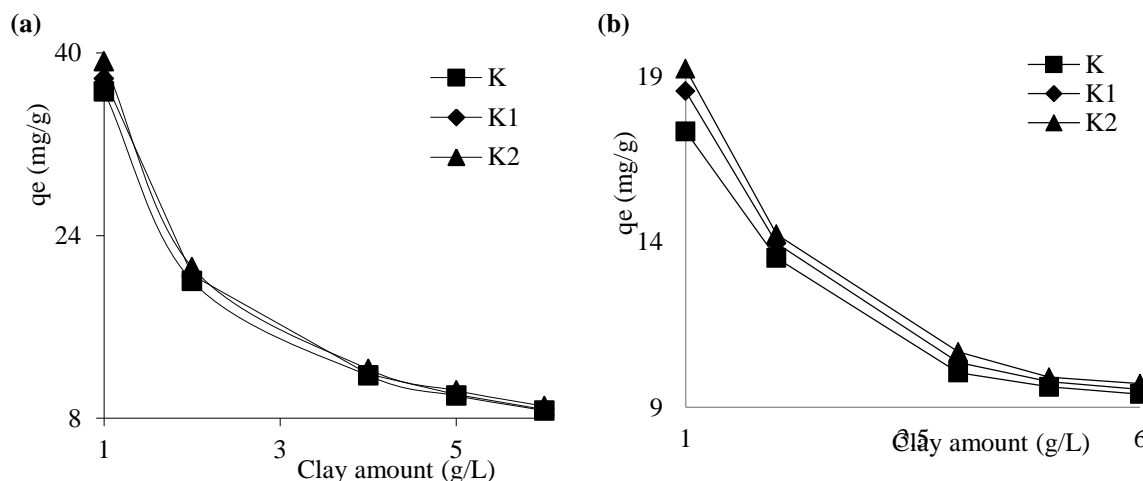


Figure 4: Effects of adsorbent loading on (a) Methylene Blue (100 mg L^{-1}) and (b) Congo Red (100 mg L^{-1}) adsorption on raw and acid treated kaolinite ($1.0 - 6.0 \text{ g L}^{-1}$) at 303 K .

However, the increase in the extent of adsorption was not sufficient to affect an increase in the amount adsorbed per unit mass. Thus, q_e showed a decreasing trend (Fig. 4). Several factors may be responsible for such behaviour. Two major considerations may be:

- (i) a large adsorbent amount reduces the unsaturation of the adsorption sites and correspondingly, the number of such sites per unit mass comes down resulting in comparatively less adsorption at higher adsorbent amount, and
- (ii) higher adsorbent amount creates particle aggregation, resulting in a decrease in the effective surface area and an increase in diffusional path length both of which contribute to decrease in amount adsorbed per unit mass.

3.4 Adsorption isotherm:

The Freundlich plots, based on the well known isotherm equation [18]:

$$\log q_e = 1/n \log C_e + \log K_f \tag{3}$$

were linear for both Methylene Blue and Congo Red ($r \sim + 0.94$ to $+ 0.98$). This isotherm is generally considered applicable to non-specific adsorption on heterogeneous solid surfaces. The values of the adsorption coefficients obtained from the plots were given in Table 3. At 303 K , the coefficient, $1/n$, varied from 0.38 to 0.41 for Methylene Blue and 0.29 to 0.30 for Congo Red. By definition, the adsorption intensity, $1/n$, should have values less than unity to suggest a favourable adsorption. Both Methylene Blue and Congo Red showed similar Freundlich adsorption capacity, K_f , which had values from 4.09 (K) to 4.93 (K2) $\text{mg}^{1-1/n} \text{L}^{1/n} \text{g}^{-1}$ for Methylene Blue and 3.28 (K) to 4.23 (K2) $\text{mg}^{1-1/n} \text{L}^{1/n} \text{g}^{-1}$ for Congo Red. Acid-treatment slightly enhanced the adsorption capacity of raw kaolinite and are in the order of $K2 > K1 > K$ with respect to adsorption of both the dye.

Monolayer chemisorption type of interactions usually follows the Langmuir equation [19]:

$$C_e/q_e = 1/(bq_m) + (1/q_m) C_e \tag{4}$$

more closely. The plots were linear (Fig. 5) in the present work. Values of b (Table 3) are small so a weak bond can be suggested for both dye clay complex.

Acid activation had resulted in an increase in the Langmuir monolayer capacity, q_m , for raw kaolinite, but the percentage increase was not very high. Acid activation caused partial loss of Mg^{2+} , Fe^{3+} and Al^{3+} from the layers and increased the porosity of the clay. This should enhance the adsorption[20]. However, the low impact of acid activation indicated that the big dye cations and anions could hardly enter into the pores created by eviction of divalent and trivalent ions. On the other hand, treatment with a strong acid dissolved out soluble mineral impurities from the surface [21] and this might have reduced the number of adsorption sites which might have acted against the likely increase expected from the creation of pores. q_m had a similar order as the Freundlich adsorption capacity, i.e. $K_2 > K_1 > K$. However, kaolinite showed higher monolayer adsorption capacity for Methylene Blue compared to Congo Red. Zeta potential study showed that raw kaolinite (K) and its acid treated forms K1 and K2 had point of zero charge (pH_{zpc}) at pH 2.9, 4.0 and 4.2 respectively. This signified that, at $pH < pH_{zpc}$ the clay mineral surface would be positively charged and at pH above that value it will be negatively charged. Since the studies were conducted at the natural pH of both the dye solution, i.e. at pH 7.5 for Methylene Blue and pH 6.94 for Congo Red the surfaces of the clay minerals would be negatively charged and it would favour adsorption of Methylene Blue compared to Congo red. Furthermore, the bigger size of Congo Red molecule compared to Methylene Blue could play an important role for the reduced adsorption capacity of Congo Red. Similar results were shown by other researcher also where they studied the adsorption of some cationic and anionic dye on modified montmorillonite[22].

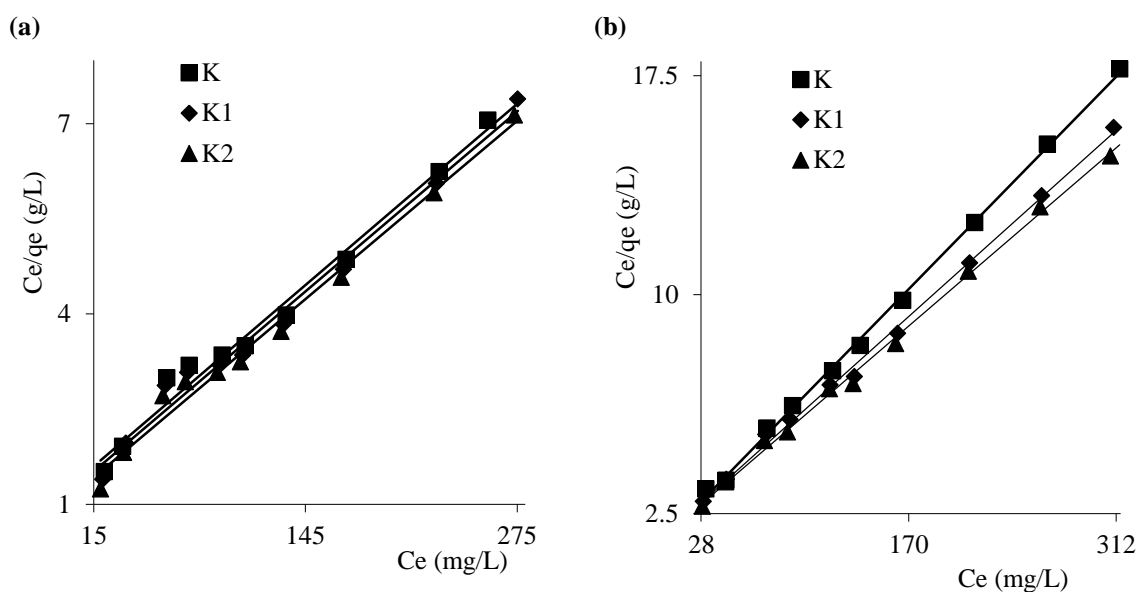


Figure 5: Langmuir plots for adsorption of (a) Methylene Blue and (b) Congo red on raw and acid-treated kaolinite (2.0 g L^{-1} , dye $50 - 350 \text{ mg L}^{-1}$) at 303 K.

Table 3: Freundlich and Langmuir isotherm parameters for adsorption of Methylene Blue and Congo Red from aqueous solution on clay minerals at 303 K. [Methylene blue $50 - 350 \text{ mg L}^{-1}$ for kaolinite K, K1, K2 (2.0 g L^{-1})] K_f in $\text{mg}^{1-1/n} \text{ L}^{1/n} \text{ g}^{-1}$, q_m and b are in mg g^{-1} and L mg^{-1} .

Parameters	Methylene Blue			Congo Red		
	K	K1	K2	K	K1	K2
Freundlich isotherm						
k_f	4.09	4.38	4.93	3.28	4.13	4.23
$1/n$	0.41	0.40	0.38	0.30	0.29	0.29
r	+ 0.98	+ 0.97	+ 0.98	+0.94	+0.97	+0.97
Langmuir isotherm						
q_m	45.45	45.87	46.30	19.53	22.27	23.26
b	0.017	0.018	0.020	0.035	0.028	0.027
r	+ 0.99	+ 0.99	+ 0.99	+0.99	+0.99	+0.99

4. Conclusions:

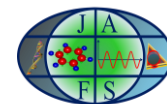
The kaolinite clay mineral had shown satisfactory performance as adsorbents to remove both Methylene Blue and Congo Red from aqueous solution and acid treatment successfully enhanced the adsorption capacity of kaolinite clay. However, kaolinite and its acid-treated forms were much more successful to remove cationic dye than anionic dye. The clay-dye interactions were very fast in the first 45 min and attained equilibrium within 180 and 120 min for Methylene Blue and Congo Red respectively. The kinetics was much more close to the second order for both the cases. The validity of the Langmuir isotherm with respect to clay-dye interactions indicated that dye species were held to clay surface by largely chemical forces. Similarly, good fits obtained with the Freundlich isotherms pointed to non-specific and energetically non-uniform nature of the adsorption sites.

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