
REMOVAL OF SOME ADVANCED DYES FROM AQUEOUS SOLUTION USING MODIFIED KAOLINITE CLAY

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ABSTRACT

Kaolin mineral and its modified forms were used for dye removal from aqueous solutions. The affecting parameters such as pH, dye concentration and contact time on the removal performance were investigated. Three different dyes (acid Green 25, Basic Blue 3 and Disperse Orange 13) were studied. The removal has a higher rate at initial period of contact time. The equilibrium is achieved at 120 min. The adsorption is occurring through transport of dye molecules from solution to solid surface. Then, they diffused into the pores. The order of adsorption was: Basic blue 3 > Acid Green 25 > Disperse Orange 13. The adsorption process follows the pseudo-second-order kinetics. The rate controlling step is not depending on the intra-particle diffusion. A Freundlich isotherm model could describe the adsorption. The calculated (R_L) factor confirmed the variability of the adsorption process.

Key words: Kaolin, Treatment, Adsorption, Dyes, Kinetics.

INTRODUCTION

Kaolin is a natural material. It has wide applications due to its composition. It may contain small amounts of silica and mica [1]. It is composed of two sheet layer structure of hydrous aluminum silicate. It has unlocked crystal structure. It contains many replaceable positive ions and water molecules. They are replaced physical or by ion exchange [2]. It is composed of tetrahedral sheet of silica (SiO_2) and an octahedral sheet of aluminum oxy-hydroxide $[\text{Al}(\text{O},\text{OH})_6]$. It can be expressed as $[\text{Si}_2\text{Al}_2\text{O}_5(\text{OH})_4]$ or $[\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}]$ [3-4].

The different applications of kaolin are due to its special surface character. Thus, the surface treatment such as mechanical or chemical activation [5-15], intercalation [16-18], thermal and chemical treatment [19-21] and chemical activation improves them [22-24].

Acid treatment can improve the surface and catalytic properties of different types of clays such as sepeolite, palygorskite, saoponite, etc. [1-4, 12-15]. It is carried out by mixing the clay with inorganic acids. It leads to particles desegregation, impurity elimination, and dissolution of the external layers [12-15]. As a result, the surface area, porosity and the

number of acid centers are increased. The treated clay contains hydrous, amorphous, and partially protonated silica. It can be used as absorber or as catalytic supports [25].

The kaolin solubility depends on the acid type and concentration, temperature and contact time. Sulfuric acid has higher effects than other mineral acids [26].

Wastewater treatment needs more development to reduce the absorber cost and increasing removal efficiency. The dyes in wastewater cause higher toxicity. Many types of dyes are used in different industries such as textile, paints, etc. It causes water pollution due to highly colored. Dyes can be classified based on chemical structure. Thus, there are many types such as anionic, cationic and non-ionic dyes depending on its ionic charge [27]. In this study, the performance of kaolin and its treated forms as absorbers of dyes were investigated.

2. EXPERIMENTAL

2.1. Chemicals

Acid green 25, Basic blue 3 and Disperse orange 13 dyes, were employed in this study to represent the different types of dyes. Dyes were

purchased from Aldrich, Milwaukee, WI, USA, and used as received. All other chemicals such as, hydrochloric acid and sodium hydroxide were reagent grade.

2.2. Kaolin preparation

Kaolin employed in this study is brought from Wade Kalapsha which is near to Aswan, Egypt. It is washed aggressively to separate the silica as a hard component. Coloring material as iron is removed by the intensive magnetic separation. Other impurities especially titanium mineral is separated using the flotation technique.

2.3. Kaolin treatment

Treatment of the kaolin is carried out by mix 200 g of washed sample with 500 ml of 1 M NaOH solution as alkali treatment. Also, the kaolin is treating by mixing with 1 M of potassium di-hydrogen phosphate/sulfuric acid mixture solution. Mixing is continued for 1 day at normal temperature. The treated kaolin is filtered and washed with pure water till pH \approx 7. The moisture is removed using an air dryer at 90°C for 4 hours. It is pulverized to powder size of less than 74 μ m. It is used as absorber in dye removal study.

2.4. Characterization of adsorbents

The treated samples were dissolved in a digestive mixture of nitric and hydro-fluoric acids using microwave digester. The chemical composition is determined by atomic absorption spectrophotometry (Perkin Elmer, AAnalyst-2 series).

The surface area is determined according to the Seer's method [28]. A 0.5 g of sample is mixed with 50 ml of HCl solution at pH about 3. A 10g of sodium chloride salt was added, followed by 0.1 M NaOH solution gradually until pH reaches to 4. Again, the pH is increased to pH = 9. The quantity of alkali is consumed to raise the pH from 4 to 9 is recorded. It is calculated as follows:

$$\text{Surface area (m}^2\text{/g)} = 32 V - 25 \quad (1) [28]$$

X-ray diffraction investigation for kaolin is carried out using the X-ray diffract-meter (Brokar, Darmsadet, Germany). X-PEIRT PREIO-MPEID, with Copper-potassium alpha

radiation ($\lambda = 1.5416 \text{ \AA}$). The porosity of the treated samples was determined using nitrogen adsorption technique. It is carried out in a micro-metrics accelerator surface-area and a porous-meter system 2011 model analyzer.

2.5. Batch adsorption

A 100 ml round bottom flask is used for mixing dye solution with absorber. A 500 mg of treated sample is mixed with 50 ml of desired concentration of the dye solution. The effect of temperature is investigated up to 60°C. Also, initial dye concentration in the range up to 250 ppm is investigated. The mixture was agitated in thermo-stated water-bath at 250 RPM for desire time up to 180 min in thermo-state water bath. The pH of the solution is adjusted using 0.01 M NaOH or 0.01 M HCl. At the end of the experiment, the aqueous solution is separated using centrifuged. The concentration of dyes was determined through measuring the absorbance at 608, 654 and 427 nm for acid green-25, Basic Blue-3 and Disperse Orange-13, respectively. The UV/Vis-Spectrometer, Lambada-2500 was employed for this purpose using a calibration curve for each dye

The amount adsorbed of dye in mg by 1 g of absorber is calculated using the following equation:

$$q_e = \frac{(C_0 - C_e)}{m} \times V \quad (2)[27]$$

Where q_e (the amount adsorbed dye, mg/g), C_0 and C_t (the initial and final concentrations of dye (mg/l), V (the volume of solution in liter), and m (the weight of absorber, g).

The removal percent is calculated using the following equation:

$$\text{Removal \%} = \frac{(C_0 - C_t)}{C_0} \times 100 \quad (3) [27]$$

3. RESULTS AND DISCUSSION

3.1. Characterization of kaolin

Mineralogy and microscopic study showed that the sample contains a small amount of quartz. The iron and titanium were found in the

form of ilminite and anatase minerals. They have very small grains of rhombic shape forming and as a network structure. Table 1, shows the composition of kaolin sample.

Table 1: Complete chemical analysis of the kaolin clay sample.

Constituents	%
SiO ₂	52.6
Al ₂ O ₃	34.4
Fe ₂ O ₃	0.25
TiO ₂	0.75
CaO	0.21
MgO	0.13
Na ₂ O	0.17
K ₂ O	0.08
Cl ⁻	0.04
Loss on ignition	11.35
Total	99.98

The surface area of untreated kaolin is 16.2 m²g⁻¹ while it is 82.5 and 159.3 m²g⁻¹ of treated kaolin, basic or acidic, respectively. It is noted that, it is up to 25 m²g⁻¹ for kaolin clays [29]. The lattice of clay is opened as a result of acid treatment. It leads to increases of pore size and surface area [30].

Fig.1 shows the XRD of the untreated and treated kaolin. There are two peaks at 2-theta of 12° and 25° (it is equivalent to d value 7.15 and 3.57). They confirm the presence of kaolin mineral.

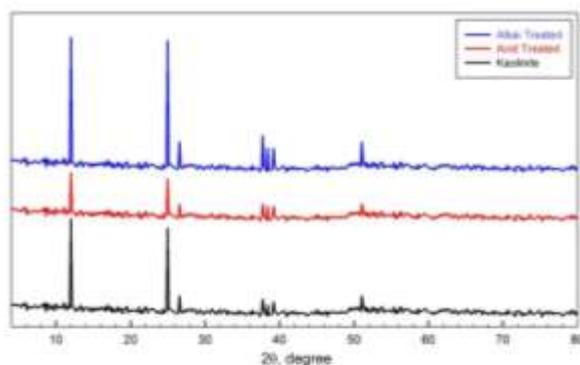


Fig.1. X-Ray Diffraction spectra of kaolin and treated forms.

The peaks at 2-theta = 34-36°, 38-42° and 45-50° are also confirming the composition of kaolin mineral [31]. As a result of treatment, the peak intensity of kaolin is sharply decreased. It may be due to the structure deficiency. Moreover, it affects the crystal degree of the sample [32]. The slim peak may

be due to increasing of the crystal degree and decreasing of the main lattice exertion [33].

On the other hand, for the alkali treated sample, the intensity of the peak is increased. It confirms that there is no effect on kaolin silicate rather than the free silica. X-ray diffraction can be considered as a tool for measuring the degree of crystallinity [34]. The non-crystalline mineral of alkali-treated sample permits to permeate the dye molecules into kaolin surface. It leads to high adsorption [35-36].

3.2. Adsorption Study

3.2.1. The effect of pH

The pH has a serious function on the removal efficiency. It has influenced the charged surface of the adsorber, the charged of adsorbed molecules in aqueous medium and the behavior effective locations at adsorbent surface. Also, it may change the form of dye molecules [37-39]. The efficiency of dye removal using untreated, alkaline-treated and acid-treated clay was investigated at pH 2 – 10, Fig.2. The acid green 25 dye showed high stability in acidic medium. There is a slight decreasing of dye removal by untreated kaolin and alkaline-treated clay by increasing the pH. It may be due to the ecstatic repudiation between dye molecules and locations on adsorber surface.

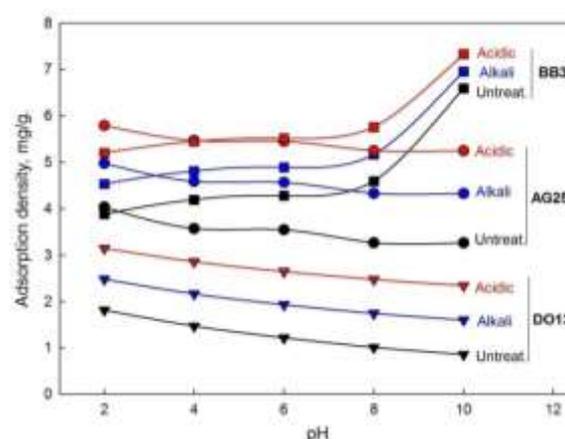


Fig.2. Effect of pH on adsorption performance of untreated and treated forms.

The removal of Basic Blue 3 dye is reinforced with increasing pH. The drop of dye uptake at higher pH may be due to the chemical structure transform the dye molecules and to

the zero point of charge of solid surface, Fig.3. The alkali-treated clay has zero surface charge at pH 5.2. The pH 6 is considered as the best possible pH to investigate other affecting parameters. The presence of much hydroxyl ion in alkaline medium, leads to rival with the negative molecules of anionic dye with the negative locations on absorber surface. Hence, low adsorption of Blue 3 dye is expected. In acidic medium, the hydrogen ions have a competitive ability with the dye molecules on the absorber surface. Thus, the lower the pH is unfavorable for efficient removal. In much alkaline medium there is no much hydrogen ion to enhance the adsorption. Moreover, at alkaline medium, the positivity of solid surface is reduced which leads to low ecstastic repudiation with the dye molecules [40].

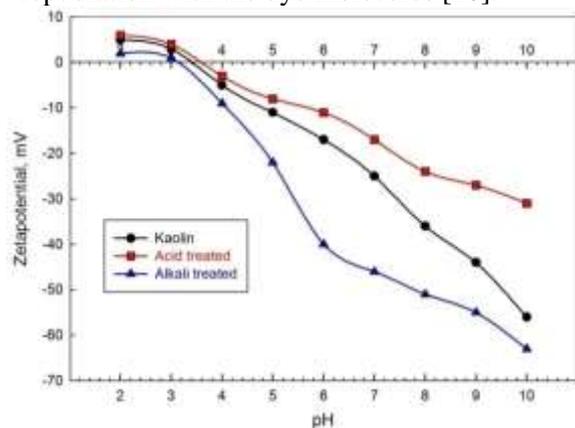


Fig.3. Zeta potential of untreated and treated forms as a function of pH.

The adsorption of Disperse orange-13 is slightly reduced with increasing pH for untreated kaolin, alkali-treated and acid-treated forms. The best removal is appeared at pH = 2 for acid-treated kaolin. The higher adsorption capacity of treated forms compared with that for untreated form confirms the distinction and needs to the chemical treatments. The higher adsorption for acid-modified kaolin may be due to the significant high surface area. The moderate adsorption for alkali-treated form may be due to increasing of the exchangeability of cations compared with original kaolin.

3.2.2. The effect of contact time

The effect of contact time on the adsorption of dyes is shown in Fig.4. The highest removal is achieved at 120 min. The higher adsorption

rate at the initial stages might be due to the presence of great active locations on the solid surface of clay. It becomes saturated with time. Vander Waals forces and ecstastic attractions; fast diffusion through the surface followed by fast diffusion into the matrix to reaching the balance at 60 min [41]. Initially, sorption is controlled by moving the adsorbed species from the aqueous solution to the solid surface of kaolin. Whereas, sorption is an adhesion-controlled process due to the presence of inactive points [17]. The experimental results indicated that the order of the adsorption capacity of kaolin and treated forms for all types of dyes follows: Basic blue 3 > Acid Green 25 > Disperse Orange 13. This may be due to the negativity of Basic blue-3 molecules.

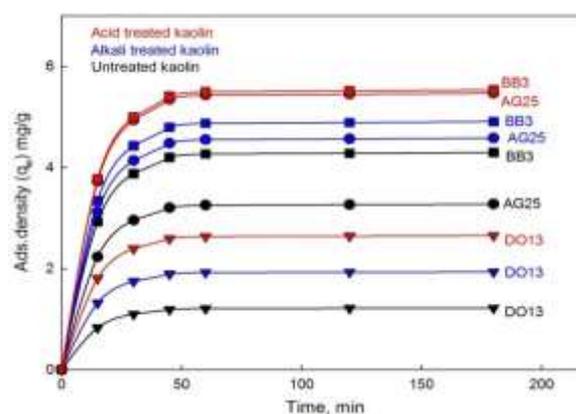


Fig.4. Effect of contact time on the adsorption performance of untreated and treated kaolin.

To investigate the mechanism of adsorption, the rate-controlling step, pseudo-first, pseudo-second-order kinetic and intra-particle diffusion models were applied.

3.2.2.1. Pseudo-first-order model

The pseudo-first-order model is stated as: [42–44]

$$\log(q_e - q_t) = \left(\frac{k_1}{2.303} \right) t \quad (4) [43]$$

Where q_t and q_e (the dye adsorbed at time t and at equilibrium time). K_1 (the rate constant). The K_1 and q_e are calculated, from plotting of $\log(q_e - q_t)$ with time, Table 2.

Plotting of $\log(q_e - q_t)$ versus time, according to pseudo-first-order kinetics allowed

to calculate the rate constant K_1 with poor linear regression coefficient (R^2). It indicates that the pseudo first-order kinetics cannot be applied, Fig.5. This model estimated higher value of the adsorption capacity compared with the experimental data.

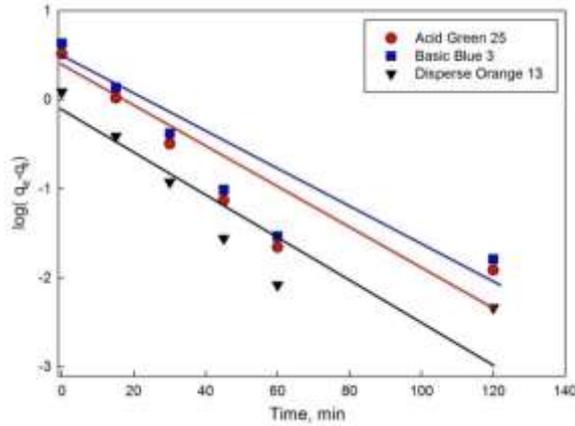


Fig.5. Plotting data using Pseudo-first order model.

3.2.2.2. Pseudo-second-order model

The adsorption data are analyzed using pseudo second-order model, which is described by:

$$\frac{dq}{dt} = K_2 ([q_e - q_t])^2 \tag{5} [42]$$

Where K_2 : the rate constant of pseudo-second-order (g/mg min)

Integrating and applying boundary conditions from $t = 0$ to $t = t$, thus:

$$\frac{t}{qt} = \frac{1}{K_2 q_e^2} + \left(\frac{1}{q_e}\right)t \tag{6} [44]$$

Thus, the rate constant (K_2), adsorption rate (h) and estimated (q_e) can be determined from the plotting of t/q with time, Fig.6. Moreover pseudo-second-order kinetic model predicts a closer value of the adsorption compared with the experimental results, Table 3. Hence, it confirms the suitability of applying this model.

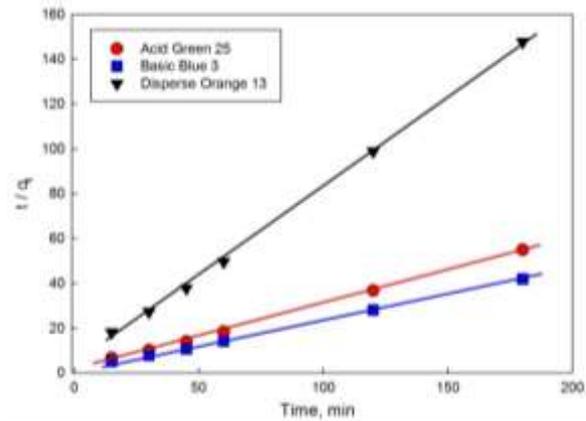


Fig.6. Plotting data using Pseudo-second order model.

3.2.2.3. Intra-particle diffusion model

This model states that the adsorption is occurring through transfer of the dye molecules from the aqueous solution to the solid surface. It can be also occurred by penetration of the dye molecules through the pores. The latter is usually a slow process. It is stated that the

Table 2: Parameters of Pseudo-first-order model.

Item	Acid Green25			Basic Blue 3			Disperse orange 13		
	Untreated	Alkali-treated	Acid-treated	Untreated	Alkali-treated	Acid-treated	Untreated	Alkali-treated	Acid-treated
R^2	0.8288	0.8279	0.8281	0.8282	0.8281	0.828	0.8282	0.8278	0.828
K_1	-0.0089	-0.0089	-0.0089	-0.0089	-0.0089	-0.0089	-0.0089	-0.0089	-0.0089
Exp. q_e	3.2763	4.5813	5.4679	4.2958	4.9061	5.5352	1.2187	1.9357	2.6527
Cal. q_e	1.4006	1.9548	2.3345	1.8336	2.0941	2.3621	0.5204	0.8258	1.1321

Table 3: Parameters of Pseudo-second-order model.

Item	Acid Green25			Basic Blue 3			Disperse orange 13		
	Untreated	Alkali-treated	Acid-treated	Untreated	Alkali-treated	Acid-treated	Untreated	Alkali-treated	Acid-treated
R^2	0.999	0.999	0.999	0.999	0.999	0.999	0.999	0.999	0.999
K_2	0.072	0.051	0.043	0.054	0.048	0.042	0.193	0.121	0.089
Exp. q_e	3.276	4.581	5.467	4.295	4.906	5.535	1.218	1.935	2.652
Cal. q_e	3.276	4.581	5.467	4.295	4.906	5.535	1.218	1.935	2.652

adsorption process is usually proportional to the square root of time, which can be represented as follows: [45]

$$q_t = K_{id} t^{0.5} + I \quad (7) [46]$$

Where q_t (the dye adsorbed at time t), $t^{0.5}$ (the square root of the time), K_{id} (the rate constant of intra-particle diffusion) and I (the intercept which reflects the thickness of the boundary layer). The higher intercept indicates the higher the boundary layer.

Fig.7 shows very poor linear regression coefficients (R^2) indicates the inapplicability of this model. Thus, intra-particle diffusion was not only the rate-controlling step.

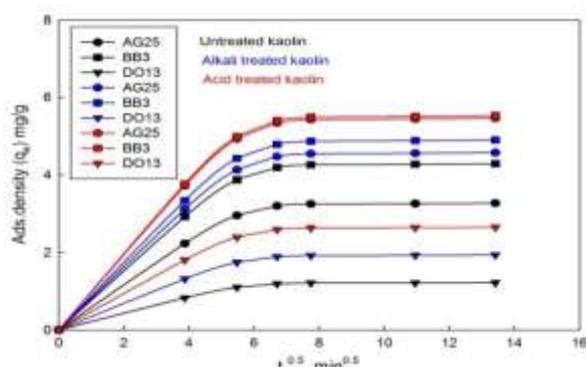


Fig.7. Plot of Intra-particle diffusion model for different dyes.

3.2.3. The effect of initial dye concentration

The amount of dye uptake is increased as a result of increasing initial concentration, Fig.8. The higher dye species molecules concentration vanquishes the impedance to transfer of adsorbed species from the aqueous solution to the solid surface [39]. The permeation through pores restrains the adsorption process. As a

result of no linearity between the initial concentration and the adsorption rate [47], the diffusion process does not limit the adsorption process. There are different isotherms can be used to explain the correlativity between the dye in the aqueous solution and on the solid surface as follows:

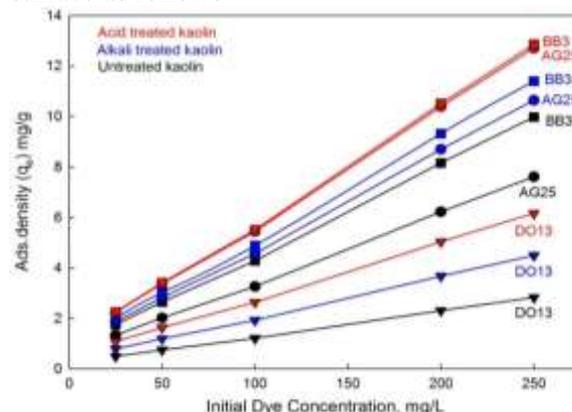


Fig.8. Effect of dye concentration on the adsorption capacity of untreated and treated kaolin.

3.2.3.1. Freundlich isotherm

Freundlich adsorption isotherm model, states that the adsorption occurred on the uniform surface, as: [42, 48].

$$\ln q_e = \ln K_1 + \frac{1}{n} (\ln C_e) \quad (8)[42]$$

Where q_e (dye adsorbed at time “t”), C_e (final concentration of dye). K_1 and n are the isotherm constants. They reflect the capacity and the intensity of the adsorption, respectively [42, 48]. The isotherm constants can be determined from the plotting of $\ln q_e$ and $\ln C_e$, Fig.9. The value of ‘n’ is higher than one which confirms the favorability nature of the process, Table 4 [49, 50]. Thus, it implies *the physical adsorption*.

Table 4: Freundlich isotherm constants.

Item	Untreated kaolin			Alkali treated			Acid treated		
	Acid Green25	Basic Blue 3	Disperse orange 13	Acid Green25	Basic Blue 3	Disperse orange 13	Acid Green25	Basic Blue 3	Disperse orange 13
R^2	0.977	0.964	0.988	0.958	0.949	0.985	0.921	0.920	0.982
n	1.542	1.715	1.370	1.789	1.899	1.415	2.221	2.221	1.475
K_1	0.2458	0.4790	0.0517	0.5850	0.7452	0.0978	1.2128	1.2128	0.1633

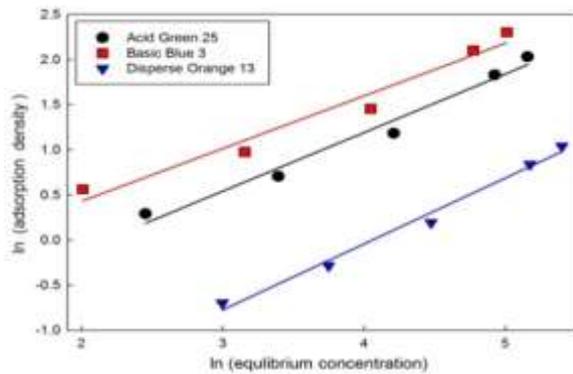


Fig.9. Fitting of data on Freundlich isotherm model.

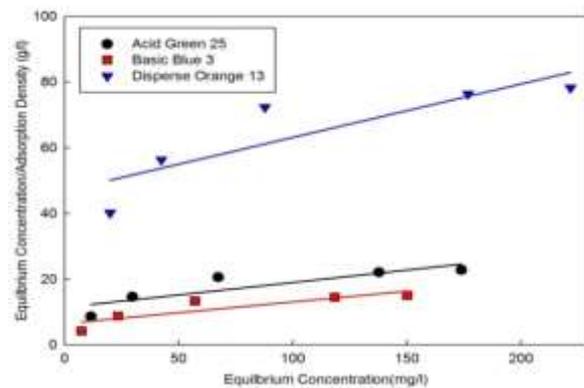


Fig.10. Fitting data on Langmuir isotherm model.

3.2.3.2. Langmuir isotherm

Langmuir model states that the adsorption occurs unitarily on the activated locations of the solid surface. Then, no further adsorption can occur at these locations [51]. The straight form of Langmuir can be written as: [42, 48]

$$\frac{1}{q_e} = \left(\frac{1}{K_2 q_{max}} \right) \frac{1}{C_e} + \frac{1}{q_{max}} \quad (9) [48]$$

q_{max} (maximum adsorption capacity) and K_2 can be calculated from the plot between $1/q_e$ versus $1/C_e$. Fig.10 shows that the Langmuir model did not fit the data for all dyes. Thus, it does not represent the mono-layer sorption onto the homogenous solid surface (*It is not chemical adsorption*). The (q_{max}) and (K_2) are represented in Table 5.

The degree of favorability of adsorption process for the Langmuir isotherm is stated in terms of dimension-less separation factor as follow: [49].

$$R_L = \frac{1}{(1 + K_2 C_0)} \quad (10) [49]$$

Where K_2 (Langmuir constant) and C_0 (initial dye concentration). It is noted that, if R_L values is less than one and higher than zero, it indicates the favorable adsorption. If it is equal one, it suggests unfavorable adsorption. While, if R_L equal zero, it represents irreversible adsorption [49].

The calculated values of separation factor, R_L (from Langmuir plot, Table 6) are range between 0 and 1. It confirmed the availability of the adsorption process.

Table 5: Langmuir isotherm constants.

Item	Untreated kaolin			Alkali treated			Acid treated		
	Acid Green25	Basic Blue 3	Disperse orange 13	Acid Green25	Basic Blue 3	Disperse orange 13	Acid Green25	Basic Blue 3	Disperse orange 13
R^2	0.764	0.768	0.759	0.768	0.770	0.761	0.773	0.773	0.762
Cal. q_{max}	13.227	15.221	6.146	15.576	15.923	9.083	16.234	16.260	11.520
Exp. q_{max}	7.612	7.612	2.831	10.644	11.398	4.497	12.704	12.860	6.163
b	0.0066	0.0101	0.0035	0.0116	0.0138	0.0042	0.0195	0.0204	0.0053

Table 6: The dimension-less separation factor.

B	Kaolin			Alkali treated			Acid treated		
	Acid Green25	Basic Blue 3	Disperse Orange 13	Acid Green25	Basic Blue 3	Disperse Orange 13	Acid Green25	Basic Blue 3	Disperse Orange 13
25	0.8582	0.9914	0.9966	0.7751	0.9894	0.9958	0.6726	0.8511	0.8829
50	0.7517	0.6646	0.8521	0.6327	0.5922	0.8250	0.5067	0.0894	0.7903
100	0.6022	0.4977	0.7423	0.4628	0.4206	0.7021	0.3393	0.0468	0.6533
200	0.4308	0.3313	0.5902	0.3010	0.2663	0.5409	0.2043	0.0239	0.4851
250	0.3771	0.2838	0.5353	0.2563	0.2250	0.4853	0.1704	0.0192	0.4298

5. CONCLUSIONS

The removal of Acid Green 25 (AG25), Basic Blue 3 (BB3) and Disperse orange 13 (DO13) dyes from their aqueous solution using by kaolin and its treated forms showed that:

- The adsorption of dyes is strongly affected by the pH, initial dye concentration and treatment type. The adsorption increases with increasing dye concentration and adsorption time. The acidic treatment produces the higher dye absorber followed by alkali-treatment.
- The adsorption is increasing with increasing contact time at all initial dye concentrations. The equilibrium is attained within 120 min. The adsorption process is highly pH dependent.
- The order of dye adsorption for kaolin and its modified forms was: AG25 > BB3 > DO13.
- Kinetic study indicated that the adsorption of AG25, BB3 and DO13 is occurring through a two steps process: a rapid adsorption of dye molecule to the surface followed by intra-particle diffusion into the interior of adsorbent. The adsorption follows the pseudo-second-order.
- The intra-particle diffusion is not only the control rate step.
- The adsorption obeys Freundlich isotherm model which indicates its physical nature.
- The R_L value (low separation factor) confirmed the favorable adsorption.

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إزالة بعض الأصباغ المتقدمة من المحاليل المائية باستخدام طفلة الكاولين المعالج

الملخص

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** مركز بحوث الفلزات بالتبين- القاهرة

تم استخدام طفلة الكاولين ، سواء الطبيعي أو المعالج كيميائياً في إزالة الصبغات من المحاليل المائية ، ثم تم دراسة تأثير الأس الهيدروجيني وتركيز الصبغة وزمن المعالجة على كفاءة إزالة الصبغات التالية: (Acid Green 25) و (Basic blue 3) و (Disperse 13) و (Orange 13).

وقد وجد أن كفاءة الإزالة تزداد مع زيادة تركيز الصبغة في المحلول ، وزمن المعالجة ، كما تم ملاحظة أن معدل الإزالة العالي عند بدء المعالجة ، والذي يقل تدريجياً حتى يصل للثبات عند 120 دقيقة.

وقد تبين أن إمتزاز الصبغات يحدث من خلال نقل جزيئات الصبغة من المحلول إلى سطح الكاولين ، ثم من خلال دخوله للمسام الداخلية. وقد كانت ترتيب الإمتزاز كالتالي:

Basic blue 3 > Acid Green 25 > Disperse)
(Orange 13

وقد وجد أن عملية الإمتزاز تتبع الرتبة الثانية ، كما أنها لاتعتمد على معدل الانتشار داخل الجسيمات ، وقد تبين إمكانية تطبيق نموذج و فريندلش لتفسير عملية الإمتزاز (أي أن الإمتزاز فيزيائي) ، وقد أكد معامل الفصل (R_L) إمكانية حدوث الإمتزاز.