

REMOVAL OF MALACHITE GREEN DYE POLLUTANT FROM WATER USING NANO-POROUS STRUCTURE OF MODEFIED NATURAL SOURCE

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ABSTRACT

Dyes are pollutants resulted from the textile, paper, and leather industries, are considered sources of environmental contamination. This study is devoted to utilize a low-cost modified local natural source, for removing the Malachite Green cationic dye (MG) from aqueous solution. Zeolite-A (ZA) was prepared in a good Crystallinity via hydrothermal heating from local kaolin at mild conditions. The mineralogical, structural, and chemical properties of both, the precursor rock and ZA that formed were identified via X-ray Diffraction (XRD), scanning electron microscope (SEM), and *X-Ray Fluorescence* (XRF) techniques. To identify the impact of operational parameters, a series of adsorption studies were performed, such as initial concentration, pH, adsorbent dose, initial dyes concentration, contact time, ionic strength and temperature on the complete dye removal. The thermodynamic parameters (ΔH , ΔS and ΔG) of adsorption systems were also determined and evaluated. The resulting degrees of dye removal were 59–86.5% for initial dye concentration of 10 mg/L and for ZA loadings of 0.01–1.00 g. It was found that the adsorption of MG on ZA followed a pseudo-second order model, the data proved well fitted to the Langmuir isotherm model and thermodynamic studies showed that the dye adsorption onto ZA is a spontaneous and endothermic. The experimental

results indicated that, the adsorption capacity of ZA for removing the cationic dye MG was 98 mg/g, which is being probably dependent on the geometry of the dye molecules.

Keywords: Zeolite-A, Local source, Malachite green, Adsorption and Thermodynamic parameters.

INTRODUCTION

Many industries use dyes for coloring their products. The discharge of effluents from such manufacturing processes contains large amount of dyes. Those hazardous materials are, not only damaging the aesthetic nature of receiving water bodies, but also are being toxic to aquatic life (Chakraborty, 2010; Bulut *et al.*, 2008). Malachite green MG is an organic cationic dye, a kind of tri-phenyl methane ($C_{23}H_{25}N_2Cl$). It is widely used in production of the textile, ceramic, leather, food and cell coloring, along with paper formation (Daneshvar *et al.*, 2007; Kaith *et al.*, 2015). MG dye has negative effect on human health, as it can cause harmful effects on liver, gill, kidney, intestine and gonads of aquatic organisms. Contact of malachite green with skin causes irritation with redness and pain. Therefore, the use of malachite green in aquaculture was banned in many countries. It is also considered as carcinogenic and mutagenic source due to the presence of nitrogen in its composition (Lu *et al.*, 2015). Therefore, its efficient removal from wastewater is of priority. Generally, the removal of organic dyes from aqueous solutions is highly challenging to decrease this hazardousness (Zhuang *et al.*, 2016; Hosseinzadeh and Abdi, 2017). It has also become

necessary to have inexpensive and efficient substitute materials which are capable of simultaneously removing organic and inorganic contaminants. Zeolites are aluminosilicate minerals that show crystalline porous identity with exceptional connected pore and channel systems in the molecular size range which designate a relied contribution in catalysis, separation and ion exchange (Bekkum *et al.*, 1991). Zeolite-A is one of the man-made zeolites (also called molecular sieves) that has various and important industrial applications such as desiccation, detergency, adsorption, separation, catalysis, and ion exchanging (Flanigen *et al.*, 1991). Zeolites are usually prepared from Na-silicate and Na-aluminate of pure chemical sources. However, their construction from low-priced resources is of economic importance with good capability of optimizing their synthetic parameters (Roozeboom *et al.*, 1984).

Many attempts were carried out to investigate the ability of both natural (NZ) and synthetic Zeolites (SZ) in eliminating MG from wastewater. It has been reported that NZ (Chinese Zeolite) can effectively adsorb MG in aqueous solution with a higher adsorption capacity of 10×10^{-5} mol/g at 30 °C and pH=6. In a single component system of this study, the adsorption is found to obey the first-order kinetics, whereas the isotherm is following the Langmuir model (Wang and Ariyanto, 2007). In contrast, using NZ, initial concentration, Clinoptilolite (obtained from Xinyang city in China) in a batch mode testing of the same dye revealed a pseudo second order kinetic and spontaneous endothermic process. The kinetic data were analyzed by

the Langmuir, Freundlich, Redlich–Peterson, and Koble–Corrigan isothermal models. The better fit for the equilibrium process was Koble–Corrigan model with maximum adsorption capacity of 22.17 mg/g (Han *et al.*, 2010). Similarly, different Zeolite nanostructures were also tested to get rid of malachite green dye from aqueous media using a batch method. Obtained data implied that, the adsorption processes fitted well with the pseudo-second-order kinetic model and Langmuir adsorption isotherm. Moreover, the thermodynamic parameters showed spontaneous adsorption process of physisorption and exothermic nature. The maximum adsorption capacity of MG dye was found to reach 29.74 mg/g (Abd El-Rahman, 2018). In the same context, Zeolite-3A was examined for removing Rhodamine B (RhB) and Malachite green dyes from water samples. The percentage contribution of each parameter on the removal for RhB and MG was determined using ANOVA. It has been found that, the most effective parameters in RhB and MG elimination under optimizing conditions were the initial concentration of dye 47.715% and the pH 6.485%, respectively (Rahmani, 2018). Finally, preparing ZA from low-grade Egyptian kaolin indicated high efficiency in many pollutants removal through less energy consuming with low energy consuming through hydrothermal conversion.

MATERIALS AND METHODS

1) Materials: Local kaolin rock, delivered by Middle East Mining Investments Company (MEMCO) was used as the Al and Si source for

Zeolite-A synthesis. Malachite green MG dye 99.9% was purchased from Sigma Aldrich. Potassium phosphate Mono-basic (KH_2PO_4), Potassium phosphate di-basic (K_2HPO_4) and Calcium Chloride (CaCl_2) were purchased from Scharlau. Sodium hydroxide pellets (NaOH) 98.9% and Hydrochloric acid (HCl) 37 % were obtained from VWR.

2) Methods

- **Preparation of Zeolite A:** Synthesis of Zeolites from crystalline clays such as Kaolin encountered two steps: 1. Thermal activation of the rock for getting an amorphous material (metakaolinite), and 2. Attacking activated clay with an alkaline solution to maintain the Zeolite phase. The formation of ZA in the current work was done following the method of (Youssef et al., 2008). Typically, Kaolin was heated at 700 oC for 4 h, and then reacted with 3.0 M of NaOH aqueous solution with a solid/liquid ratio of 1:10. The mixture was charged in a Teflon-lined stainless steel vessel of 100 ml capacity and treated in an electric oven at 80 oC for 4 h. The reaction powder was collected, washed severally with distilled water up to pH 7-8 and centrifuged for solid- liquid separation. The solid powder was dried at 80 oC for 24 h and collected in dry, clean plastic containers for phase characterization.
- **Instrumentation:** A pH meter model (Hach, Sension1) equipped with reference electrode was used to adjust the solutions pH, rotor shaker 15 position model (THERMO, SHKE 2000) equipped with timer was used in batch experiments, centrifuge model (Hermle, Z206A) used for sample

centrifuging at 6000 rpm, electric muffle model (Carbolite, CWF 1200) and residual MG dye in aqueous phase was detected using (Shimadzu UV-VIS) spectrophotometer.

- **Adsorption batch experiments:** The batch experiments of MG removal by ZA were carried out to study the optimal conditions that governing the efficient elimination of dye from the contaminated water. The studied parameters were: solution pH, adsorbent ZA dose, initial MG concentration, contact time, ionic strength and temperature. Lab. experiments were performed using a rotatory shaker at a constant shaking rate of 250 rpm. The process was done by adding 50ml solution of MG, a desired quantity of ZA in 250ml Erlenmeyer flasks. The mixture was agitated in a shaker at the desired temperature and speed for predetermined time intervals. The supernatant was agitated by centrifugation at 6000 rpm for 15 min. The residual concentration in the supernatant was determined and the dye concentration was then detected by UV-VIS Spectrophotometer at a wavelength of $\lambda \sim 620\text{nm}$. It is worth mentioning that the percent removal of MG dye (R % Removal) calculated with the following eq. (1) at different pH (3-10), ZA dose (0.01-1.0 gm.), concentrations of MG dye (5-2000 mg/L), time (5-300 min) and concentrations of CaCl_2 (0.01- 0.5 M).

$$(\mathbf{R \%}) = \frac{(\mathbf{C_o - C_e})}{\mathbf{C_o}} \times \mathbf{100} \quad (1)$$

Where : C_0 (mg/l) is the initial conc. of MG dye solution and C_e is the residual concentration.

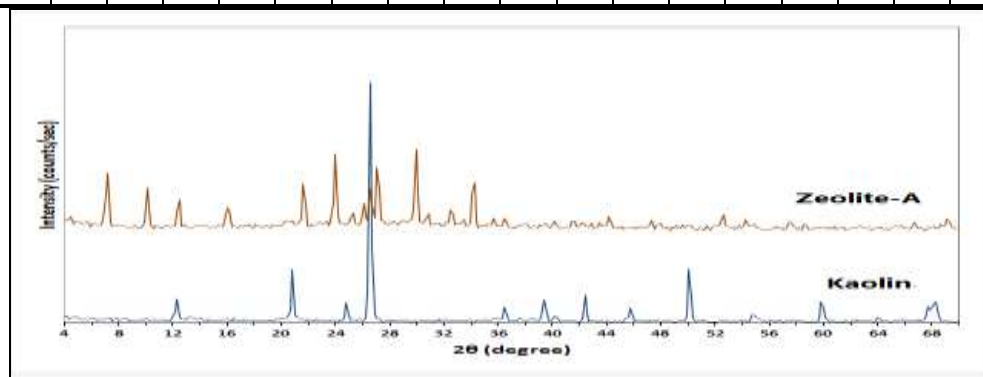
3. Characterization techniques: The X-Ray Diffraction XRD tool was used to identify the mineralogical composition of both; parent kaolin and the prepared ZA powder using BRUKER apparatus, Axs, D8-ADVANCE (Germany 2001) by applying Cu-K α radiation. The patterns of all synthesized phases were compared to the PDF data. The internal structure of the prepared Zeolite samples was investigated using Scanning Electron Microscope SEM model Philips XL30 attached with EDX unit, with accelerating voltage 30 K.V., magnification 10 x up to 400,000x and resolution for W 3.5nm. Whereas, the main chemical constituents of the original rock material were detected by the Wavelength Dispersive X-Ray Fluorescence Spectroscopy, Axios advanced, sequential WD XRF spectrometer, PANalytical 2005.

4. Results and Discussions

A. Characterization of Zeolite (adsorbent synthesis): The composition of the starting kaolin, from which the Zeolite adsorbent was prepared, is given by the XRF chemical analysis of Table 1. The oxide contents (in weight percentage, Wt %) of the analyzed rock implied an amount of silicon/aluminum ratio of 1.24. This is suitably close to the unity, which is the same Si/Al ratio in most of the synthetic forms of Zeolite-A (Bougard *et.al*, 2000).

Table(1): Chemical Oxide analysis of kaolin

Oxides	Elemental analysis (Wt%)													Total			
	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO	MgO	CaO	SrO	K ₂ O	P ₂ O ₅	Y ₂ O ₃	CeO ₂	PbO		ThO ₂	P ₂ O ₅	SO ₂
Kaolin	53.25	1.62	42.94	0.41	<0.01	0.05	0.37	0.28	0.05	0.05	0.01	0.09	0.04	<0.01	0.758	0.05	99.94



Figure(1): XRD pattern for kaolin and developed Zeolite A.

The XRF analysis for the rock indicated Si/Al contents of nearly 1.24 which is so close to the same ratio of the two elements in the crystalline Zeolite-A (Bougeard *et.al*, 2000). Figure 1 displays the XRD data for the mineralogy of the starting material (kaolin) and the as-synthesized ZA, developed from attacking calcined kaolin with 3.0M NaOH under hydrothermal conditions of 80 °C for 4h. The X-ray peaks are so sharp with strong and complete positioning and perfect matching with the reference PDF card # 73-2340. The absence of remnant peaks of the originally treated rock is indicating a well crystalline product and a complete crystallization process.

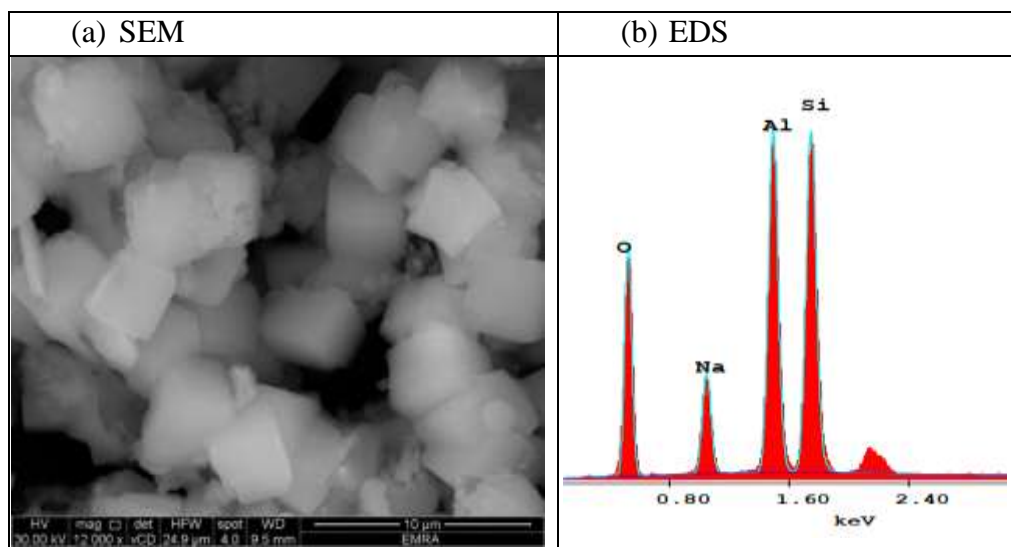


Figure (2): (A) SEM micrographs and (B) EDS chemical microanalysis of the as-prepared ZA powder.

Figure 2 is monitoring the microstructure and the elemental chemical composition of the formed Zeolite-A, obtained from the thermally activated kaolin. Figure 2a is showing the common cubic morphology of ZA, with crystals of unequal sizes in the range of 1-5 microns. Some of the particles are spherical and in a minute sizes, others are very well shaped in a big and small cubic morphology. The different crystallite sizes of the formed Zeolite can be explained by the continuous, successive nucleation and crystallization of the slurry during the whole reaction duration of the conventional heating process. The presence of different crystal generations is explained by the slow temperature rise of the reaction under the

conventional hydrothermal processing of Zeolites (Bonaccorsi and Proverbio, 2008).

Table(2): EDS elemental analysis of the product

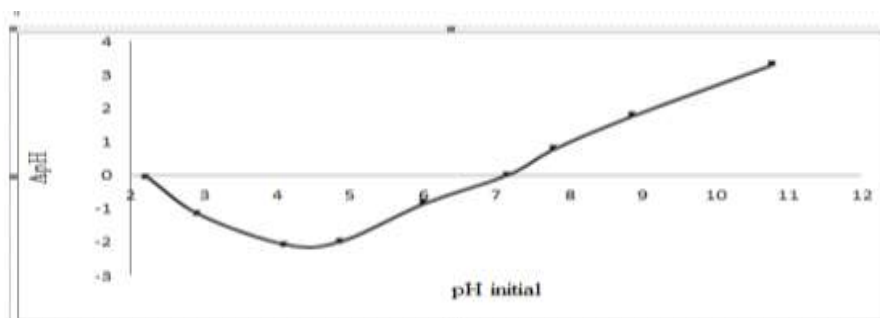
Element	Weight %	Atomic %
O K	37.84	50.48
Na K	9.42	8.75
Al K	22.13	17.51
Si K	30.61	23.27
Total	100	100

On the other hand, Figure 2b presents the atomic percentages of Si, Al, Na, and O which constitute the main elements that contributed to form ZA framework. It is clear that, the EDS measured value for the Si/Al contents of the monitored Zeolite crystals (average of 5 crystals) was 1.33 which is so close to the previously given Si/Al value (1.24) of XRF analysis. This result is reflecting the siliceous nature of the starting kaolin, see Table 2. It is well known that, the amount of Al content of a given Zeolite is the determining factor for the cation exchange capacity of such Zeolite type. It is a fact that, the decrease in Al content resulted in reducing the number of developing negative sites on the porous construction, and in turn, those (negative) charges usually originate from the normal replacement of Si by Al during Zeolite formation. Accordingly, the chemical analysis of Zeolites with deficient in aluminum content may show reduced amounts of compensating positive cations, accompanied by some reduction in the whole cation exchange capacity of the micro porous material (Munthali *et al.*, 2014). In

this work, EDS microanalysis of the obtained ZA (Table 2 & Figure 2b) is showing an amount of 8.75 % Na⁺ cations/ unite cell of Zeolite-A, which is less than the theoretical amount of the cationic contents of the fully compensated ZA structure per unite cell (12 Na⁺ %/ unite cell) (Munthali *et al.*, 2014).

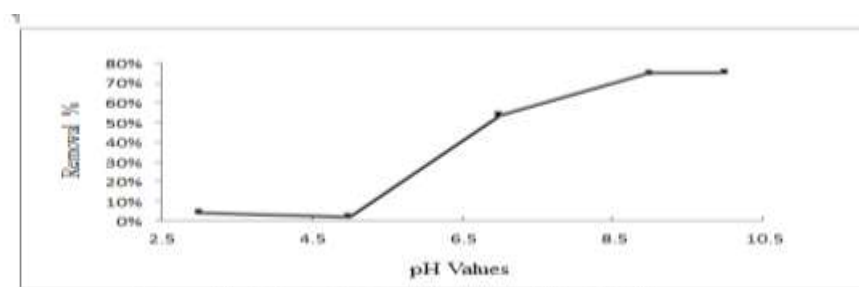
- **Adsorption studies**

A). Determination of zero-point charge (pHZPC): The point of zero charge (pHpzc) means the pH at which the surface charge of the material equals to zero. To get this value, ZA powder was thermally activated at 105 °C for 24 h to eliminate any environmental contaminants that may find their way into the open pores and channels of Zeolite, such as the attached water vapor and CO₂. The (pH_{pzc}) of Zeolite was determined by adding 0.1mg of ZA to 100 ml of water with varying pH values in the range of 3 to 10, and adjusted using 0.1 M HCl or 0.1 M NaOH on stirring for 24 h. The $\Delta \text{pH} = (\text{pH}_{\text{final}} - \text{pH}_{\text{initial}})$ was plotted against the pH_i as shown in Figure 3, and the point where pH_f - pH_i = 0 was taken as the pHpzc (Neag *et al.*, 2020). The (pH_{ZPC}) for ZA was found at basic pH 7.18, it was proved that, the pH_{PZC} of Na-X Zeolite was found to be 7.5 (Kiwan *et al.*, 2021).



Figure(3): Zero-point-of-charge for Zeolite

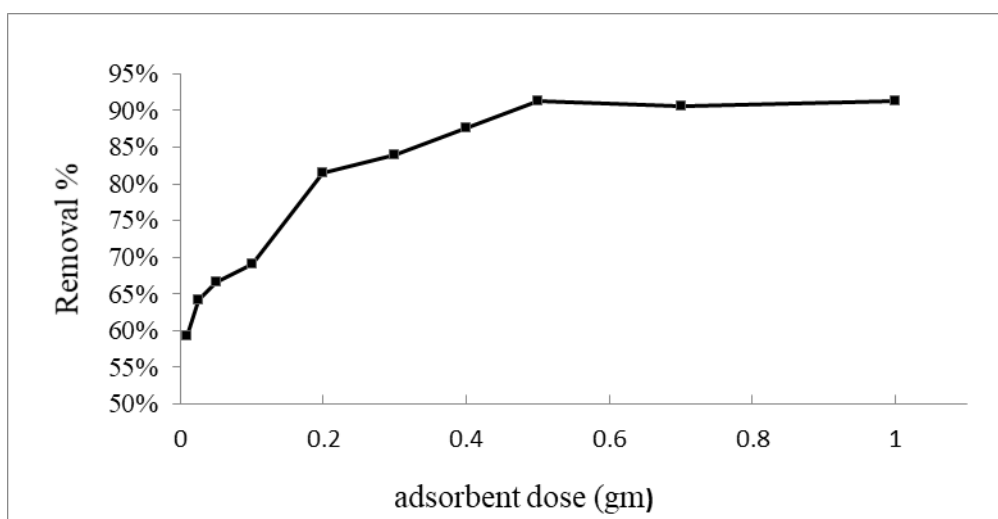
B) Effect of pH: The effect of pH of the solution on the adsorption capacity of the dye into Zeolite surfaces was conducted to by shaking 0.1g of ZA at different pH values from 3 to 10 in 50ml of MG solution 10 mg/L in 250ml glass conical flasks sealed with aluminum foil on a rotary shaker at 250 rpm for 15 min. pH values were adjusted by phosphate buffer solution and 0.1 M HCl or 0.1 M NaOH, then centrifuged at 6000 rpm for 15 min. Separate liquid phase followed by samples analyses to determine the optimum pH value using spectrophotometer.



Figure(4): Effect of pH on the removal % of MG

Figure 4 illustrates the adsorption of MG onto ZA at various pH values based on initial MG concentration 10.0 mg/L, adsorbent dose 0.1g and contact time 15min. It was noticed from the curve that, the best adsorptions of MG were obtained in basic pH values 9 to 10. The variation in the dye uptake with respect to the initial solution pH can be explained based on the structure of dye molecule and the point of zero charge (pH_{ZPC}) of ZA. For ZA, the point of zero charge is found to be 7.18 and the carboxylic groups of MG $pK_a = 10.3$ were protonated and had high positive charge density at a lower pH (Garg *et al.*, 2003). At a pH higher than pH_{ZPC} , the ZA particle acquires a negative surface charge and favors uptake of cationic dyes due to the increase of the electrostatic force of attraction. At a pH lower than pH_{ZPC} , on additional, the ZA surface acquires a positive charge, and dye molecules gain a positive charge as well. Due to this explanation, there is an electrostatic repulsion between dye molecules and ZA that causes the reduction in dye uptake. It also has been reported that adsorption of MG onto NZ (Natural Zeolite) increases as pH is enhanced (Wang and Ariyanto, 2007). The best adsorption of MG dye was obtained in basic pH. At low pH values, due to formation of positive charge on the surface of adsorbent and protonation of dyes little electrostatic interaction occurs between 3A Zeolite and dyes (Rahmani *et al.*, 2018), and this result complies with (Kiwani *et al.*, 2021).

C): Effect of adsorbent dose: The effect of adsorbent dosage was conducted by adding desired amounts of ZA 0.01, 0.025, 0.05, 0.1, 0.2, 0.3, 0.4, 0.5, 0.7 and 1g at the optimum pH 9 and 50ml of MG solution concentration 10mg/L in distilled water shaken for 15 min at 250 rpm.



Figure(5): Effect of Adsorbent Dose on the removal % of MG

Figure 5: shows the adsorption behavior of MG versus various adsorbent amounts in the range of 0.01–1.0 g/50 ml with initial concentration 10.0 mg/L and contact time 15min. It is clear that the percentage of MG removal has been increased with the increase of adsorbent dose. Such a trend is mostly attributed to an enlargement in the adsorbent surface area and the availability of more active adsorption sites. Although the percentage removal of dye is increased with the increasing of adsorbent dose, the equilibrium adsorption capacity (q_e) for MG is

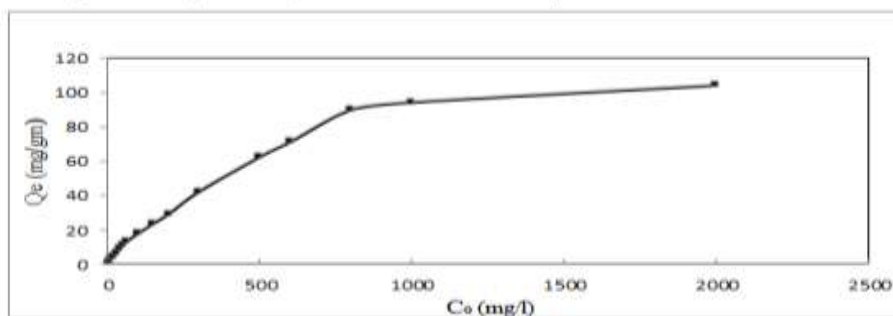
decreased (as explained equation 2). This might be related to the decrease in the total adsorption surface area available to dye molecules resulting from overlapping or aggregation of adsorption sites. Thus by increasing the adsorbent mass, the amount of dye adsorbed onto unit mass of adsorbent could be reduced. Furthermore, the maximum dye removal 91.35% for ZA was recorded at 0.5g/50ml and the optimal dosage was 0.2g/50ml with removal ratio 81.48% to reduce the economic effect between the two dosages and any further increase in adsorbent dose will not significantly change the adsorption yield. This is due to the binding of almost all dye molecules to adsorbent surface and the establishment of equilibrium between the dye molecules on the adsorbent and in the solution. Han et al. also confirmed this result for using Zeolite to remove MG by microwave irradiation (Han *et al.*, 2010). The amount of adsorbent dose (3A Zeolite) significantly affects the adsorption of MG dye. With increasing of adsorbent dosage, the removal efficiency was increased because of the increase in the available sorption surface sites (Rahmani *et al.*, 2018).

The adsorption capacity of the ZA adsorbent q_e (mg/g) can be estimated using following Eq. (2):

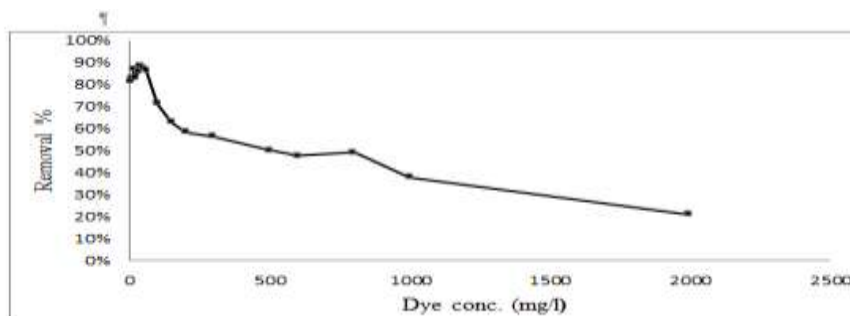
$$q_e = \frac{(C_o - C_e)}{m} \times V \quad (2)$$

Where, C_o (mg/l) is the initial conc. of MG dye solution, C_e is the residual concentration of MG, V (L) is the volume of solution and m (g) is the weight of the ZA.

D) Effect of MG Dye concentrations: To investigate the effect of MG concentration, experiments were carried out by adding 0.2g of ZA at optimum pH 9 to 50ml of MG with different concentrations 5, 10, 15, 20, 30, 40, 50, 60, 100, 150, 200, 300, 500, 600, 800, 1000 and 2000 mg/L using the same previously mentioned conditions.



Figure(6): Effect of adsorption capacity of Zeolite-A against initial concentration of MG

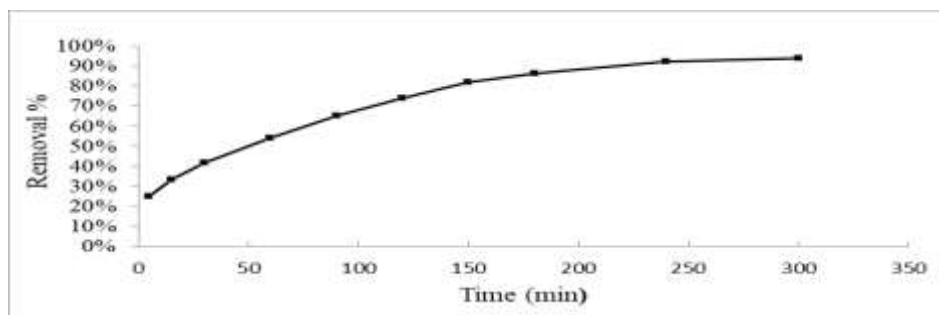


Figure(7): Effect of initial dye (MG) concentration on removal %

In Figures 6&7 the effect of different initial dye concentrations adsorption ZA is presented. It's worth mentioning that increasing the initial

dye concentration reduced the percentage of MG removed. This can clarify that the ZA has a limited number of active sites, which become saturated at a certain concentration. However, the adsorption capacity at equilibrium could increase by growing initial MG dye concentration. This will lead to an increasing in equilibrium sorption until sorbent saturation is achieved with maximum adsorption capacity (q_{max}) 98 mg/g for ZA, this result shows an agreement with (Rahmani *et al.*, 2018). The percent removal over the as-prepared different types of Zeolite nanostructures increase as the concentration of the malachite green dye decrease (Abdelrahman, 2018).

E) Effect of agitation time: To explain equilibrium time it was conducted by shaking 0.2g of ZA at optimum pH 9 and MG solutions of (800 mg/L) in distilled water for different time intervals of (5, 15, 30, 60, 90, 120, 150, 180, 240 and 300 min) then centrifuged at 6000 rpm for 15 min.

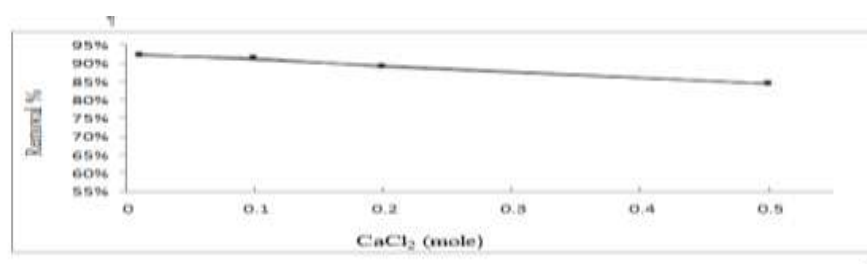


Figure(8): Effect of agitation time on removal % of MG

In the sorption experiment, the effect of contact time is important, as the data will allow confirmation on the length of agitation time. This will get the adsorption processes between the solid phase (adsorbent) and aqueous

phases (adsorbates) into a state of balance. Figure 8 summarized the data of the contact time effect of MG removal. The adsorption of MG 800mg/L over ZA has presented a similar process in which the adsorption of MG dye has increased with the agitation time raise. The equilibrium has been reached in the adsorption phase after 240min for ZA. The initial rapid adsorption rate could be explained by an increase in the number of active binding sites on the surface of adsorbent. This result shows conformity with (Jain *et al.*, 2015). The removal efficiency increases as the contact time increases (Rahmani *et al.*, 2018).

f) Effect of ionic strength: Adsorption efficiency depends on the electrostatic interactions between the cationic dye molecules and ZA binding sites. MG solutions were prepared with CaCl_2 salt to clarify the effect of ionic strength on adsorption to remove MG, the experiments were carried out at different conc. of CaCl_2 (0.01, 0.05, 0.1, 0.3, and 0.5M) in 50ml MG soln. 800 mg/L, 0.2 gm. ZA, pH 9, shaking at 250 rpm for 240min and centrifuged at 6000 rpm for 15 min.



Figure(10): Effect of ions strength on removal% of MG over Zeolite-A

The effect of calcium chloride on the adsorption of MG over ZA has been shown in Figure 10. With calcium chloride concentration increase from 0.01 to 0.50 mol/L, we found that, the adsorption percentage of MG has decreased from 92.2 to 84.5% this behavior could be attributed due to the competitive effect between dyes cations and ions from the salt (Ca^{2+}) for the sites available for the sorption process, this result has conformity with (Mittal *et al.*, 2020).

- **Adsorption kinetic:** For comprehending more data about the adsorption mechanism, different kinetic models are applied; pseudo-first- or pseudo-second-order reaction (Seen Eq. (3) and Eq. (4))

Pseudo first order:

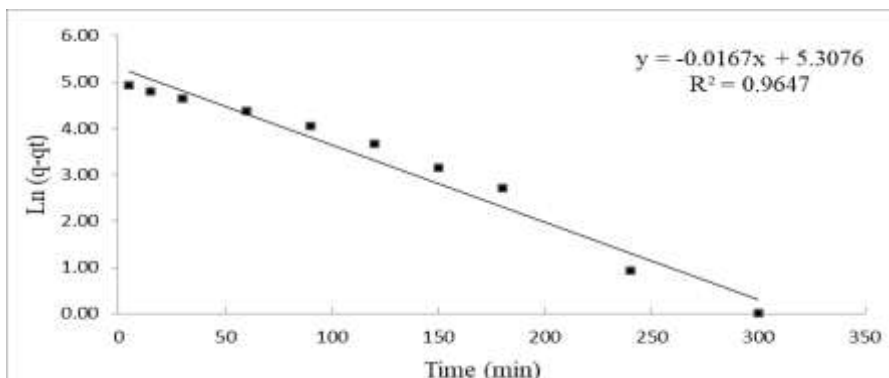
$$\ln (q_e - q_t) = \ln q_e - K_1 t \quad (3)$$

Where, q_t is the amount adsorbed at time t , and k_1 is the first-order rate constant (Gupta *et al.*, 2016; Wang *et al.*, 2018; Farghali *et al.*, 2021).

Pseudo second order:

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

Where, t is the adsorption time, q_e and q , (mg/g) are the adsorbed amount of MG at equilibrium, k_2 is the second-order rate constant (Ho & McKay 1999; Wu *et al.*, 2009; Yao *et al.*, 2010).



Figure(9.a): Kinetic plots of pseudo First order for the adsorption of MG over ZA

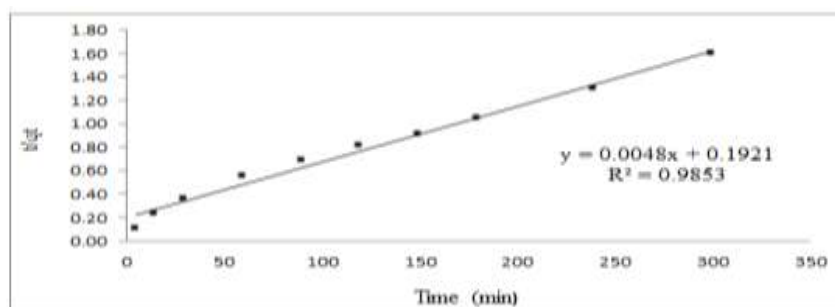


Figure (9.b): Kinetic plots of pseudo second order for the adsorption of MG over ZA

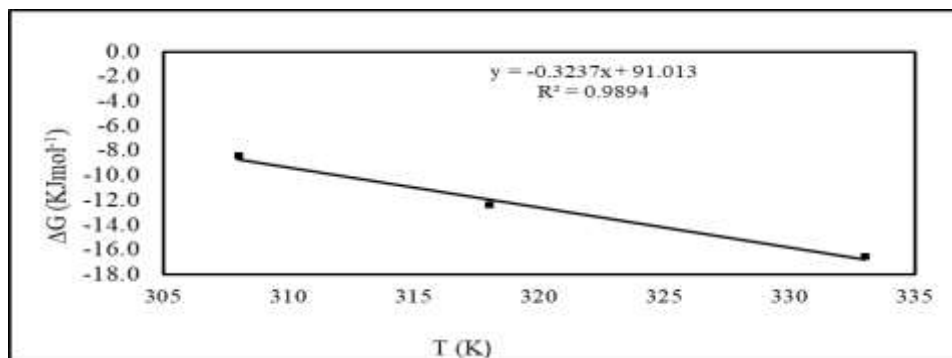
Figure 9 (a,b) demonstrates pseudo first-order and pseudo second-order graphics for the adsorption kinetics of studied MG dye. The accordance between the experimental data and the model-predicted values was defined using the correlation coefficients (R^2). When the values R^2 are significantly higher, it means that the model has stated successfully the kinetics of MG adsorption. The data outcomes indicate good accordance with the second-

order kinetic model with correlation coefficients 0.9853 for ZA. In Table 4, the regression coefficient (R^2) for second-order model is detected higher than first-order one. This result also has an agreement that adsorption of MG over Zeolite is fitted well with the pseudo-second-order kinetic model (Han *et al.*, 2010; Abdelrahman, 2018). Adsorption kinetics followed the pseudo-second-order type kinetic and intra-particle diffusion played an important role onto adsorption mechanism of malachite green and natural Zeolite (Tanyol, 2017).

Table(3): Kinetics parameters of MG adsorption by ZA

Adsorbent	Parameters	Pseudo First order	Pseudo Second order
ZA	R^2	0.9647	0.9853
	q_e calc.	203048.4	203048.4
	q_e exp.		180000

- **Effect of Temperature on the Adsorption and Thermodynamics:** To explain the effect of temperature, thermodynamic experiment carried out at optimum points of pH 9, concentration of MG 800 mg/L, dose of adsorbent 0.2g and time 240min at 308, 318 and 333K.



Figure(11): Plots ΔG° versus T for adsorption of MG over ZA

The adsorption of MG on ZA was carried out at different temperatures (35, 45 and 60 0C) for the initial concentration of 800 mg/L. The free energy of adsorption ΔG° was calculated from the following equation:

$$\Delta G = -RT \ln K \quad (5)$$

Where, K is the equilibrium constant, T is the solution temperature and R is gas constant 8.314 J= mol K.

The apparent enthalpy of adsorption ΔH° and entropy of adsorption ΔS° were calculated from adsorption data at different temperatures using the Van't Hoff Eq. (5).

$$\ln K = \frac{\Delta S^\circ}{R} - \left(\frac{\Delta H^\circ}{T} \right) \quad (6)$$

Data obtained from the experiments are presented in Figure 11. Temperature is a well-known factor that has a significant impact on any adsorption process. Therefore, batch adsorption experiments were performed at a variety of temperatures, from 308 to 333K. The findings clearly showed that, adsorption of MG over ZA have risen in parallel with

the rise in temperature. The observed increase in the adsorption capacity with temperature rise shows that, the removal is assisted by a high temperature of MG molecules by ZA. This is because a high temperature could thicken the boundary layer, reducing the dye molecules' tendency to escape from the adsorbent surface and enter the solution process. The ΔH° and ΔS° values were determined from the slope and intercept of the plot of ΔG° versus T. The obtained results as showed in Table 4 that the (negative) values of ΔG° and positive value of ΔH° mean that the MG adsorption process is a spontaneous and endothermic process. The positive value of ΔS° means the adsorption changes with temp. Increase, this result has an accordance with (Han et al., 2010) who reported that the adsorption of MG and natural Zeolite was spontaneous and endothermic process. The change in free energy for physisorption and chemisorption is recorded between -20 and 0 kJ/mol, and 80 to -400 kJ/mol, respectively (Tehrani-Bagha et al., 2011). In this study, the values rang of ΔG° for ZA is obtained equal to (-8.39 to -16.58 kJ/mol) these (negative) values indicate that the physisorption is the dominating mechanism which is also has a conformity with (Abd-elrahman, 2018).

Table(4): Thermodynamic parameters for MG adsorption on ZA under different temperatures

ZA				
T	Ka	ΔG°	Slope (ΔS°) KJ/mol.k	Intercept (ΔH°) KJ/mol
308	26.50	-8.39	0.32	91.01
318	109.00	-12.40		
333	399.00	-16.58		

• **Adsorption Equilibrium**

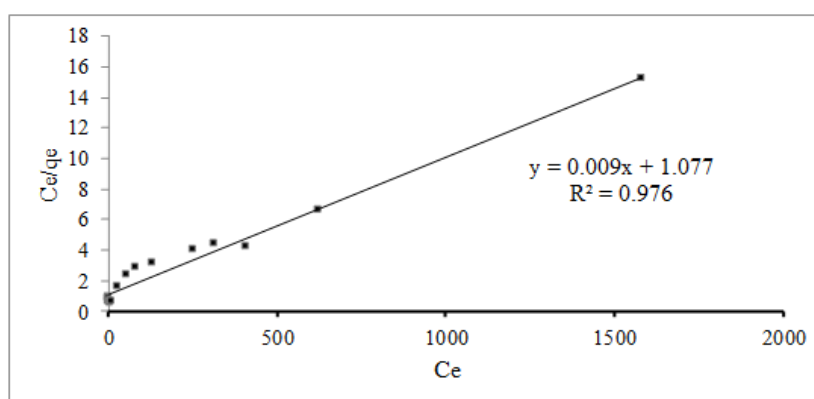


Figure (12.a): Langmuir adsorption isotherm of MG on ZA

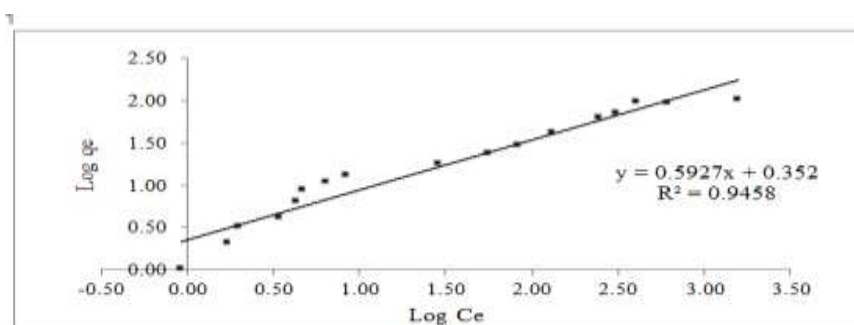


Figure (12.b): Freundlich adsorption isotherm of MG on ZA

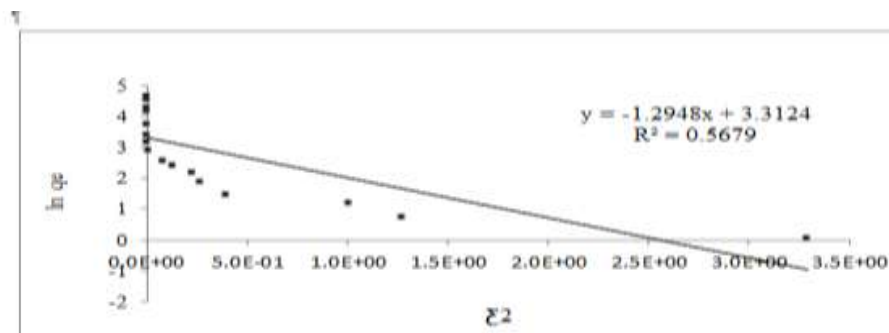


Figure (12.c): (D-R) adsorption isotherm of MG on ZA

An adsorption isotherm is a curve relating the equilibrium of an adsorbate on the surface of an adsorbent, (q_e), to the concentration of the adsorbate in the Liquid, (C_e). Langmuir, Freundlich, and Dubinin-Raduskevitch (D-R) isotherm equations were used to analyze the equilibrium data in order to disclose the adsorption behavior of MG to ZA. Linear forms of Langmuir, Freundlich, and D-R isotherm equations are given below as equations. (7), (8), and (9) respectively. Related constants were calculated and given in Table 4.

$$\frac{C_e}{q_e} = \frac{C_e}{q_{max}} + \frac{1}{Kq_{max}} \quad (7)$$

$$\text{Log } q = \text{log}K_f + n \cdot \text{log}C_e \quad (8)$$

$$\ln q = \ln q_m - K \epsilon^2 P \quad (9)$$

where, q_m is the maximum adsorption at monolayer coverage in mg/L; K is the adsorption equilibrium constant related to the energy of adsorption in l/mg; K_f and n , Freundlich constants representing the adsorption capacity and intensity respectively; K is the equilibrium constant related to the

adsorption energy; ϵ_p is the Polanyi potential and it was calculated using the following equation:

$$\epsilon_p = RT \ln\left(1 + \frac{1}{C_e}\right) \quad (10)$$

Where, R is the gas constant (8.13 J) and T is temperature in kelvin.

E is the mean free energy of adsorption and can be calculated using the following equation:

$$E = (-2K)^{-0.5} \quad (11)$$

Table(5): adsorption isotherm parameters of MG on ZA

ZA		
Langmuir isotherm		
qm(mg/g)	K(l/mg)	R2
110.4	0.01	0.9670
Freundlich isotherm		
KF	N	R2
2.26	1.69	0.9458
D-R isotherm		
Qm(mg/g)	E (kJ/mol)	R2
27.28	0.62	0.5679

In the present study, the Langmuir, Freundlich and Dubbin-Radushkevich isotherm models were performed. Detailed descriptions about fitted isotherm models on the experimental data are summarized in Table 5 the main objective is to describe the adsorption process of MG on ZA. According to the R^2 values in Table 5, Langmuir was selected as the best isotherm model with $R^2=0.967$, with calculated adsorption capacity $V_m = 110.4$ mg/g that derived from Langumuir model are obtained close to the experimental values $q_{max} = 98$ mg/g for ZA. It can be worthy concluded

that langumuir describes monolayer coverage of MG over ZA. The model has also suggested that ZA surface is homogenous and uniform distribution of sites and their energies. As well confirmed by Abdelrahman, who informed that the adsorption of MG over a synthesized Zeolite nanostructures fitted well with langmuir model (Abdelrahman, 2018), This result is in accordance with those of the study (Ariyanto, 2009; Tanyol, 2017). In order to comprehend the adsorption type, an equilibrium data has been examined by D-R isotherm. Straight lines are created by plotting $(\ln q_e)$ versus $(\frac{E}{2P})$, which indicates that the adsorption of MG over ZA obeys the D-R isothermal equation in the whole concentration range investigated. Values q_m and K' can be calculated from the intercepts and slopes of the plots are shown in Figure 12. Based on K' values, it might be possible to estimate the free energy of adsorption (E), which is described by the free energy change when 1.0 mole of ion is transferred to the surface of the solid from infinity in solution. E value is beneficial for the type of adsorption calculations and if this value is found between 8.0 and 16 KJ/mol, the adsorption type can be explained by ion exchange. The value of E in this study is found within the energy range of physical adsorption $E < 8.0$ KJ/mol. As shown in Table 6 the calculated values of E are smaller than 8.0 KJ/mol = 0.62 for MG, this indicating that adsorption of MG onto ZA is physical in nature, which has an accordance with (Abdelrahman, 2018).

Table(6): Explains different types of Zeolites and MG dye removal

Zeolite Type		Materials & Method	Dye	Efficiency	References
Natural		Clinoptilolite With particle size = 0.5–2 mm.	MG	5×10 ⁻⁵ mol/g	Wang and Ariyanto, 2007
		Mordenite, 0.5-2 mm	MG	3.24×10 ⁻⁵ mol/g	Ariyanto, 2009
		Clinoptilolite (~68.50%) + montmorillonite and quartz, size average= 0.4-0.25 mm	MG	23.94 mg/g	Han <i>et al.</i> , 2010
		Clinoptilolite 85%+ gang minerals, size < 45 µm	Basic Dye	> 82 %	Amin <i>et al.</i> , 2017
		Clinoptilolite, Particle size =0.25mm	MG	98 mg/g	Tanyol, 2017
Synthetic	3A	Commercial 3A- Zeolite, pure chemicals	MG	87.40 %	Rahmani <i>et al.</i> , 2018
	4A	Linde Zeolite type A (LTA)-based on kaolin. 80 OC/24h, 5mol/l with 8:1 of NaOH/metakaolin.	MG	55 mg/g	Pereira <i>et al.</i> , 2018
	Na+	Calcined bentonite, 70 OC/2h Product was a mixture of bentonite + NaP Zeolite	Methylene Blue	36.23 mg/g	Shaban <i>et al.</i> , 2018
	Y-Zeolite	Pure chemicals, 100 °C/12h,	Brilliant Green dye	1461.35 mg/g	Mittal <i>et al.</i> , 2020
	Na-X	Commercial type formula, Na ₈₆ [(AlO ₂) ₈₆ (SiO ₂) ₁₀₆].nH ₂ O). The crystallite size was 37.8 nm	Brilliant Green (BG)	24.13 mg/g	Kiwan <i>et al.</i> , 2021
	ZA	From kaolin (mentioned previously)	MG	98 mg/g	This study

Where,3A; is 3A-Zeolite, 4A; is Na-A Zeolite, NaP; is Gismondine-type Zeolite, Y-Zeolite; is Faujasite Na-Y Zeolite, and Na-X; is Faujasite Na-X Zeolite.

CONCLUSION

The study investigates low cost technique to remove MG using adsorption based on synthetic ZA. Synthetic ZA that obtained through previous illustrated stages in this study shows well developed crystals with almost uniform particle size distribution. XRD and SEM confirmed suitability of the selected reduced pilot-scale conditions for ZA production. The adsorption results of MG demonstrated that the high removal was found at pH 9 MG adsorption has been fulfilled using pseudo-second-order kinetic model rather than pseudo-first-order with $R^2=0.9853$. The adsorption of MG based on ZA was well fitted by Langmuir isotherms rather than Freundlich isotherm model with correlation coefficient $R^2=0.9760$. Furthermore, Dubinin-Radushkevich model has indicated that the adsorption of MG by ZA is a physical process. Thermodynamic calculation has revealed that the adsorption of MG over ZA is spontaneous and the process is endothermic with adsorption capacity 98 mg/g. To conclude, the ZA could be considered as an excellent candidate to be used as coagulant aid and sorbent for the removal of MG in drinking water treatment plant and wastewater and the reduced conditions in terms of less energy consumption, along with using the low-grade Egyptian kaolin in terms of lowering costs were the main economic interest and priority for the current study. Overall, taking green chemistry requirements into account, Zeolites prepared from natural clays (Kaolin) are promising materials for the removal of many environmental pollutants.

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إزالة صبغة الملائكة الخضراء من الماء باستخدام مصدر طبيعي معدل ذو مسام نانوية

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المستخلص

تعد الأصباغ من الملوثات البيئية الأساسية الناتجة من صناعات " النسيج - الورق - الجلود ". وهذه الدراسة تختص باستخدام مصدر طبيعي محلي منخفض التكلفة لإزالة صبغة " الملائكة الخضراء " من المحاليل، حيث تم تحضير (الزيوليت - أ) ذو خصائص بلورية جيدة من خلال عمليات تحويل حرارية في ظروف متوسة باستخدام خام الكاولين المحلي. تم تحديد الخصائص الكيميائية و التركيبية لكلا المادتين عن طريق إجراء بعض الفحوصات المتخصصة مثل " حيود الأشعة السينية - الأشعة السينية الفلورية - مجهر إلكتروني ماسح ". تم إجراء مجموعة من التجارب المعملية للتعرف علي المعايير الفيزيوكيميائية مثل (الأس الهيدروجيني - تحديد جرعة الممتز - تحديد جرعة الصبغة - تحديد درجة الحرارة المثلي - تحديد زمن التلامس الأمثل -

تحديد تأثير القوة الأيونية (وذلك للوصول الي إزالة تامة للصبغة. ايضا تحديد بعض المعايير الديناميكية الحرارية لنظام الأمتزاز مثل (التغير في المحتوي الحراري - القصور الحراري - الطاقة الحرة الديناميكية). أوضحت نتائج الإزالة للصبغة وصلت الي (٥٩-٨٦,٥ %) وذلك بإستخدام تركيز مبدئي (١٠ مجم/ل)، وتركيزات تتراوح بين (٠,٠١-١ جم) لزيوليت-أ. كما اوضحت التجارب المعملية ايضا أن سعة امتزاز (زيوليت- أ) لصبغة الملاكيت الخضراء تصل إلي (٩٨ مجم/جم)، ويتبع نموذج إمتزاز " لانجومير " للتساوي الحراري ومعادلة التفاعل من الدرجة الثانية . كما اوضحت الدراسات الديناميكية الحرارية لإمتزاز الصبغة علي الزيوليت (أ) انها تحدث تلقائيا ويصحبها إمتصاص حرارة.

الكلمات المفتاحية: زيوليت (أ)، مصدر محلي، صبغة الملاكيت الخضراء، الإمتزاز و القياسات الديناميكية الحرارية.