

## Comparative Investigation of Indigo Blue Dye Removal Efficiency of Methylmethacrylate/Sodium-Y-Zeolite Composite and Amidoximated Acrylonitrile / Na-Y-Zeolite Composite

M. Salem<sup>1</sup>, A.Z. El-Sonbati<sup>2</sup>, M.A. Diab<sup>2</sup> and T.Y. Al-Said<sup>\*1</sup>

<sup>1</sup>Environmental Sciences Department, faculty of Science, Damietta University, Damietta, Egypt

<sup>2</sup>Chemistry Department, faculty of Science, Damietta University, Damietta, Egypt.

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\* Corresponding author's E-mail: tamer\_eaaa2@yahoo.com

### Abstract

**Objectives:** The adsorption of indigo dye onto methylmethacrylate/sodium-Y-Zeolite composite and amidoximated acrylonitrile / Na-Y-Zeolite composite has been evaluated in watery solutions studying some different parameters namely, contact period, measure of the acidity or alkalinity of a solution, adsorbent dosage and thermal factor was also examined.

**Methods:** Two sorption isotherm imitations namely, Langmuir and Freundlich sorption imitations had been utilized for describing equilibria isotherm. Evaluation of the activating forces of sorption were carried out regarding sorption of indigo dye on both composites. Kinetics of the sorption model were studied and two kinetic imitations were utilized in an attempt for describing the kinetics of the process with regard to the practically obtained information.

**Key findings:** Regarding both composites, the pseudo-second order kinetics imitation was suitable and is consistent with the practically obtained information. The activating force ( $E_a$ ), difference in liberated energies ( $\Delta G$ ), enthalpy ( $\Delta H$ ) and entropy ( $\Delta S$ ) of sorption methodology had been determined regarding the sorption of the indigo dye via both composites. The thermodynamics of the sorption proved that the process regarding both composites had been both spontaneously and endothermically happening.

**Conclusion:** The practically obtained information indicated that both of methylmethacrylate/sodium-Y-Zeolite composite and amidoximated polyacrylonitrile/sodium-Y-Zeolite composite might serve well as inexpensive, efficient and reproducible adsorbents to get rid of indigo dyes from wastewaters.

**Keywords:** *Indigo dye, sodium-Y-Zeolite composite, adsorption, kinetics, thermodynamically factors.*

### Introduction

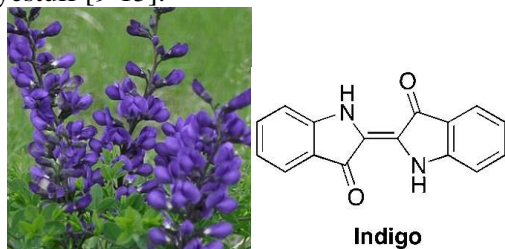
Dyes are colored substances that could impart

color to textile, leather, paper, or other materials via forming actual chemical bonds with the materials to which they impart colors. This is the major difference that distinguishes dyes from pigments. Dyes could be considered as ionizing

aromatic and/or heteroaromatic compounds with electron system that is delocalized in a resonance system. They are applied for the dyeing process in aqueous solutions [1-3].

Dyes are colored because they can absorb light in the visible region that usually at wavelength of the range of (300-750 nm). It was assumed that dyes are capable to absorb light due to the presence of a chromophore which is responsible for imparting the light absorption character to the dye. In addition, an auxochrome may be present to impart depth to the color. Recent theories suppress this assumption by the fact that dyes are colored due to the delocalized electron system of the aromatic and heteroaromatic ring systems [4-8].

Back to 3000 BC, indigo dye was used by Egyptians and Persians. This is proved by the presence of blue-colored belts discovered within ancient tombs of Egypt. Moreover, a cuneal writing explaining the methodology adopted for the dyeing fleece to be blue-colored had been discovered in ancient Meso-potamia. The technique was explained via repeatedly and continuously soaking and leaving the fleece textiles to dry in air. Some archaeological excavations showed the application of indigo on the Indian sub-continent for over four thousand years. It seems that indigo plant cultivation spread from India. Historically, indigo dye was obtained from a natural source where it was initially obtained from the organic extract of the leaf of a number of vegetations belonging to the genus namely, *Indigofera* genus. *Indigofera tinctorial* is one of the most widely used species (figure 1). This is a dye-bearing plant that was widely planted and utilized worldwide, especially in the Asian continent, because of its economical benefits. This is due to the fact that it was not an easy task to find the indigo dyestuff [9-15].



**Figure 1:** Indigo plant and structure of indigo dye.

Textile industry technologies and procedures require the utilization of massive amount of water and also utilize many toxic products. These effluents have hazardous effects as they

badly affect the ecosystem by speeding the degradation process of the surrounding environment. This occurs *via* the release of contaminated industrial discharges in surrounding environments as a polluted residue. Ultimate discharge for these effluents still challenging risk regarding their toxicological effects. So, it is a crucial need to assess its ecotoxicological effects and hazards to minimize its environmental effects. The conventional treatment techniques of these toxic effluents do not completely remove and detoxicate the dye discharges. Indigo dye is considered as a widely used dyestuff that is utilized for dyeing of textile, papers, leathers, plastics. In addition, it is used for other specific applications such as foods, pharmaceutical agents, cosmetics and photo-chemical products. Textile industry discharges containing indigo dye and other dyestuffs cause the wastewater to be eco-toxic and unsuitable for human and animal usance. Moreover, it causes imbalanced aquatic eco-systems. Recently, many scientists identified different carcinogenic and mutagenic effects of samples of textiles' industries wastewaters. These results illustrated that the dyes used during the industrial processes are the main cause of both carcinogenic and mutagenic effects. The nature of the discharges from textile industry dyeing is complex, containing various dissolved and suspended solid substances, organic chemicals, and heavy metals. The exact composition of these discharges defines the extent to which they cause hazardous environmental impacts. So, indigos dye's complicated properties effluents are considered as the main cause of high toxic impacts in addition to the other xenobiotics found in the discharges [16-20].

It has been estimated that textile and dyeing industries comprises more than 70% of the discharged dyes in the environment. This might be attributed to the fact that not all the dye amount used in the process is taken up by the textile or the dyed material. Only about 80% of the added dye is consumed while the rest is discharged in the effluent wastewater. This discharged unfixed dye is then become a threat to the environment exerting its hazardous impacts on the eco-system [18-22].

Indigo is widely used in the denim and other textile industries. It has been estimated that about 40,000,000 kilograms of indigo dyes are synthesized each year for industrial purposes. This, in turn, necessitates the research for a

suitable method for its removal from wastewater because the conventional primary treatment protocols are not enough. Otherwise, it would be discharged into the ecosystem causing various environmental and health impacts. For example, cornea and conjunctivas could be greatly harmed, may be completely damaged, if the dye comes in direct contact with these tissues. Moreover, indigo dye is very harmful for the human skin and respiratory tract, causing severe irritation to them. In fact, nourished denim industries in the Asia enhances the extensive application of indigo dyes in these regions. As a result, several serious environmental hazards were detected, especially water pollution and contamination because of the extensive use of indigo dyes in these regions. In addition to that, contamination of water with indigo dyestuff causes water to become turbid. This results in a great decrease of the photosynthetic processes which results in a dangerous threat to aquatic ecosystem [23-25].

Over the years, different methods of wastewater treatment had been developed. Among these methods, biotechnological applications were also reported and utilized such as fungal and bacterial depolarization methods. In general, treatment techniques are categorized in three main classes: biological, chemical and physical. Of course, each method of them has its pros and cons. Despite there are many reported methods for wastewater treatment, many conventional techniques could not be widely applied for the treatment of effluent discharges of the dye. This is mainly due to the high cost and sophistication of the technique. At the recent era, there is no single technique is globally approved and utilized that adequately for the treatment process. This is greatly attributed to the complex nature of the discharges, containing not only residual dye, but also different discharges such as heavy metals [26, 30].

The present study is a comparative investigation of the removal of indigo dye adopting the adsorption technique. Comparison was performed of adsorption by two different composites. For the determination of optimal circumstances towards the carrying out the adsorption technique using both composites, different parameters were investigated namely, firstly-added quantity of adsorbete, sorbent added quantity, interaction period, solution's pH value, and thermal effects had been investigated. Moreover, both dynamic and

thermos-dynamic boundaries had been likewise determined for proper selection of the reaction consitants and sorption components. Exploratory information had been investigated for fitting in Langmuier and Frenlich conditions for figuring out what model of them correlates perfectly with trial information regarding both composites.

## Experimental

### *Zero-charge mark*

The mark of zero-charge (pH pzc) was resolved through strong expansion technique. Solutions of  $1 \times 10^{-1}$  Molar potassium nitrate of volumes of exactly fifty milliliters had been prepared and their pH's values were controlled via addition of  $1 \times 10^{-1}$  Molar hydrochloric acid and  $1 \times 10^{-1}$  Molar sodium hydroxide to a range of 1.0 to 11.0. then,  $1 \times 10^{-1}$  gram of methylmethacrylate/sodium-Y-Zeolite composite or amidoximated acrylonitrile / Na-Y-Zeolite composite were gradually incorporated into the mixture and the mixtures should be then, shaken and left for exactly forty eight hours. At predetermined periods, the mixtures were agitated. At the end of the experiment, final pH of the mixtures had been determined. This readings were plotted against the differenced pH (between initial and final reading)  $\Delta$ pH . The intercept of that plot gave the pH<sub>pzc</sub> [31].

### *Establishment of solutions*

All watery mixtures were prepared using distilled water. A stock solution (0.5 ml/L) of indigo had been ready in refined H<sub>2</sub>O. Afterthat, predecided dilutions had been attained via diluting the mixtures with other solution. Hydrochloric acid ( $1 \times 10^{-2}$  to  $1 \times 10^{-1}$  N) or sodium hydroxide ( $1 \times 10^{-2}$  to  $1 \times 10^{-1}$  N) had been gradually added for proper adjustment of medium's pHvalue.

### *Sorption investigations*

Batched sorption investigations had been performed via agitation of mixtures of 0.25 gram of metnylmethacrylate/sodium-Y-Zeolite composite or amidoximated acrylonitrile / Na-

Y-Zeolite composite and twenty five milliliters of indigo dye's dilutions of predetermined concentrations controlling the value of solution's pH via magnetic stirrer device acting with capacity of two hundred rounds per minutes at 25°C. pH's values were controlled via addition of  $1 \times 10^{-1}$  Molar hydrochloric acid and  $1 \times 10^{-1}$  Molar sodium hydroxide to a range of 1.0 to 11.0. When the sorption experiment was ended, the mixtures were filtered and the filtrates were admitted to a spectrophotometry which was adjusted to 613 nm exact wavelength to determine the absorbance of them. This measurement gave the amount of indigo dye that is remaining in the clear filtrate. Percentile of removed dye removal had been obtained via applying equation 1:

$$R = \frac{100(C_i - C_t)}{C_i} \quad (1)$$

In this equation,  $C_i$  was the initial concentration of indigo dye in mg/L,  $C_t$  was final concentration after certain period in mg/L. regarding sorption isotherms, various adsorbate's concentrations which were mixed with certain quantities of sorbates should be shaken till the system attains equilibria. Equilibria sorption capacities,  $Q_e$  that is measured in milligram of adsorbate for each gram of sorbent had been computed via applying equation 2:

$$q_e = \frac{V(C_0 - C_t)}{W} \quad (2)$$

$C_t$  (mg L<sup>-1</sup>) is the measured quantity of indigo dye after equilibria states were attained, V is the volume of solution in liters while W was the weight of composite in grams.

The methodologies of kinetics were the same as that of equilibria experiments. Intermittent measurements of the quantity of indigo dye remaining was estimated via extracting a specific volume of the mixture at specific time intervals. The quantity of remaining indigo dye at specific time t,  $q_t$  (mg/g) has been estimated via the equation 3:

$$q_t = \frac{V(C_0 - C_t)}{m} \quad (3)$$

$C_0$  was the first dye quantity at time = zero in mg/L, and  $C_t$  (mg /L) the dye amount at specific time interval t, while V the volume of the extracted mixture in liters and m was the weight of the added composite in grams.

The equilibrium sorption data of the investigation were fitted adopting various sorption isotherm imitates and kinetics equations for the determining the analyses and designates of the sorption techniques. Various

hypothetical imitates might been utilized to deal with practically obtained information, that is to decide a model that properly expects kinetical and isothermal information. Validation of the designs had been performed via computing the coefficient of determination ( $r^2$ ) [32].

Recovery productivity (RE, %) was determined by the accompanying condition:

$$RE \% = \frac{\text{Amount of sorbed metal(mg) at run (n+1)}}{\text{Amount of sorbed metal(mg) at run (n)}} \times 100 \quad (4)$$

## Experimental Results

### Sorption trials

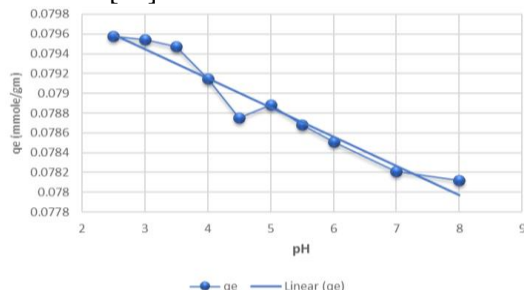
#### Influence of pH

The values of pH of fluid arrangements was considered as a significant boundary influencing color sorption. Impact of pH upon sorption of indigo color on the methylmethacrylate/sodium-Y-zeolite composite and amidoximated acrylonitrile/sodium-Y-Zeolite composite has been explored within the underlying pH scope of 1-8.

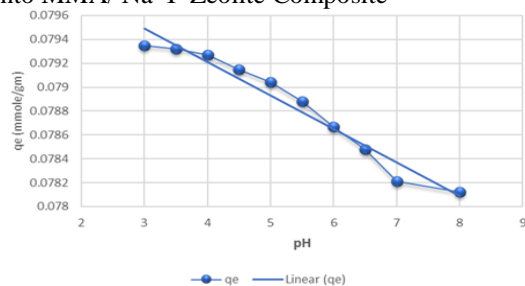
The removal of the tested dye applying various pHs has been investigated using starting concentrations of 0.5 ml/L of the colored substance at 25 °C and 5 g/L sorbent quantities. pH's values regarding the mixture had been considered as a crucial determining factors concerning the sorption experiment. Both composites were shown to be efficient sorbents for the dye's clearance. This had been performed by sorption of watery mixtures concerning methylmethacrylate/sodium-Y zeolite and amidoximated acrylonitrile / Na-Y-Zeolite composite at pH 4 and 3, respectively (Fig. 2, 3). It was shown that sorption capacities of investigated dye on both composites elevates considerably by lowering the pH. Maximal sorption after period of two hours had been performed at pH 4 for methylmethacrylate/sodium-Y-zeolite composite. On the other hand, it was maximal sorption for contact period two hours have been performed at pH 3 regarding amidoximated acrylonitrile / Na-Y-Zeolite composite.

Generally, the sites that bear negative charges is directly proportional to pH of sorption mixture. Also, inversely proportional to number of sites bearing positive charges. Due to electrostatic repulsion, negative charges on the sites at the

surfaces of composites do not aid the sorption of dye negatively charged ions. Moreover, reduced sorption of indigo in alkaline circumstances could be attributed to very high numbers of OH<sup>-</sup> that compete with the negatively charged ions for the sorption surfaces [33].



**Figure 2:** Effect of pH on the adsorption of the dye onto MMA/ Na-Y-Zeolite Composite



**Figure 3:** Effect of pH on the adsorption of the dye onto amidoximated Polyacrylonitrile/ Na-Y-Zeolite composite

### Kinetic studies

Sorption kinetics of indigo dye utilizing both investigated composites are illustrated in (Fig. 4, 5). It very well may be seen that adsorption cycle for the color is quick at introductory stage and diminishes continuously arriving at harmony at 95 and 75 min. for methymethacrylate/ Na – Y zeolite and amidoximated acrylonitrile / Na-Y-Zeolite composite, respectively. This might be because of the way that at starting stage there are enormous number of dynamic destinations accessible for expulsion of color, and evacuation is troublesome as time expands due to repugnance among solutes and strong.

Uptake kinetics of dye adsorption by these two sorbents had been studied using two models namely, so-called pseudo-first order rate equation (PFORE) [34] in addition to the pseudo-second order rate equation (PSORE) [35]. These imitations plus the linearity forms were illustrated in Table 1 for methymethacrylate/sodium-Y zeolite and amidoximated acrylonitrile /sodium-Y-Zeolite composite (see Supplementary Material

Section)  $k_1$  was the pseudo-first-order-rate constant measured in 1/min.,  $q_e$  and  $q_t$  both were measured in mg/g were the quantities of sorbed dyes at equilibria's and time  $t$ , respectively,  $k_2$  was the pseudo-second order rate constant measured in g/mg.min. validation of the data was studied via correlate coefficient of the computed linear form. The finest model for explaining the kinetic information could be chosen on a condition that  $R^2$  is about 1. The factors included in the various applied models for the investigated sorbents were illustrated in Table 2. Regularly, the finest correlating coefficients had been fitted applying PSORE isotherm; that was assured via plotting the practically obtained information concerning the linear arrangements for these models: (Figure 6, 7) for PFORE and PSORE, models with respect to both composites showed a finest fitting kinetic profiles by PSORE. Moreover, comparing equilibria's sorption capacity regarding computed values and the practically obtained data were compatible with the PSORE. Regarding methymethacrylate/sodium -Y- Zeolite composite, the equilibrium sorption capacities were found to be 0.07913, and PSORE modeling gave value of 0.07948, closer from experimental value than PFORE 1.9039. while regarding the amidoximated acrylonitrile /Na-Y- Zeolite composite, the equilibrium sorption capacities are found to be 0.08, and PSORE modeling gave value of 0.0799, closer from experimental value than PFORE 1.77815. In any case, the PSORE depicts motor information through a worldwide methodology, and doesn't consider the commitment of dispersion components in the control of the energy. Under these circumstances, the active boundaries ought to be considered as obvious rate coefficients.

### Equilibrium sorption isotherms

Different sorption isotherm uncover the particular connection between the grouping of adsorbate and the adsorption limit of an adsorbant at a specific consistent temperature. sorption isotherms give valuable data on how a sorption cycle continues, and decide the way in which adsorbate atoms interface with adsorbent. A few imitation models were utilized to portray exploratory information for adsorption isotherms. The Langmuir [36] and Freundlich [37] imitations have been utilized for explaining adsorption of the dye onto both



tested composites. These models and their linearized forms were summarized in Table 2,  $q_e$  was the sorbed quantity of the indigo dye when equilibrium conditions were attained measured in mg/g,  $q_{m,L}$  was the maximal adsorption capacities, measured in mg/g and  $K_i$  is the Langmuir binding constant that was

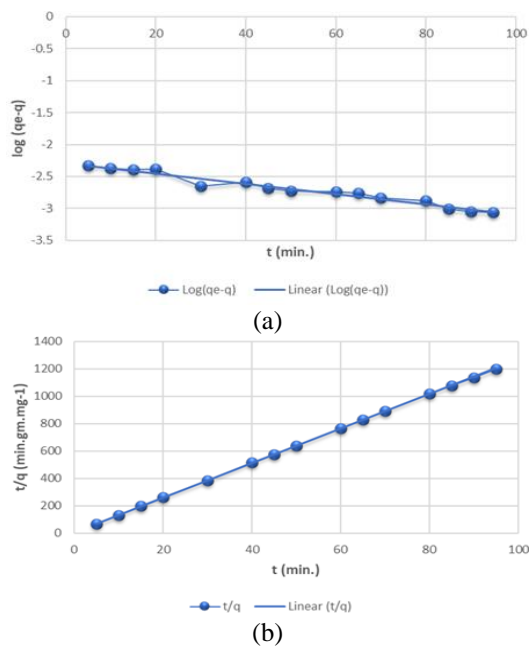
connected to the forces of adsorption measured in liter per gram,  $C_e$  stands for the equilibrium situation of the indigo dye in mixtures, measured in milligram per liter. Finally,  $n$  stands for the Freundlich constant that is attributed to adsorption capacities and intensities.

**Table 1:** Kinetic parameters for indigo dye adsorption

	$q_{e, exp}$ ( $mg\ g^{-1}$ )	PFORE			PSORE		
		$k_1$ ( $min^{-1}$ )	$q_{e, calc}$ ( $mg\ g^{-1}$ )	$R^2$	$k_2$ ( $g\ mg^{-1}\ min^{-1}$ )	$q_{e, calc}$ ( $mg\ g^{-1}$ )	$R^2$
MMA/Na-Y-zeolite composite	0.07913	-0.008	1.9039	0.9616	17.31301	0.079479	0.9949
Amidoximated acrylonitrile/ Na-Y-zeolite composite	0.08	-0.0122	1.778151	0.9035	28.5695	0.079917	0.9953

**Table 2:** Kinetics models and their linear forms

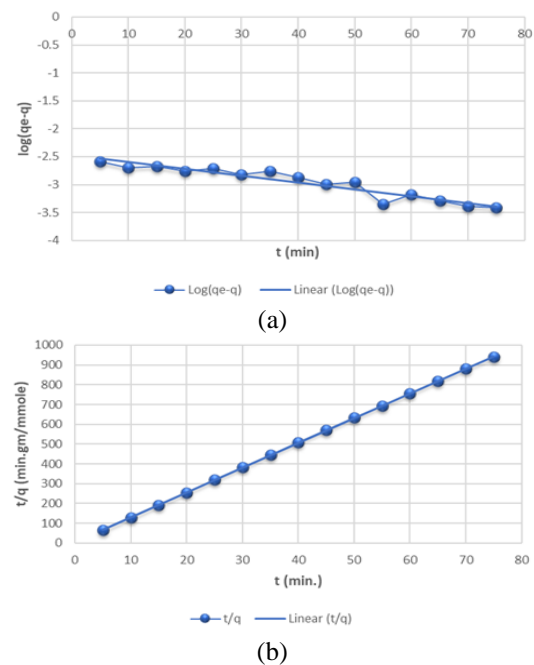
Kinetic model	Non-Linear form	Linear form	Plot	Author	References
Pseudo-First order	$q_t = q_e [1 - e^{-k_1 t}]$	$\log(q_e - q_t) = \log q_e - (\frac{k_1}{2.303})t$	$\log(q_e - q_t)$ vs. $t$	(Lagergren, 1898)	[34]
Pseudo-Second order	$q_t = \frac{k_2 t}{1 + k_2 q_e t}$	$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + (\frac{1}{q_e})t$	$(t/q_t)$ vs. $t$	(Ho and McKay, 1999)	[35]



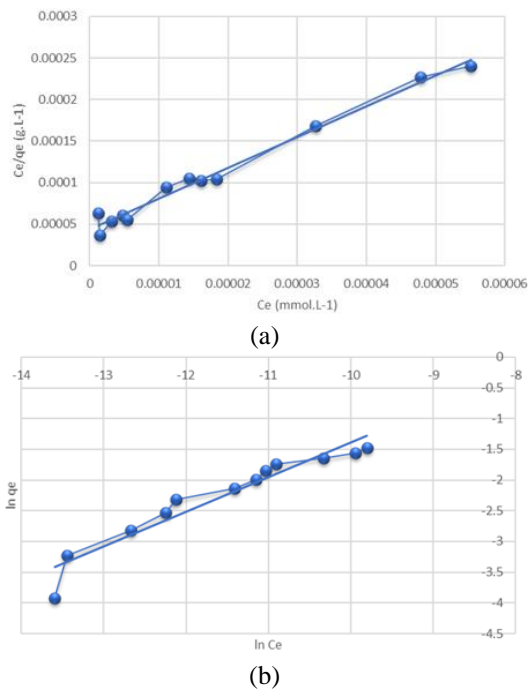
**Figure 4:** Indigo dye uptake kinetics using MMA/Na-Y-Z Composite

The Langmuir isotherms had been proved to be mostly proper models for the description of the isotherm regarding sorption of the indigo onto both composites (Fig. 6a,b, and 7a,b (see Supplementary Material Section)). By comparing  $R^2$  combutes, the Langmuir isotherm showed to be best fitted, with  $R^2$  being more than 0.90 that were higher than that of Freundlich isotherms. Moreover,  $Q_m$

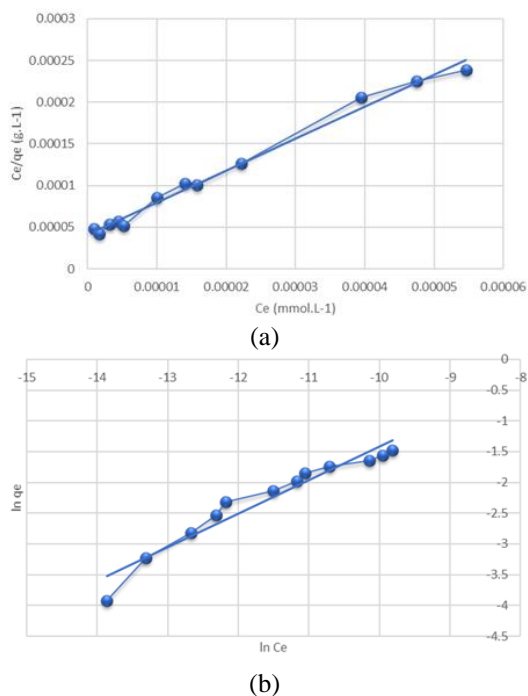
determined by applying Langmuir isotherm has been closer to the practically obtained value of  $Q_{max}$ .



**Figure 5:** Indigo dye uptake kinetics using amidoximated polyacrylonitrile/ Na-Y-Zeolite composite



**Figure 6:** Dye sorption isotherms onto MMA/Na-Y-Z Composite: (a) Langmuir isotherm (b) Freundlich Isotherm



**Figure 7:** Dye sorption isotherms onto amidoximated Polyacrylonitrile/ Na-Y-Zeolite composite: (a) Langmuir isotherm (b) Freundlich Isotherm

*Influence of temperature*

Researching the thermal impact regarding sorption in a perspective on commonsense utilization is significant. Sorption tests have

been completed for six different thermal degrees namely, 25, 30, 35, 40, 45 and 50 °C. The adsorption capacity slightly increases with the increase in the temperature from 25 to 50 °C. that attitude of results assured the endothermic nature of the sorption method. The sorption equilibril constant,  $K_c$  was calculated via applying equation 7 and combined with the van't Hoff equation 10 and regular thermodynamical equation 10 for assessing the thermodynamical constants of the adsorbents. These constants includes  $\Delta H^\circ$  which stands for the stander entalpy changes,  $\Delta G^\circ$  which stands for stander free Gibbs energy, in addition to  $\Delta S^\circ$  which stands forthe standard entropical change.

$$K_c = \frac{q_e}{C_e} \tag{7}$$

In this equation,  $q_e$  was the equilibril concentration of adsorbant and  $C_e$  stands for the concentration of adsorbat.

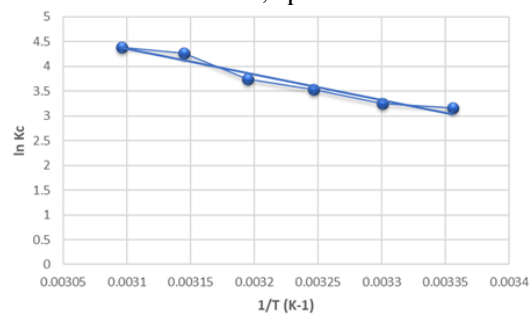
$$\Delta G^\circ = - RT \ln K_c \tag{8}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{9}$$

As a consequence, vant's Hoff equation became:

$$\ln K_c = \frac{-\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \tag{10}$$

The upsides of standardized entalpy changes ( $\Delta H_o$ ) and standard enthalpy change ( $\Delta S_o$ ) for the sorption not set in stone from the incline and block for the plotting that represents  $\ln K_c$  against  $1/T$  (Fig. 8, 9). Values of thermodynamical factors were illustrated within Table 5. Positive values of enthalpy assured that the process was endothermic. In addition, its negative values proved exothermic reaction. Moreover, positive values of  $\Delta G^\circ$  indicate that the sorption reaction is nonspontaneous. In the present study, as could be concluded for both composites under investigation, the adsorption process is endothermic, spontaneous one.



**Figure 8:** Effect of temperature on dye sorption using MMA/Na-Y-Z composite

**Table 3:** Parameters of the models for adsorption isotherms

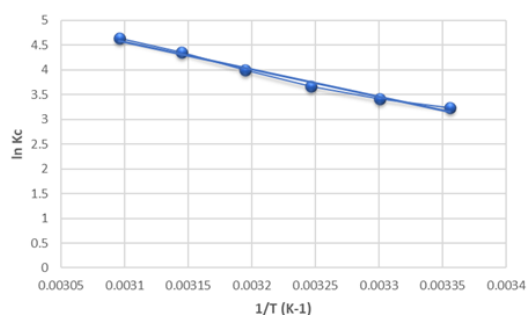
	Langmuir model				Freundlich model		
	$q_{m, \text{exp}}$ (mmol g <sup>-1</sup> )	$q_{m,L}$ (mmol g <sup>-1</sup> )	$K_L$ (L mmol <sup>-1</sup> )	$R^2$	n	$K_F$ (mmol g <sup>-1</sup> ) (L mmol <sup>-1</sup> ) <sup>1/n</sup>	$R^2$
MMA/Na-Y-zeolite composite	0.22898	0.363	92610	0.9846	1.776199	4.2372	0.9122
Amidoximated acrylonitrile/ Na-Y-zeolite composite	0.3808	0.47372	84407.46	0.99416	2.040233	1.84717	0.94688

**Table 4:** Sorption isotherms and their linear forms

Isotherm	Non-Linear form	Linear form	Plot	Author	References
Langmuir	$q_e = \frac{q_{m,L} K_L C_e}{1 + K_L C_e}$	$\frac{C_e}{q_e} = \frac{C_e}{q_{m,L}} + \frac{1}{K_L q_{m,L}}$	$\frac{C_e}{q_e}$ vs. $C_e$	(Langmuir, 1918)	[36]
Freundlich	$q_e = K_F C_e^{1/n}$	$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e$	$\ln q_e$ vs. $\ln C_e$	(Freundlich, 1906)	[37]

**Table 5:** Standard enthalpy, entropy and free energy changes for adsorption.

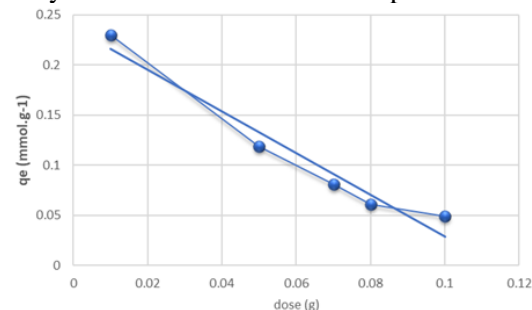
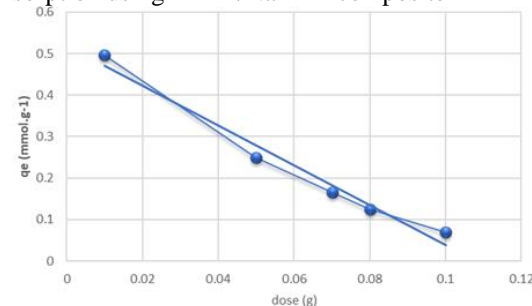
Composite	$\Delta H^\circ$ (kJ mol <sup>-1</sup> )	$\Delta S^\circ$ (J mol <sup>-1</sup> K <sup>-1</sup> )	$R^2$	$\Delta G^\circ$ (kJ mol <sup>-1</sup> )					
				298 K	303 K	308 K	313 K	318 K	323 K
MMA/Na-Y-zeolite composite	42.8296	0.16898	0.953	-7.53	-8.37	-9.22	-10.06	-10.91	-11.75
Amidoximated acrylonitrile/ Na-Y-zeolite composite	40.1884	0.18118	0.985	-7.80	-8.71	-9.61	-10.52	-11.43	-12.33


**Figure 9:** Effect of temperature on dye sorption using amidoximated polyacrylonitrile/ Na-Y-Zeolite Composite.

#### *Influence of adsorbent dosage*

Adsorption of the colored substance onto the surface of each of the investigated composites was investigated via varying the amount of adsorbent reach of  $1 \times 10^{-2}$  to  $1 \times 10^{-1}$  grams, while the dye concentration was fixed at  $4 \times 10^{-4}$  Molar at twenty five °C and pH 4 for methmethacrylate/sodium-Y-Zeolite composite, and pH 3 for amidoximated acrylonitrile/ sodium-Y- zeolite composite, respectively. The data in Figures 10, 11 proved dye sorption capacities as a behaviour of sorbent quantity. It was deduced that the sorption capacities reduced from 50 to 10 mg /g by elevating the quantity of composite from  $1 \times 10^{-2}$  to  $1 \times 10^{-1}$  gram. Based to the practically

obtained data, maximum removal efficiency was 80% for methymethacrylate/sodium-Y-Zeolite composite, and 86% for amidoximated acrylonitrile/ Na-Y- zeolite composite.


**Figure 10:** Effect of sorbent dose (SD) on dye sorption using MMA/Na-Y-Z composite

**Figure 11:** Effect of sorbent dose (SD) on dye sorption using amidoximated polyacrylonitrile/ Na-Y-Zeolite composite.



### *Regenerating the composites*

pH value is a crucial factor that was proved to control the de-sorption process of dyes regenerating the free composite to be used again for another treatment cycle. Regeneration process of composites usually is carried out in alkaline conditions. Desorption of methymethacrylate/sodium-Y-Zeolite composite and amidoximated acrylonitrile/sodium-Y- zeolite composite had been performed via allowing 20 mL of 0.1 N sodium hydroxide to be in contact with each composite for one hour. Application of equation 4 was then performed to obtain the regeneration efficiency. Washing of the regenerated composites using distilled waters is another important step to ensure that the regenerated composite is suitable for reusing them in other sorption experiments. Efficiency of regenerating composites had been calculated and it was 78% regarding methymethacrylate/sodium-Y- zeolite composite. While it is 84% for amidoximated acrylonitrile/ Na-Y- zeolite composite.

### *Estimation of point of zerocharge*

The point of zerocharge demonstrates important huge data regarding the kind of surface-dynamic focuses. pH of methymethacrylate/sodium-Y-Zeolite composite had been viewed as 7.5 while it had been 4 for amidoximated acrylonitrile/ Na-Y- zeolite composite. This demonstrated that beneath that pH, both composites became positively charged because of that practical gatherings became protonated at this pH. On the other hand, outer layers of the composites became negatively charged.

### **Conclusion**

This current investigation concentrate obviously at both MMA-Na-Y-Zeolite and amidoximated acrylonitrile/ Na-Y- zeolite composites as powerful adsorbents for the expulsion of indigo color from fluid discharges and dirtied water. Characterization of the tested composites was performed via effective discriminatory adsorption of the dye at approximated pH of 4 for methymethacrylate/sodium-Y-Zeolite and pH of 3 for amidoximated acrylonitrile/ sodium-Y-zeolite composite.

Adsorption equilibrium information was fitted finely with Langmuir equation for the adsorption of the dye by both composites. In addition, kinetics of the adsorption process was found to be fitted perfectly with the pseudo-second-order kinetic models with high correlation coefficients again for both investigates. Moreover, the thermodynamical data of the sorption showed spontaneous and endothermic reaction.

Regeneration investigates have been performed and the practically obtained data proved the composites could be used in sorption of the dye many times by the desorption process using 0.1 N NaOH solution.

The obtained findings illustrated that the both composites represent a promising adsorbent for indigo dye from aqueous solutions and wastewaters of textile industry..

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## الملخص العربي

### عنوان البحث: تحقيق مقارن لكفاءة إزالة صبغة الانديجو للبوليمر المتراكب ميثيل ميثاكريلات / صوديوم- واى- زيوليت والبوليمر المتراكب أميدوكزيم أكريلونيتريل / صوديوم- واى- زيوليت

محمود سالم إبراهيم<sup>١</sup> ، عادل زكي السنباطي<sup>٢</sup>، مصطفى أمين دياب<sup>٢</sup> ، تامر يس السعيد<sup>١\*</sup>  
<sup>١</sup> قسم العلوم البيئية – كلية العلوم – جامعة دمياط – دمياط – مصر  
<sup>٢</sup> قسم الكيمياء – كلية العلوم – جامعة دمياط – دمياط – مصر

الأهداف: تم تقييم امتزاز صبغة الانديجو على البوليمر المتراكب ميثيل ميثاكريلات / صوديوم- واى- زيوليت والبوليمر المتراكب أميدوكزيم أكريلونيتريل / صوديوم- واى- زيوليت في المحاليل المائية بدراسة بعض المؤثرات المختلفة وهي الفترة الزمنية، ومقياس الحموضة أو القلوية للمحلول كما تم فحص جرعة الممتزات والعامل الحراري. الطريقة: تم استخدام طريقتان لوصف الامتزاز وهما لانجمير وفريندليش. تم تقييم القوى المنشطة لامتزاز الصبغة النيلية على كلا المركبين. تمت دراسة الخواص الحركية لنموذج الامتزاز في محاولة لوصف حركية العملية. النتائج الرئيسية: فيما يتعلق بكلا البوليمرات المتراكبة، كان التقليد الحركي من الرتبة الثانية الزائفة مناسباً ومتوافقاً مع المعلومات التي تم الحصول عليها عملياً. أثبتت ديناميكيات الامتزاز أن العملية المتعلقة بكلا المركبين كانت تحدث تلقائياً وبصفة ماصة للحرارة. الخلاصة: أشارت المعلومات التي تم الحصول عليها عملياً إلى أن كلا من البوليمرات المتراكبة ميثيل ميثاكريلات / صوديوم- واى- زيوليت وأميدوكزيم أكريلونيتريل / صوديوم- واى- زيوليت يمكن أن يعمل بشكل جيد وغير مكلف وفعال للتخلص من صبغة الانديجو من مياه الصرف.