

Removal of Indigo Dyes from Aqueous Solution using Methylmethacrylate/Sodium-Y-Zeolite Composite

M. Salem¹, A.Z. El-Sonbati², M.A. Diab² and T.Y. Al-Said*¹

¹Environmental Sciences Department, faculty of Science, Damietta University, Damietta, Egypt

²Chemistry Department, faculty of Science, Damietta University, Damietta, Egypt.

Received: 23 April 2022 /Accepted: 15 May 2022

* Corresponding author's E-mail: tamer_eaa2@yahoo.com

Abstract

The sorption of indigo dye onto methylmethacrylate/sodium-Y-Zeolite composite had been evaluated in watery solutions studying different parameters namely, period of the experiment, pH, adsorbent dosage and thermal effect on the experiment. Different properties of methylmethacrylate/sodium-Y-Zeolite composite as forier-transformation IR spectroscopy, X-rays deffraction had been investigated. Langmier and Frenlich sorption imitations had been utilized for describing equilibrial isotherm. In addition, evaluation of the activating force of sorption has been carried out regarding the sorption of indigo dye on the surface of methylmethacrylate/sodium-Y-Zeolite composite. Kinetics information of the reaction were also studied.. These experimentally obtained information was nicely compatible and consistent with the pseudo-second-order kinetics for adsorption of indigo dye. The activating force (E_a), difference in liberated energies (ΔG), entalpy (ΔH) and entrophy (ΔS) of sorption methodology had been determined regarding the sorption of the indigo dye via composites.methylmethacrylate/sodium-Y-Zeolite composite. The thermodynamics of the sorption proved that the process had been both spontaneously and endothermically happening.

The results indicated that methylmethacrylate/sodium-Y-Zeolite composite would be successfully applied as efficient, reproducible, and inexpensive adsorbent regarding the sorption of indigo dye from industrial wastewaters.

Keywords: *Indigo dye, sodium-Y-Zeolite, adsorption, adsorption kinetic, tehrmodynamic properties*

Introduction

During last few decades, pollution became a major environmental issue. This is attributed to the rapidly developing anthropogenic activities including industry, un-planned urbanization, rapid population growth, sewage, agricultural

activities and rural wastewater. In this context, there is global concern about treatment of wastewater in order to protect natural water resources and protect humans and ecosystems [1-4]. Current techniques of wastewater treatment include a combination of physical, chemical and biological methods, and transactions to remove insoluble solids in addition to soluble contaminants from industrial

effluents. The reported techniques include adsorption, precipitation, oxidation, evaporation, ion exchange, membrane filtration, electrochemistry, bio-degradation and phyto-remediation [5-12].

Dyes comprises an extensively used material in many industrial processes such as textile, pharmaceutical products, cosmetics, foodstuff and paints. Dyes may originate from either natural or synthetic source. Both of which discharged with effluent water from factories and cause water pollution. This pollution adversely affects human, flora, soil, fauna and entire ecosystem. Thus, the United States-Environmental Protection Agencies put guidelines for environment guidelines regarding textile dyeing industry [13-16]. Dyes, especially those with aromatic and heterocyclic structures are stable chemical compounds and are used in textile industries. They comprise great environmental threat when present in textile wastewaters [17,18]. 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.

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 dyes are bluish colored organic compound which was historically known as naturally occurring dyes and was obtained by extraction process of the crushed leaf of certain vegetations belonging to *Indigofera* genus. In particular, *Indigofera tenctoria* is the main

natural source of indigo dye. Indigo plant grows in tropical regions and also grow in the hot and humid areas but it depends upon the fertility of the soil. It is a shrub one to two meters high. It has light green pinnate leaves and bearing pink or violet flowers [19-21].

Physically, indigo is a bluish crystals. It is sublimable between a temperature of 390 and 392°C, do not dissolve in water, and alcohols, but dissolves in dimethyl sulfoxide, CHCl_3 , nitro-benzene and H_2SO_4 . This dye has absorption properties towards certain wavelength within the visible region where its λ_{max} is 613 nm. This compound has deep blue color due to conjugation system in the molecule which are adjacent to each other. Also, the molecule has a planar structure [22, 23].

Indigo dye is applied primarily in the dyeing purposes regarding cottons fibers; especially for denim textiles [24].

It has been proven that presence of this dye and its products and effluents in wastewater are carcinogens and mutagens. Also, it causes aesthetic deterioration of the natural water resources. Moreover, it is considered as hazardous material to the flora and fauna in the natural eco-system. Thus, industrial effluents, such as wastewater from textile industries must be treated before discharging them into the environment. Industrial and commercial importance of textile dyeing processes is the driving force for the extensive studies of the treatment of wastewater before its discharge in the eco-system [25-27]. There is a wide variety of effluents treatment techniques [28]. Sorption techniques are regarded as a very efficient methodologies because of its advantages such as ease of application, low cost and simplicity of the design [29,30].

Here in, we aimed at investigating the sorption of indigo dyes on methymethacrylate/sodium-Y-Zeolite composites. Different parameters and conditions had been evaluated to determine the optimal conditions for the adsorption processes. For example, first used dye's dilution, adsorbant dosing, period of the process, solution's pH and temperature influence had been all evaluated. Both dynamic and thermodynamic boundaries had been likewise determined for deciding the process's rates constant. Exploratory information had been fit for Langmuer and Freundlich conditions for figuring out which one give rise to the finest relationship towards the practically obtained information.

Experimental

Chemical compounds and reagent

Synthetic substances utilized had been of insightful reagents grade and refined water has been utilized for readiness for every single fluid arrangement. Sodium bisulfite was Fluka scientific item. Na-Y-Zeolite, Potassium persulfate and Methyl methacrylate (MMA) were Loba Analytical item.

Characterization of methymethacrylate/sodium-Y-Zeolite composite

Confirmation of the sorbent's functionalization had been done in dry KBr disc via assignment of its infrared spectra regarding wavelengths from four thousand to four hundred cm^{-1} using a Forier transformation IR spectrophotometer (Jaso FT/IR-4100 spectrophotometer device). The structural characterization of the adsorbent has been elucidated by X-rays diffracting measurements on X-ray diffractometer with diffracting angles $2\theta = 5 - 80^\circ$. These analyses were performed applied copper $\text{K}\alpha 1$ radiation ($\lambda = 1.540598 \text{ \AA}$).

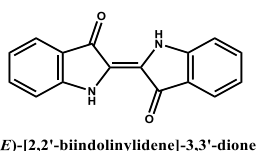


Figure 1: Indigo plant and structure of indigo dye.

Calculation of zero-charge mark

Mark of zero-charge which is abbreviated as pHpzc had been resolved through the strong expansion technique. Series of 1×10^{-1} molar potassium nitrate solutions had been prepared and pH values had been kept constant and controlled via addition of 1×10^{-1} molar hydrochloric acid and 1×10^{-1} molar sodium hydroxide to the range of 1.0 to 11.0. Then, 1×10^{-1} gram of methymethacrylate/sodium-Y-Zeolite composite was mixed and the resulted mixtures had been agitated for two days. From time to time, the agitated mixture had been shaken and checked. 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) ΔpH . The intercept of that plot gave the pHpzc [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_2O . Afterthat, predecided dilutions had been attained via diluting the mixtures with other solution. Hydrochloric acid (1×10^{-2} to 1×10^{-1} N) or sodium hydroxide (1×10^{-2} to 1×10^{-1} N) had been gradually added for proper adjustment of medium's pHvalue.

Sorption experiments

Batched sorption investigations had been performed via agitation of mixtures of 0.25 gram of metnylmethacrylate/sodium-Y-Zeolite composite o 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 1×10^{-1} Molar hydrochloric acid and 1×10^{-1} Molar sodium hydroxide to a range of 1.0 to 11.0. When the sorption experiment was ended, the mixtures were fileted and the filterates were admitted to a spectro-photo-metry 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 filerate. 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 sarbates 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^{-1}) 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 be 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:

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

Results and discussion

Sorbant characterization

FTIR spectrophotometry

FTIR spectrophotometry had been applied to elucidate structural form of the methymethacrylate/sodium-Y-Zeolite composite (**Figure 2a,b**). The FTIR spectral data of PMMA showed a powerful absorption peaks at 1146.34 to 1271.76 cm^{-1} . This band indicated the carbon bonded to oxygen functionalities stretching vibration. Also, peak at 1732.68 cm^{-1} confirmed that $-\text{C}=\text{O}$ moiety of acrylate is present in the molecule. Moreover, a peak at 1447.27 cm^{-1} indicated the binding vibration of carbon-hydrogen bonds in methyl functionalities. In addition, 2-peaks of 2997.56 - 2953.32 cm^{-1} could be attributed to the carbon-hydrogen bond stretching vibrations of methyl, methynyl functionalities. On other hand, the infrared spectral plot of methymethacrylate/sodium-Y-Zeolite

composite showed shifted $-\text{C}=\text{O}$ peaks about 100 cm^{-1} that attitude resembles that reported and described via Kabanove [33] and Diabe and coworkers [34] in polymerizing MMA in the presence of zinc chloride, AlCl_3 .

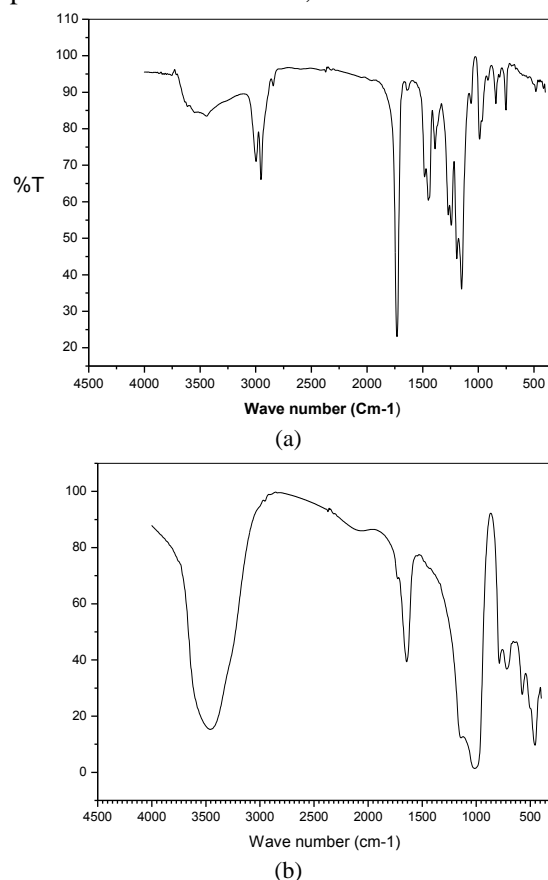


Figure 2: FT-IR analysis of (a) PMMA and (b) MMA/Na-Y-Zeolite composite.

X-ray of methymethacrylate/sodium-Y-Zeolite composite

The X-ray diffracting analyses of methymethacrylate/sodium-Y-Zeolite sorbent had been illustrated (**Figure 3a,b**) showing numerous diffraction tops which affirm the polycrystalline stage. The normal crystallite size (ξ) and disengagement thickness (δ) can be determined from the XRD as indicated by the accompanying condition [35, 36].

$$\xi = \frac{K\lambda}{\beta_{1/2} \cos \theta} \quad (5)$$

$$\delta = \frac{1}{\xi^2} \quad (6)$$

Where λ is 1.541874 \AA , and K stands for constants calculated to be 0.95 regarding organomaterials. In addition, $\beta_{1/2}$ stands for fill wethd when 1/2 max of reference diffracting

band was determined in radius, theta stands for the diffracting angles. For methymethacrylate/sodium-Y-Zeolite composite, calculated values for ζ were found to be 470.75, 485.11, 478.92 and 492.515.

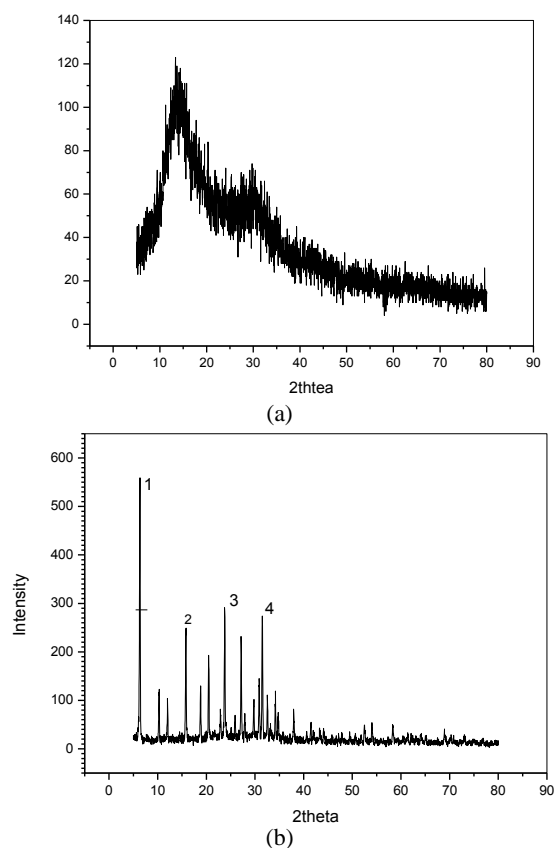


Figure 3: XRD analysis of (a) PMMA and (b) MMA / Na-Y-Zeolite composite.

Sorption experiments of methymethacrylate /sodium-Y-Zeolite composite

pH influence on the experiment

The pH value for fluids were proved to be significantly influencing color sorption. Consequently, impact of pH on sorption of indigo color on methymethacrylate/sodium-Y-Zeolite composite had been explored in underlying pH scope of 1-8.

The sorption of indigo dye via methymethacrylate/sodium-Y-Zeolite composite at varying pH value had been investigated at first dilution of 1/2 ml/L of indigo dye at ambient temperature and 5 gram/liter sorbent quantities. pH's values regarding the mixture had been considered as a crucial determining factors concerning the sorption experiment. Methymethacrylate/sodium-Y-Zeolite composite had been shown to be efficient sorbent for the dye's clearance.

This had been performed by sorption of watery mixtures concerning methymethacrylate/sodium-Y zeolite at pH 4 (Figure 4). It was shown that sorption capacities of investigated dye on tested composite elevates considerably by lowering the pH. Maximal sorption after period of two hours had been performed at pH 4 for methymethacrylate/sodium-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⁻ that compete with the negatively charged ions for the sorption surfaces [37].

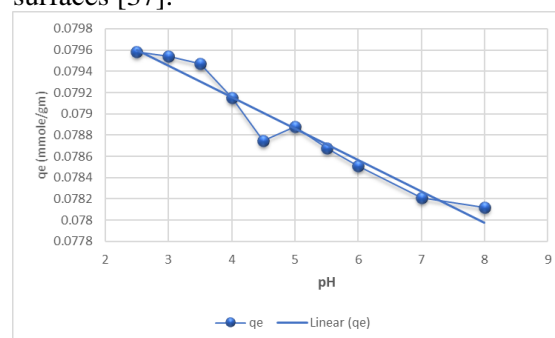


Figure 4: Effect of pH on the adsorption of the dye onto MMA/ Na-Y-Zeolite Composite.

Kinetic studies

The uptake kinetics of indigo dye utilizing the methymethacrylate/sodium-Y-Zeolite sorbent had been illustrated in (Figure 5). It had been very well considered that sorption cycle regarding color is quick firstly, and diminishes continuously arriving at harmony at 95 min. 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.

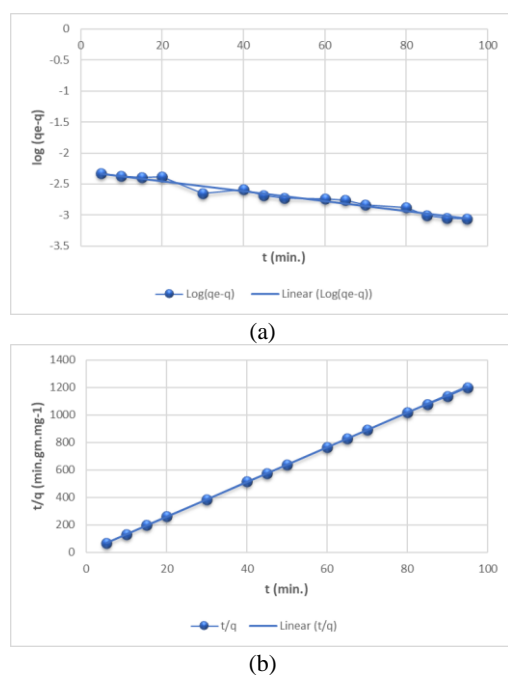


Figure 5: Indigo dye uptake kinetics using MMA/Na-Y-Z Composite.

Uptake kinetics of dye adsorption by these two sorbents had been studied using two models namely, so-called pseudo-first order rate equation (PFORE) [38] in addition to the pseudo-second order rate equation (PSORE) [39]. These imitations plus the linearity forms were illustrated in **Table 1** for methacrylate/sodium-Y zeolite (see supplementary material sections) k_1 was the pseudo-first-order-rate constant measured in $1/\text{min.}$, q_e and q_t both were measured in mg/g were the quantities of sorbed dyes at equilibrium'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 correlation 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 two. 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**) for PFORE and PSORE, models with respect to both composites showed a finest fitting kinetic profiles by PSORE. Moreover, comparing

equilibrium's sorption capacity regarding computed values and the practically obtained data were compatible with the PSORE. Regarding methacrylate/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. 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

The sorption isotherms uncover a particular connection regarding the grouping of adsorbate and adsorption limit of sorbent at a consistent temperature. Sorption isotherms provide valuable data about the sorption mechanism, and decide the way in which adsorbate atoms interface with adsorbent. A few isotherm imitations were utilized so as to portray exploratory information about the isotherms. The Langmuir [40] and Freundlich [41] methods had been utilized for explaining dye's sorption onto methacrylate/sodium-Y-Zeolite composite. Summarization of both and their linearized forms were illustrated in **Table 2** (Supplementary Material Section), the q_e stands for sorbed dye amount measure in mg g^{-1} , $q_{m,L}$ is the maximal sorption capacities measured in mg g^{-1} and K is the Langmuir bonding constant that had been referred to forces to adsorption measured in L g^{-1} , C_e stands for dye's equilibrium concentration in solution measured in (mgL^{-1}) . $K_f (\text{mg g}^{-1}) (\text{L mg}^{-1})^{1/n}$ and n stand for Freundlich constant referred to adsorption capacities and intensities.

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 (**Figure 6** (see Supplementary Material Section)). By comparing R^2 computes, 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} .

Table 1: Kinetic parameters for indigo dye adsorption by MMA/Na-Y-Z Composite

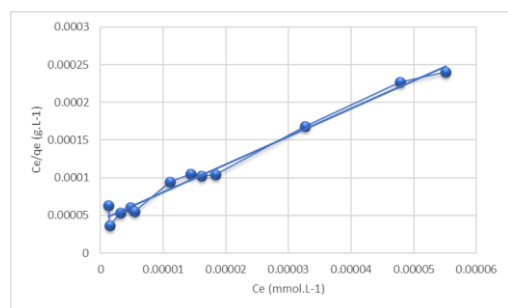
$q_{e, exp}$ ($mg\ g^{-1}$)	PFORE			PSORE		
	k_1 (min^{-1})	$q_{e, calc}$ ($mg\ g^{-1}$)	R^2	k_2 ($g\ mg^{-1}\ min^{-1}$)	$q_{e, calc}$ ($mg\ g^{-1}$)	R^2
0.07913	-0.008	1.9039	0.9616	17.31301	0.079479	0.9949

Table 2: Kinetics models and their linear forms

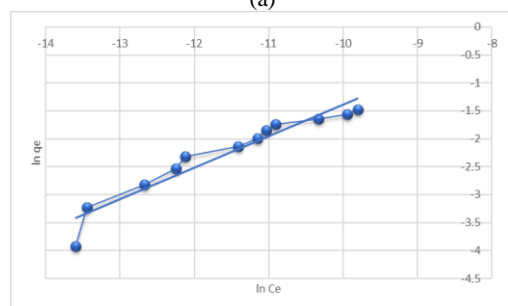
Kinetic model	Non-Linear form	Linear form	Plot	Author	References
Pseudo-First order	$q_t = q_e [1 - e^{-k_1 t}]$	$\log(q_e - q_t) = \log q_e - (\frac{k_1}{2.303}) t$	$\log(q_e - q_t)$ vs. t	(Lagergren, 1898)	[38]
Pseudo-Second order	$q_t = \frac{k_2 t}{1 + k_2 q_e t}$	$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + (\frac{1}{q_e}) t$	(t/q_t) vs. t	(Ho and McKay, 1999)	[39]

Table 3: Parameters of the models for adsorption isotherms

$q_{m, exp}$ ($mmol\ g^{-1}$)	Langmuir model			n	Freundlich model	
	$q_{m, L}$ ($mmol\ g^{-1}$)	K_L ($L\ mmol^{-1}$)	R^2		K_F ($mmol\ g^{-1}$) ($L\ mmol^{-1}$) ^{1/n}	R^2
0.22898	0.363	92610	0.9846	1.776199	4.2372	0.9122



(a)



(b)

Figure 6: Dye sorption isotherms onto MMA/Na-Y-Z 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 equilibrium 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 ΔH_0 which stands for the standard enthalpy changes, ΔG_0 which stands for standard free Gibbs energy, in addition to ΔS_0 which stands for the standard entropical change.

$$K_c = \frac{q_e}{C_e} \quad (7)$$

In this equation, q_e was the equilibrium concentration of adsorbant and C_e stands for the concentration of adsorbant.

$$\Delta G^0 = -RT \ln K_c \quad (8)$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad (9)$$

As a consequence, van't's Hoff equation became:

$$\ln K_c = \frac{-\Delta H^0}{RT} + \frac{\Delta S^0}{R} \quad (10)$$

The upsides of standardized enthalpy changes (ΔH_0) and standard enthalpy change (ΔS_0) for the sorption not set in stone from the incline and block for the plotting that represents $\ln K_c$ against $1/T$ (Figure 7). 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 ΔG^0 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.

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)	[40]
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)	[41]

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

ΔH° (kJ mol ⁻¹)	ΔS° (J mol ⁻¹ K ⁻¹)	R ²	ΔG° (kJ mol ⁻¹)					
			298 K	303 K	308 K	313 K	318 K	323 K
42.8296	0.16898	0.953	-7.53	-8.37	-9.22	-10.06	-10.91	-11.75

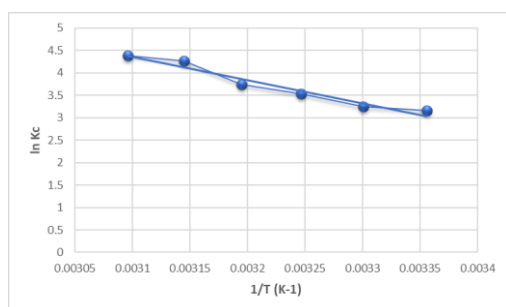


Figure 7: Effect of temperature on dye sorption using MMA/Na-Y-Z composite

Sorbent dosage's influence

Adsorption of the colored substance onto the surface of each of the investigated composites was investigated via varying the amount of adsorbent reach of 1×10^{-2} to 1×10^{-1} grams, while the dye concentration was fixed at 4×10^{-4} Molar at twenty five °C and pH 4 for methmethacrylate/sodium-Y-Zeolite composite. The data in **Figure 8** 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 1×10^{-2} to 1×10^{-1} gram. Based to the practically obtained data, maximum removal efficiency was 80% for methmethacrylate/sodium-Y-Zeolite composite.

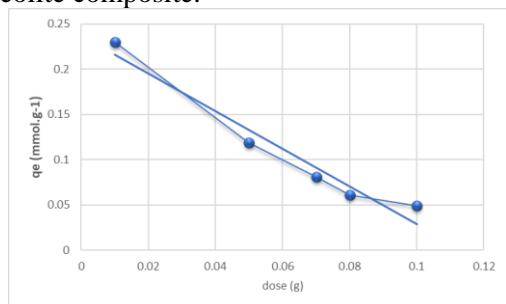


Figure 8: Effect of sorbent dose (SD) on dye sorption using MMA/Na-Y-Z composite

Regenerating the composite

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 methmethacrylate/sodium-Y-Zeolite composite had been performed via allowing 20 mL of 0.1 N sodium hydroxide to be in contact with 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 composite had been calculated and it was 78% regarding methmethacrylate/sodium-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 methmethacrylate/sodium-Y-Zeolite composite had been viewed as 7.5. This demonstrated that beneath that pH, composite 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 methmethacrylate/sodium-Y-Zeolite composite as powerful adsorbent for the

expulsion of indigo color from fluid discharges and dirtied water. Characterization of the tested composite was performed via effective discriminatory adsorption of the dye at approximated pH of 4 for methymethacrylate/sodium-Y-Zeolite.

Adsorption equilibrium information was fitted finely with Langmuir equation for the adsorption of the dye. 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 the investigate. Moreover, the thermodynamical data of the sorption showed spontaneous and endothermic reaction.

Regeneration investigates have been performed and the practically obtained data proved the composite 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 methymethacrylate/sodium-Y-Zeolite composite represent a promising adsorbent for indigo dye from aqueous solutions and wastewaters of textile industry.

References

- Goel PK. Water pollution: causes, effects and control. New Age International; 2006.
- Hanchang SH. Industrial wastewater-types, amounts and effects. Point sources of pollution: Local effects and their control. 2009 Aug 17;2:191.
- Abdel-Shafy HI, Aly RO. Water issue in Egypt: Resources, pollution and protection endeavors. Central European Journal of Occupational and Environmental Medicine. 2002;8(1):3-21.
- Crini G, Lichtfouse E. Advantages and disadvantages of techniques used for wastewater treatment. Environmental Chemistry Letters. 2019 Mar;17(1):145-55.
- Benefield LD, Judkins JF, Weand BL. Process chemistry for water and wastewater treatment.
- Samer M. Biological and chemical wastewater treatment processes. Wastewater treatment engineering. 2015 Oct 14;150.
- Chen G. Electrochemical technologies in wastewater treatment. Separation and purification Technology. 2004 Jul 15;38(1):11-41.
- Forgacs E, Cserhati T, Oros G. Removal of synthetic dyes from wastewaters: a review. Environment international. 2004 Sep 1;30(7):953-71.
- Anjaneyulu Y, Chary NS, Raj DS. Decolourization of industrial effluents—available methods and emerging technologies—a review. Reviews in Environmental Science and Bio/Technology. 2005 Nov;4(4):245-73.
- Hai FI, Yamamoto K, Fukushi K. Hybrid treatment systems for dye wastewater. Critical Reviews in Environmental Science and Technology. 2007 May 16;37(4):315-77.
- Barakat MA. New trends in removing heavy metals from industrial wastewater. Arabian journal of chemistry. 2011 Oct 1;4(4):361-77.
- Rathoure AK, editor. Toxicity and waste management using bioremediation. IGI Global; 2015 Dec 2.
- Mani S, Chowdhary P, Bharagava RN. Textile wastewater dyes: toxicity profile and treatment approaches. In: Emerging and eco-friendly approaches for waste management 2019 (pp. 219-244). Springer, Singapore.
- Gottlieb A, Shaw C, Smith A, Wheatley A, Forsythe S. The toxicity of textile reactive azo dyes after hydrolysis and decolourisation. Journal of Biotechnology. 2003 Feb 27;101(1):49-56.
- Padhi BS. Pollution due to synthetic dyes toxicity & carcinogenicity studies and remediation. International Journal of Environmental Sciences. 2012;3(3):940-55.
- <https://www.epa.gov/eg/textile-mills-effluent-guidelines>
- Ding S, Li Z, Wang R. Overview of dyeing wastewater treatment technology. Water Resour. Prot. 2010;26:73-8.
- Mani S, Bharagava RN. Isolation, screening and biochemical characterization of bacteria capable of crystal violet dye decolorization. Int. J. Appl. Adv. Sci. Res. 2017;2:70-5.
- Fox MR, Pierce JH. Indigo--past and present. Textile chemist and colorist. 1990 Apr 1;22(4):13-5.
- Stasiak N, Kukula-Koch W, Glowniak K. Modern industrial and pharmacological applications of indigo dye and its derivatives-a review. Acta Pol Pharm. 2014 Mar 1;71(71):215-21.
- Głowacki ED, Voss G, Leonat L, Irimia-Vladu M, Bauer S, Sariciftci NS. Indigo and Tyrian purple—from ancient natural dyes to modern organic semiconductors. Israel journal of chemistry. 2012 Jun;52(6):540-51.
- Stasiak N, Kukula-Koch W, Glowniak K. Modern industrial and pharmacological applications of indigo dye and its derivatives-a review. Acta Pol Pharm. 2014 Mar 1;71(71):215-21.
- Franchi D, Calamante M, Coppola C, Mordini A, Reginato G, Sinicropi A, Zani L. Synthesis and characterization of new organic dyes containing the indigo core. Molecules. 2020 Jan;25(15):3377.
- Stasiak N, Kukula-Koch W, Glowniak K. Modern industrial and pharmacological applications of

- indigo dye and its derivatives-a review. *Acta Pol Pharm.* 2014 Mar 1;71(71):215-21.
- Chia MA, Musa RI. Effect of indigo dye effluent on the growth, biomass production and phenotypic plasticity of *Scenedesmus quadricauda* (Chlorococcales). *Anais da Academia Brasileira de Ciências.* 2014;86:419-28.
- Wambuguh D, Chianelli RR. Indigo dye waste recovery from blue denim textile effluent: a by-product synergy approach. *New journal of chemistry.* 2008;32(12):2189-94.
- Amutha K. Environmental impacts of denim. *InSustainability in denim 2017 Jan 1* (pp. 27-48). Woodhead Publishing.
- Tchobanoglus G, Burton F, Stensel HD. Wastewater engineering: Treatment and reuse. American Water Works Association. *Journal.* 2003 May 1;95(5):201.
- De Gisi S, Lofrano G, Grassi M, Notarnicola M. Characteristics and adsorption capacities of low-cost sorbents for wastewater treatment: A review. *Sustainable Materials and Technologies.* 2016 Sep 1;9:10-40.
- Kumar PS, Joshiba GJ, Femina CC, Varshini P, Priyadharshini S, Karthick MA, Jothirani R. A critical review on recent developments in the low-cost adsorption of dyes from wastewater. *Desalin. Water Treat.* 2019 Dec 1;172:395-416.
- M. Mullet, P. Fievet, A. Szymczyk, A. Foissy, J. C. Reggiani, J. Pagetti, A simple and accurate determination of the point of zero charge of ceramic membranes, *Desalin.* (1999),121, 41-48.
- V. A. Kabanov, IUPAC International symposium on macromolecular chemistry, Budapest, p 435-462 (1969).
- V. A. Kabanov, IUPAC International symposium on macromolecular chemistry, Budapest, p 435-462 (1969).
- M. A. Diab, A. Z. El-Sonbati, A. S. Hilali, H. M. Killa, M. M. Ghoneim, *Eur. Polym. J.*, 26 (1990) 1.
- M. M. Ghoneim, A. Z. El-Sonbati, A. A. El-Bindary, M. A. Diab, L. S. Serag, Polymer complexes. LX. Supramolecular coordination and structures of N (4-(acrylamido)-2-hydroxybenzoic acid) polymer complexes, *Polymer complexes. LX. Supramolecular coordination and structures of N (4-(acrylamido)-2-hydroxybenzoic acid) polymer complexes, Spectrochim. Acta. A.* 140 (2015) 111.
- A. A. El-Bindary, A. Z. El-Sonbati, M. A. Diab, S. M. Morgan, Geometrical structure, potentiometric and thermodynamic studies of rhodanine azo dye and its metal complexes, *J. Mol. Liq.*, 201 (2015) 36.
- D. A. Fungaro, S. I. Borrelly, T. E.M. Carvalho, Surfactant modified zeolite from cyclone ash as adsorbent for removal of reactive orange 16 from aqueous solution, *American Journal of Environmental Protection*, 1 (2013) 1.
- S. Lagergren, About the theory of so-called adsorption of soluble substances, *KunligaSwenska Vet.*, 24 (1898) 1.
- Y.S. Ho, G. McKay, Pseudo-second order model for sorption processes, *Process Biochem.*, 34 (1999) 451.
- I. Langmuir, The adsorption of gases on plane surfaces of glass, mica and platinum, *J. Amer. Chem. Soc.*, 40 (1918) 1361.
- H. M. F. Freundlich, Uber die adsorption in lasungen, *Z. Phys. Chem.*, 57 (1906) 385.

الملخص العربي

عنوان البحث: إزالة صبغة الانديجو من المحلول المائي باستخدام البوليمر المتراكب ميثيل ميثاكريلات / صوديوم- واي- زيوليت

محمود سالم إبراهيم¹ ، عادل زكي السنباطي² ، مصطفى أمين دياب² ، تامر يس السعيد^{1*}
¹ قسم العلوم البيئية - كلية العلوم - جامعة دمياط - دمياط - مصر
² قسم الكيمياء - كلية العلوم - جامعة دمياط - دمياط - مصر

تم تقييم امتزاز صبغة الانديجو على البوليمر المتراكب ميثيل ميثاكريلات / صوديوم- واي- زيوليت في المحاليل المائية بدراسة متغيرات مختلفة وهي فترة التجربة ودرجة الحموضة وجرعة الممتزات والتأثير الحراري على التجربة. تمت دراسة الخصائص المختلفة البوليمر المتراكب ميثيل ميثاكريلات / صوديوم- واي- زيوليت كالتحويل الطيفي للأشعة تحت الحمراء ، وانحراف الأشعة السينية. تم استخدام طريقتان لوصف متساويات الحرارة لدراسة الامتزاز وهما لانجمير وفريندليش. بالإضافة إلى ذلك ، تم إجراء تقييم القوة التنشيطية للامتزاز فيما يتعلق بامتصاص صبغة الانديجو على سطح البوليمر المتراكب ميثيل ميثاكريلات / صوديوم- واي- زيوليت. كما تمت دراسة المعلومات الحركية للتفاعل. كانت هذه المعلومات التي تم الحصول عليها تجريبياً متوافقة بشكل

جيد ومتسقة مع حركية المرتبة الثانية الزائفة لامتزاز صبغة الانديجو. تم تحديد قوة التنشيط ، والاختلاف في الطاقات المحررة لعملية الامتزاز. أثبتت الديناميكا الحرارية للامتزاز أن العملية كانت تحدث تلقائيًا وبصفة ماصة للحرارة. أشارت النتائج إلى أنه يمكن تطبيق البوليمر المترابك ميثيل ميثاكريلات / سوديوم- وى- زيوليت بنجاح على أنه مادة ممتزة فعالة وغير مكلفة فيما يتعلق بامتزاز صبغة الانديجو من مياه الصرف الصناعي.