



Removal of Indigo dye from Aqueous Solution using Amidoximated Acrylonitrile/Na-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: 21 April 2022 /Accepted: 13 May 2022

* Corresponding author's E-mail: tamer_eeaa2@yahoo.com

Abstract

Adsorption of indigo dye onto amidoximated acrylonitrile /Na-Y-Zeolite composite had been evaluated in aqueous-solutions studying different parameters namely, period of the experiment, pH, adsorbent dosage and thermal effect on the experiment. Different properties of amidoximated acrylonitrile/sodium-Y-Zeolite composite as forier-transformation IR spectroscopy, X-rays deffraction had been investigated. Langmier and Frendlich 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 amidoximated acrylonitrile/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 (Ea), difference in liberated energies (ΔG), entalpy (ΔH) and enthropy (ΔS) of sorption methodology had been determined regarding the sorption of the sorption proved that the process had been both spontaneously and endothermically happening.

The results indicated that amidoximated acrylonitrile/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, amidoximated acrylonitrile/sodium-Y-Zeolite composite, adsorption, sorption kinetics, thermodynamic parameters

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 precipitation. oxidation. adsorption, 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-Enviromental 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 Indigofiera genus. In particular, Indigofiera 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, CHCl₃, nitro-benzene and H₂SO₄. 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 dying 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 dying 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 indigo amidoximated of dves on polyacrylonitrile/Na-Y-Zeolite composite. Different parameters and conditions hade 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 thermaldynamic boundaries had been likewise determined for deciding the process's rates constant. Exploratory information had been fit for Langmier and Frendlich conditions for figuring out which one give rise to the finest relationship towards the practically obtained information.

Experimental

Chemicals and reagents

Synthetic substances utilized had been of insightful reagents grade and distilled water has been utilized for readiness for every single fluid arrangement. Sodium bisulfite was Fluka scientific item. Acrylonitrile (AN), sodium-Y Zeolite and Sodium bisulfite were Fluka analytical products.

Indigo dye was kindly supplied by DNM Textile for Spinning, Weaving and Dyeing. The preparation of stock solution was done with concentration of 500 mg/L. Other different dilutions of 25, 50, 100, 125 and 250 mg/L were made from the stock solution. The exact chemical structure of indigo dye has been illustrated in figure 1.

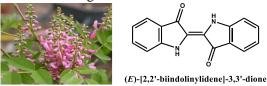


Figure 1: Indigo plant and structure of indigo dye.

Characterization of 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 diffractimeter with diffracting angles $2\theta = 5$ -80°. These analyses were performed applied copper K α 1 radiation ($\lambda = 1.540598$ Å).

Calculation of point of zero charge

The point of zero-charge which is abbreviated as pHpzcs 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 1x10⁻¹ molar hydrochloric acid and 1x10⁻¹ molar sodium hydroxide to the range of 1.0 to 11.0. Then, 1×10^{-1} gram of amidoximated polyacrylonitrile/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 shaked 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].

Preparation of solutions

All aqueous mixtures were prepared using distilled water. A stock solution (0.5 ml/L) of indigo had been ready in refined H₂O. Afterthat, predecided dilutions had been attained via diluting the mixtures with other solution. Hydrochloric acid $(1x10^{-2} \text{ to } 1x10^{-1} \text{ N})$ or sodium hydroxide $(1x10^{-2} \text{ to } 1x10^{-1} \text{ N})$ 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 amidoximated polyacrylonitrile/ sodium-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 1x10⁻¹ 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 filetred and the filterates were admitted to a specrto-photo-metery 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:

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

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 shaked till the system attains equilibriua. Equilibria sorption capacities, Q_e that is measured in milligram of adsorbate for each gram of sorbent had been computed via applying equation 2:

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

 $C_t (mg L^{-1})$ 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 tine intervals. The quantity of remaining indigo dye at specific time t, q_t (mg/g) has been estimated via the equation 3:

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

 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 equetions 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 porperly 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:

$$RE\% = \frac{Amount of sorbed metal(mg)at run(n+1)}{Amount of sorbed metal(mg)at run(n)} X100$$
(4)

Results and discussion

Sorbent characterization

FT-IR spectrometry

The FTIR spectrum of the amidoximated PAN/sodium-Y-Zeolite composite is shown in Figure 2. The absorptions' peaks of -CN functionalities had been ultimately vanished

after the amidoximation reaction. This proved a complete transformation of all -CN groups into newly formed amidoxime functionalities. Moreover, broad peak at about 3464 cm⁻¹ appeared because of the -OH moieties in amidoxime moiety. Additionally, two bands of absorption appeared at 1654 cm⁻¹ & 1014 cm⁻¹ corresponding for the -C=N & -N-O of amidoximes, respectively. The absorbtion peaks of -CN moieties were vanished after the amidoximation reaction. This ensured a complete conversion of all -CN groups into newly formed amidoxime ones.

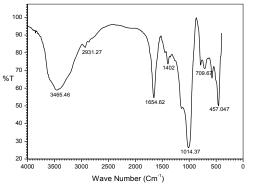


Figure 2: FT-IR analysis of) amidoximated polyacrylonitrile/ Na-Y-Zeolite composite

X-ray of amidoximated acrylonitrile /sodium-Y- Zeolite composite

The X-ray diffracting (XRD) patternes of amidoximated acrylonitrile/Na-Y- Zeolite composite as illustrated in Figure 3, showed variuos diffraction beaks which ensured its polycrystalline form. The average crystal size (ξ) and dislocation density (δ) could be computed using the x-ray-diffraction applyiong the following eq. 5 and 6 [35, 36].

$$\xi = \frac{K\lambda}{\beta_{1/2}\cos\theta}$$
(5)
$$\delta = \frac{1}{\xi^2}$$
(6)

Where λ is 1.541874 Å, and K stands for constants calculated to be 0.95 regarding organicmaterials. In addition, $\beta_{1/2}$ stands for fill wedth when 1/2 max of reference diffracting band was determined in radius, theta stands for the diffracting angles. For amidoximated acrylonitrile/sodium-Y-Zeolite composite, calculated values for ξ were found to be 567.27, 453.12, 490.70 and 513.53.

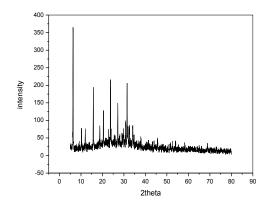


Figure 3: XRD analysis of amidoximated polyacrylonitrile/ Na-Y-Zeolite composite.

Sorption experiments of amidoximated acrylonitrile /Na-Y- Zeolite composite

Effect of pH

The pH of the solution is a critical property that is capable of controlling the sorption of dyes. This influence was studied regarding the sorption of the tested dye on the composite had been evaluated with applied pH scope of 1-8.

The sorption of indigo dye via amidoximated acrylonitrile/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. Amidoximated acrylonitrile /sodium-Y-Zeolite composite had been shown to be efficient sorbent for the dye's clearance. This had been performed by sorption of aqueous mixtures concerning amidoximated acrylonitrile/ sodium-Y zeolite at pH 3 (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 3 for amidoximated acrylonitrile/sodium-Yzeolite 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].

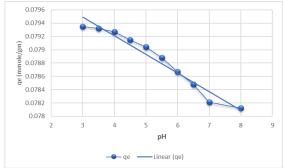


Figure 4: Effect of pH on the adsorption of the dye onto amidoximated Polyacrylonitrile/ Na-Y-Zeolite composite

Kinetic studies

The kinetics of the adsorption of indigo dye utilizing the tested sorbent is illustrated in Figure 5. A closer look at these obtained data concluded that the sorption of the tested dye was initially rapid and then, it gradually decreases until it reached an equilibrium state at **75** minutes. That was because of availability of many free active sites in the composite for the adsorption process during early stages of the process. Then, the repulsion forces between the sorbent and adsorbate dominates and causes the adsorption process harder to occur.

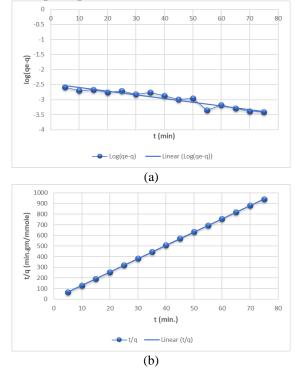


Figure 5: Indigo dye uptake kinetics using amidoximated polyacrylonitrile/ Na-Y-Zeolite composite

Uptake kintics of dye adsorbtion by the tested sorbent had been studied using two models namely, so-called pseodo-first order rate equation (PFORE) [38] in addition to the psedosecond order rate equation (PSORE) [39]. These imitations plus the linearity forms were illustrated in Table 1 for amidoximated acrylonitrile/sodium-Y zeolite (see supplementary material sections) k₁ was the pseudo-first- order-rate constant measured in $1/\min_{e}$, q_e and q_t both were measured in mg/g were the quantities of sorbed dyes at equilibria's and time t, respectively, k2 was the pseudosecond order rate constant measured in g/mg.min. validation of the data was studied via correlat coefficient of the computed linear form. The finest model for explaining the kinetic information could be chosen on a condition that R2 is about 1. The factors included in the various applied models for the investigated sorbents were illustrated in table two. Regualrily, the finest correlating coeffecients

had been fitted applying PSORE isotherm; that was assured via plotting the practically obtained information concerning the linear arrangements for these models: (Figure 5) for PFORE and PSORE, models with respect to both composites showed a finest fitting f kinetic profiles by PSORE. Moreover, comparing equilibria's sorption capacity regarding computed values and the practically obtained data were compatible with the PSORE. Regarding amidoximated acrylonitrile/sodium -Y- Zeolite composite, the equilibrium sorption capacities were 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.

Table 1: Kinetic parameters for indigo dye adsorption by amidoximated polyacrylonitrile/ Na-Y-Zeolite Composite

	PFORE			PSORE			
$q_{e, exp}$ (mg g ⁻¹)	k_1 (min ⁻¹)	$q_{e, calc}$ (mg g ⁻¹)	\mathbb{R}^2	k_2 (g mg ⁻¹ min ⁻¹)	$q_{e, calc} (mg \ g^{-1})$	\mathbb{R}^2	
0.08	-0.0122	1.778151	0.9035	28.5695	0.079917	0.9953	

Equilibrium sorption isotherm

Sorption isotherm give useful data on the progression of an adsorption process, and determine the interaction between adsorbate molecules and the adsorbent. Sorption isotherms provide valuable data about the sorption mechanism, and decide the way inwhich adsorpate atoms interface with adsorpant. A few isoterm imitates were utilized so asto portray exploratory information about the isoterms. The Langmier [40] and Frendlich [41] methods had been utilized for explaining dye's sorption onto amidoximated acrylonitrile/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 sorbtion capacities measured in mg g^{-1}) and K is the Langmier bonding constent that had been referred to forces to adsorption measured in L g^{-1} , C_e stands for dye's equilibrial concntration in solution measured in (mgL^{-1}) . K_f (mg g⁻¹) (L mg⁻¹)^{1/n} and n stand for Frendlich constant referred to adsorption capacities and intensities. The Langmier 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 R2 combutes, the Langmier isotherm showed to be best fitted, with R_2 being more than 0.90 that were higher than that of Freundlich isotherms. Moreover, O_m determined by applying Langmier isoterm has been closer to the practically obtained value of Q_{max}.

Table 2: Kinetics models and their linear forms

Kinetic model	Non-Linear form	Linear form	Plot	Author	References
Pseudo-First order	$q_t = q_e \left[1 - e^{-k_1 t}\right]$	$\log (q_e - q_t) = \log q_e - (\frac{k_1}{2.303}) t$	$\log_{v_{s}} (q_{e} - q_{t})$	(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]

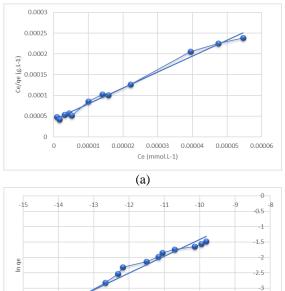




Figure 6: Dye sorption isotherms onto amidoximated Polyacrylonitrile/ Na-Y-Zeolite composite: (a) Langmuir isotherm (b) Freundlich Isotherm

Influence of temperature

It is important to investigate the effect of temperature on adsorption in a view of practical application. The adsorption experiments were carried out at six different temperatures including 25, 30, 35, 40, 45 and 50 °C. The adsorption capacity slightly increases with the increase in the temperature from 25 to 50 °C. This behavior confirms that the adsorption process is endothermic. The adsorption equilibrium constant, K_c was determined (Eq. 7) and used with the van't Hoff equation (Eq. 10) and conventional thermodynamic equation (Eq. 10) for evaluating the thermodynamic constants of the sorbents (i.e., the standard enthalpy

Table 3: Parameters of the models for adsorption isotherms

change, ΔH° , the standard free Gibbs energy, ΔG° , and the standard entropy change, ΔS°).

$$K_{c} = \frac{q_{e}}{C_{e}}$$
(7)

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

$$\Delta G^{o} = - RT \ln K_{c} \qquad (8)$$

$$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ} \qquad (9)$$

consequence, vant's Hoff equatio

As a consequence, vant's Hoff equation became:

$$\ln K_{\rm C} = \frac{-\Delta {\rm H}^{\circ}}{{\rm RT}} + \frac{\Delta {\rm S}^{\circ}}{{\rm R}} \quad (10)$$

The upsides of standardized entalpy changes (Δ Ho) and standard enthropy change (Δ So) for the sorption not set in stone from the incline and block for the plotting that represents ln Kc against 1/T (Fig. 7). Values of thermodynamical factors were illustrated within Table 5. Positive values of enthalpy assured that the process was endothermic. In addition, its negitive values proved exothermic reaction. Moreover, positive values of Δ G^o 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 7: Effect of temperature on dye sorption using amidoximated polyacrylonitrile/Na-Y-Zeolite Composite.

	Laı	ngmuir model	Freundlich model						
$q_{m, exp}$ (mmol g ⁻¹)			\mathbb{R}^2	n	${ m K_F}~({ m mmol}~{ m g}^{-1}) \ ({ m L}~{ m mmol}^{-1})^{1/n}$	\mathbb{R}^2			
0.3808	0.47372	84407.46	0.99416	2.040233	1.84717	0.94688			
Table 4: Sorption isotherms and their linear forms Plat Author Peferonces									
				Plot	Author	References			
Isotherm Isotherm	$\frac{\text{Ion isotherms and}}{\text{Non-Linear for}}$ $q_e = \frac{q_{m,L} K_L C}{1 + K_L C}$	m I	$\frac{\text{Linear form}}{\frac{C_{\text{e}}}{q_{\text{m,L}}} + \frac{1}{K_L q_{\text{m,L}}}}$	$\frac{Plot}{\frac{C_e}{q_e}} vs. C_e$	Author (Langmuir, 1918)	References [40]			

ΔH^{o}	ΔS^{o}	D 2	$\Delta G^{o} (kJ mol^{-1})$					
(kJ mol ⁻¹)	$(J \text{ mol}^{-1} \text{ K}^{-1})$	K ²	298 K	303 K	308 K	313 K	318 K	323 K
40.1884	0.18118	0.985	-7.80	-8.71	-9.61	-10.52	-11.43	-12.33

Effect of sorbent dose

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 3 for amidoximated acrylonitrile/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 86% for amidoximated acrylonitrile/sodium-Y-Zeolite composite.

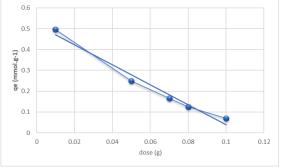


Figure 8: Effect of sorbent dose (SD) on dye sorption using amidoximated polyacrylonitrile/ Na-Y-Zeolite composite.

3.3. Regeneration

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 conditions. alkaline Desorption of amidoximated acrylonitrile/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 84% regarding amidoximated acrylonitrile/sodium-Y- zeolite composite.

3.4. Determination of point of zero charge (*pHpzc*)

The point of zerocharge demonstrates important huge data regarding the kind of surfacedynamic focuses. pH of amidoximated acrylonitrile/sodium-Y-Zeolite composite had been viewed as 4. 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 negativly charged.

Conclusion

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

Adsorption equilibrial information was fitted finely with Langmier 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 spontanous 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 desobtion process using 0.1 N NaOH solution.

The obtained findings illustrated that amidoximated acrylonitrile/sodium-Y-Zeolite composite represent a promising adsorbent for indigo dye from aqueous solutions and wastewaters of textile industry.

References

- P.K. Goel, Water pollution: causes, effects and control. New Age International; 2006.
- S.H. Hanchang, Industrial wastewater-types, amounts and effects. Point sources of pollution: Local effects and their control, 17(2009) 191.
- H.I. Abdel-Shafy, R.O. Aly, Water issue in Egypt: Resources, pollution and protection endeavors. Central Eur. J, Occupat. Envir. Med., 8(2002) 3.
- G. Crini, E. Lichtfouse, Advantages and disadvantages of techniques used for wastewater treatment, Envir. Chem. Lett., 17(2019) 145.
- Droste RL, Gehr RL. Theory and practice of water and wastewater treatment. John Wiley & Sons; 2018 Sep 12.
- M. Samer, Biological and chemical wastewater treatment processes, Wastewater treatment Eng., 14(2015) 150.
- G. Chen,. Electrochemical technologies in wastewater treatment. Separation Purif.. Tech., 15(2004) 11.
- E. Forgacs, T. Cserhati, G. Oros , Removal of synthetic dyes from wastewaters: a review, Envir. Inter., 30(2004) 953.
- Anjanevulu, N.S. Chary, Y. D.S. Raj. Decolourization of industrial effluents-available methods and emerging technologies, a review, Rev. Envir. Sci. Biotec., 4 (2005) 245.
- F.I. Hai, K. Yamamoto, K. Fukushi, Hybrid treatment systems for dye wastewater, Critical Rev. Envir. Sci. Tech., 16(2007) 315.
- M.A. Barakat, New trends in removing heavy metals from industrial wastewater. Arabian J. Chem., 4 (2011) 361.
- A.K. Rathoure, Toxicity and waste management using bioremediation. IGI Global, 2015.
- S. Mani, P. Chowdhary, R. N. Bharagava, Textile wastewater dyes: toxicity profile and treatment approaches. In Emerging and eco-friendly approaches for waste management, Springer, Singapore (2019).
- A. Gottlieb, C. Shaw, A. Smith, A. Wheatley, S. Forsythe, The toxicity of textile reactive azo dyes after hydrolysis and decolourisation, J. Biotechn.,27 (2003) 49.
- B.S. Padhi, Pollution due to synthetic dyes toxicity & carcinogenicity studies and remediation, Inter. J. Envir. Sci., 3(2012)940.
- Vaiopoulou E, Gikas P. Regulations for chromium emissions to the aquatic environment in Europe and elsewhere. Chemosphere. 2020 Sep 1;254:126876.
- S. Ding, Z. Li, R. Wang, Overview of dyeing wastewater treatment technology, Water Resour. Prot., 26(2010)73.

- S. Mani S, R.N. Bharagava, Isolation, screening and biochemical characterization of bacteria capable of crystal violet dye decolorization. Int. J. Appl. Adv. Sci. Res. 2(2017)70.
- M.R. Fox, J.H. Pierce, Indigo--past and present, Textile Chem, Color., 22(1990) 13.
- N. Stasiak, W. Kukula-Koch, K. Glowniak, Modern industrial and pharmacological applications of indigo dye and its derivatives, a review, Acta Pol. Pharm.,71(2014)215.
- E.D. Głowacki, G. Voss, L. Leonat, M. Irimia-Vladu M, S. Bauer, N.S. Sariciftci, Indigo and Tyrian purple-from ancient natural dyes to modern organic semiconductors, Israel J. Chem., 53(2012) 540.
- N. Stasiak, W. Kukula-Koch, K Glowniak. Modern industrial and pharmacological applications of indigo dye and its derivatives, a review, Acta Pol. Pharm., 71(2014) 215.
- D. Franchi, M. Calamante, C. Coppola, A. Mordini, G. Reginato, A. Sinicropi, L. Zani, Synthesis and characterization of new organic dyes containing the indigo core, Molecules. 25(2020) 3377.
- Rashid MR, Rahman MF. Study on Fabric and Seam Strength Loss of Denim Trousers for Different Washing Treatments. Journal of Textile Science and Technology. 2020 Jun 17;6(03):114.
- M.A. Chia, R.I. Musa, Effect of indigo dye effluent on the growth, biomass production and plasticity of phenotypic Scenedesmus quadricauda (Chlorococcales). Ana. da Acad. Brasileira de Ciências, 86(2014) 419.
- D. Wambuguh, R.R. Chianelli, Indigo dye waste recovery from blue denim textile effluent: a byproduct synergy approach, New J. Chem., 32(2008)2189.
- K. Amutha, Environmental impacts of denim. In Sustainability in denim, 2017 Jan 1 (pp. 27-48), Woodhead Publishing.
- Tchobanoglus, F. Burton, H.D. Stensel, G. Wastewater engineering: Treatment and reuse, Amer. Water Works Ass. J., 95(2003)201.
- S. De Gisi, G. Lofrano, M. Grassi, M. Notarnicola, Characteristics and adsorption capacities of lowcost sorbents for wastewater treatment: A review, Sustain. Mater. Techn., 9(2016) 10.
- M.R. Lutfor, S. Silong, W. M.Zin, M.Z. A. B. Rahman, M. Ahmad, J. Haron, Preparation and characterization of poly(amidoxime) chelating resin from polyacrylonitrile grafted sago starch, Eur. Polym. J., 36 (2000) 2105.
- 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., 121(1999) 41.
- V. A. Kabanov, IUPAC International symposium on macromolecular chemistry, Budapest, p 435-462

(1969).

- Jasper EE, Ajibola VO, Onwuka JC. Nonlinear regression analysis of the sorption of crystal violet and methylene blue from aqueous solutions onto an agro-waste derived activated carbon. Applied Water Science. 2020 Jun;10(6):1-1.
- Diab MA, El-Sonbati AZ, Hilali AS, Killa HM, Ghoneim MM. Polymer complexes—X. Polymerization of methyl methacrylate in the presence of some transition metal chlorides. European polymer journal. 1990 Jan 1;26(1):1-3.
- 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 rhodanineazodye and its metal complexes, J. Mol. Liq., 201 (2015) 36.

- D. A. Fungaro, S. I. Borrely, T. E.M. Carvalho, Surfactant modified zeolite from cyclone ash as adsorbent for removal of reactive orange 16 from aqueous solution, Amer. J. Envir. Protec., 1 (2013) 1.
- S. Lagergren, About the theory of so-called adsorption of soluble substances, Kungliga Swenska 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 lounge, Z. Phys. Chem., 57 (1906) 385.

الملخص العربى

عنوان البحث: إزالة صبغة الانديجو من المحلول المائى باستخدام البوليمر المتراكب أميدوكزيم أكريلونيتريل / صوديوم- واى- زيوليت

محمود سالم إبراهيم' ، عادل زكي السنباطي'، مصطفي أمين دياب' ، تامر يس السعيد*' ' قسم العلوم البينية – كلية العلوم – جامعة دمياط – دمياط – مصر ' قسم الكيمياء – كلية العلوم – جامعة دمياط – دمياط – مصر

تم تقييم امتزاز صبغة الانديجو على البوليمر المتراكب أميدوكزيم أكريلونيتريل / صوديوم- واى- زيوليت في المحاليل المائية بدر اسة متغيرات مختلفة وهي فترة التجربة ودرجة الحموضة وجرعة الممتزات والتأثير الحراري على التجربة. تمت در اسة وانصاف الاضعة السينية. تم استخدام طريقتان لوصف متساويات الحرارة لدر اسة الامتزاز وهما لانجمير وفرينديليش. بالإضافة إلى ذلك ، تم إجراء تقييم للقوة التنشيطية للامتزاز فيما يتعلق بامتصاص صبغة الانديجو على سطح اليوليم المتراكب أميدوكزيم أكريلونيتريل / صوديوم- واى- زيوليت كالتحويل الطيفي للأشعة تحت الحمراء، وانحراف الأشعة السينية. تم استخدام طريقتان لوصف متساويات الحرارة لدر اسة الامتزاز وهما لانجمير وفرينديليش. بالإضافة إلى ذلك ، تم إجراء تقييم للقوة التنشيطية للامتزاز فيما يتعلق بامتصاص صبغة الانديجو على سطح البوليمر المتراكب أميدوكزيم أكريلونيتريل / صوديوم- واى- زيوليت. كما تمت در اسة 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 و الاختلاف في الطاقات المحررة لعملية الامتزاز. أثبتت الديناميكا الحرارية للامتزاز أن العملية كانت تحدث تلقائيًا وبصفة ماصة الحرارة. أشارت النتائج إلى أنه يمكن تطبيق البوليمر المتراكب أميدوكزيم أكريلونيتريل / صوديوم- واى- زيوليت بنجاح على أنه مادتر ممتزة فعالة وغير مكلفة فيما يتعلق المتراك أميدوكزيم أكريلونيتريل / صوديوم- واى- زيوليت بنجاح على أنه مادة ممتزة فعالة وغير مكلفة فيما يتعلق بامتزاز صبغة الانديجو. من مياه الصرف الصناعي.