Removal of Sunfix Blue SF-RL dye from aqueous solution using methyl methacrylate/ Na-Y-Zeolite composite

M.S. Ibrahem¹, A.Z. El-Sonbati^{*2}, M.A. Diab², T.Y. Al-Said¹

¹Environmantal Sciences Department, Faculty of Science, Damietta University, Damietta, Egypt. ²Chemistry Department, Faculty of Science, Damietta University, Damietta, Egypt

Received: 19 March 2018 /Accepted: 25 March 2018 * Corresponding author: elsonbatisch@yahoo.com

Abstract

The adsorption of Sunfix Blue SF-RL dye onto methyl methacrylate/ Na-Y-Zeolite (MMA/Na-Y-Z) composite was investigated in aqueous solution in a batch system with respect to contact time, pH, adsorbent dosage and temperature. Physical characteristics of (MMA/Na-y-Z) composite such as Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD) were obtained. Langmuir and Freundlich adsorption models were applied to describe the equilibrium isotherms and the isotherm constants were determined. The activation energy of adsorption was evaluated for the adsorption of Sunfix Blue SF-RL dye onto (MMA/Na-Y-Z) composite. The pseudo-first-order and pseudo-second-order kinetic model for the adsorption of Sunfix Blue SF-RL dye. The activation energy (Ea), change of free energy (Δ G), enthalpy (Δ H) and entropy (Δ S) of adsorption were also evaluated for the adsorption indicated spontaneous and endothermic process for Sunfix Blue SF-RL dye. The results indicate that (MMA/Na-Y-Z) composite could be employed as low-cost material for the removal of dyes from industrial wastewater.

Keywords: Sunfix Blue SF-RL dye / Na-Y-Zeolite composite, adsorption efficiency, sorption kinetics, thermodynamic parameters.

Introduction

Water contamination caused by dye industries, including food, leather, textile, plastic, cosmetics, paper-making, printing and dye synthesis, has caused more and more attention, since most dyes are harmful to human being and environments [1]. Therefore, these industrial effluents must be treated before discharge. Currently, much attention has been paid to the removal of dyes from industrial wastewater [2]. Various treatment methods including physical, chemical and biological schemes have been developed to remove dyes from wastewater [2-4]. However, these methods mentioned above always show some disadvantages, such as the generation of large amounts of toxic and carcinogenic byproducts, intensive energy and high cost. Some of the applied techniques for the treatment of dye contaminated wastewaters are flocculation, coagulation, precipitation, adsorption, membrane filtration, electrochemical techniques, ozonation and fungal decolorization [5,6]. Among them, the adsorption-based procedure is widely utilized due to its high efficiency, capacity and ability for large scale dye removal application (with potential for adsorbent regeneration) [6-10]. The nontoxic, low cost and easy availability adsorbents are the best choice for wastewater treatment. Due to the unique properties of nanoparticles such as a high number of reactive atoms, high mechanical and thermal strength, large number of vacant reactive surface sites metallic or semi-metallic behavior and high surface area widely applied for removal of various toxic materials [11]. To our delight, adsorption is an economic, effective and easily operated process in dye removal [12]. Numerous adsorbents, such as zeolite, silica, wheat shells, orange peel, coir pith, almond shells, natural polymeric materials, etc. have been studied and applied [13].

The industrial wastewater usually contains a variety of organic compounds and toxic pulp mills and dyestuff manufacturing discharge highly colored wastewater which have provoked serious environmental concerns all over the world [14]. Several methods including adsorption [15], coagulation [16], membrane filtration [17] and advanced oxidation [18] have been employed to eliminate dyes from wastewaters. Among them, adsorption has been recognized as a promising technique due to its high efficiency, simplicity of design, ease of operation as well as the wide suitability for diverse types of dyes [19,20]. Because the dye effluent may cause damage to aquatic biota and human by mutagenic and carcinogenic effects, the removal of dye pollutants from wastewater is of great importance [21].

Adsorption is considered to be relatively superior to other techniques because of its low cost, simplicity of design, ease of operation, flexibility, high efficiency, availability and ability to separate wide range of chemical compounds [22, 23]. Currently, zeolite is the most common adsorbent [24,25]. Because zeolites are crystalline alluminosilicates with the structure based on tetrahedral SiO₄ and AlO₄ units, connected by shared oxygen atoms, and the isomorphous replacement of Si⁴⁺ by Al³⁺ produces a negative charge in the lattices. Which is compensated by alkali and alkaline-earth metal cations within the frame work. Thus, each mole of aluminum produces one equivalent of cation exchange capacity for the zeolite frame work. [26, 27]. Polymeric adsorbents are generally preferred due to their high efficiency, easy handling, availability of different adsorbents reusability and the cost effectiveness.

The aim of this study is to investigate the adsorption of hazardous Sunfix Blue SF-RL dye onto methyl methacrylate/ Na-Y-Zeolite

(MMA/Na-Y-Z) composite. Effects of different parameters such as initial adsorbate concentration, adsorbent dosage, contact time, solution pH and temperature were studied. The kinetic and thermodynamic parameters were also calculated to determine rate constants and adsorption mechanism. The experimental data were fitted into Langmuir and Freundlich equations to determine which isotherm gives the best correlation to experimental data.

Experimental

Chemicals and reagents

All chemicals used were of analytical reagent grade and distilled water was used for the preparation of all aqueous solutions, Methyl methacrylate (MMA) was Loba Analytical products. It was washed with caustic soda solution to remove the inhibitor, subsequently with distilled water and dried over calcium hydride. The monomer was vacuum-distilled, the first and last 20% being eliminated. Na-Y Zeolite and sodium bisulfite were Fluka Analytical products.

Preparation of poly (methyl methacrylate) (*PMMA*).

PMMA was prepared by free radical initiation of MMA monomer using 0.1 g of sodium bisulfite and 50 ml distilled water in 250 ml conical flask. The polymerization was carried out in a thermostate at 50°C for 24 hours. The formed PMMA was isolated by filtration, washed with distilled water followed by ethanol and dried in drying oven for four days at 50°C yield 95% of PMMA.

Preparation of methyl methacrylate /Na-Y-Zeolite (MMA/Na-Y-Zeolite) composite.

MMA/ Na-Y-Zeolite composite was prepared through solution polymerization of MMA (20 ml) monomer and Na-Y Zeolite (20g) using 0.3 g of Sodium bisulfite as initiator in 50 ml distilled water. The polymerization was carried out at 50°C with continuous stirring for 24 hours and the product was isolated by filtration and washed with distilled water followed by ethanol then air dried. The product was grinded to fine particles.

q_e

Characterization of the sorbents

In order to confirm the functionalization of the sorbent; methyl methacrylate / Na-Y-Zeolite resin was examined in dried KBr powder by recording the infrared spectra over the range of 4000–400 cm⁻¹ using a Fourier transform infrared spectrophotometer (FTIR) (Jasco FT/IR-4100 spectrophotometer). The structure of the synthesized adsorbent was examined by X-ray diffraction measurement (XRD) is recorded on X-ray diffract meter in the range of diffraction angle $2\theta = 5-80^{\circ}$. This analysis is carried out using Cu K α 1 radiation ($\lambda = 1.540598$ Å).

Determination of point of zero charge

The point of zero charge (pHpzc) was determined by solid addition method. A series of 0.1 M KNO₃ solution (50 ml each) were prepared and their pH values were adjusted in the range of 1.0 to 11.0 by addition of 0.1 M HCl and 0.1 M NaOH. To each solution, 0.1 g of MMA/Zeolite composite was added and the suspensions were shaked manually and the solution was kept for a period of 48 h with intermittent manual shaking. The final pH of the solution was recorded and the difference between initial and final pH (Δ pH) (Y-axis) was plotted against the initial pH (X-axis). The point of this curve yielded pHpzc [28].

Preparation of solutions

Distilled water was used for the preparation of all aqueous solutions. A stock solution (1000 mgL⁻¹) of Sunfix Blue SF-RL dye was prepared in distilled water. The desired concentrations were then obtained by dilution. HCl (0.01-0.1 N) and NaOH (0.01-0.1 N) were used to control the pH of the medium.

Sorption experiments

Batch adsorption studies were carried out by shaking 50 ml conical flasks containing 0.25 g of MMA/ Na-Y-Zeolite composite and 25 mL of dye solutions of desired concentration with adjusted pH on an orbital shaker machine at 200 rpm at 25°C. The solution pH was adjusted with 0.1 mol L⁻¹ HCl and 0.1 mol L⁻¹ NaOH solutions. At the end of the adsorption period, the clear solution was separated by filtration. Then the concentration of the residual dye was determined spectrophotometrically by monitoring the absorbance at 613 nm for dye using UV–Vis

spectrophotometer. Percentage of Dye removal (R) was calculated using eq. (1):

$$= V (C_0 - C_t) / W$$
 (2)

where $C_t (mg L^{-1})$ is the dye concentration at equilibrium, V (L) is the volume of solution and W (g) is the weight of adsorbent.

The procedures of kinetic experiments were identical with those of equilibrium tests. At predetermined moments, aqueous samples (5 mL) were taken from the solution, the liquid was separated from the adsorbent magnetically and concentration of dye in solution was determined spectrophotometrically at a wavelength of 613 nm. The amount of dye adsorbed at time t, q_t $(mg.g^{-1})$ was calculated by following eq. (3): $q_t = V (C_0 - C_t) / m$ (3) where $C_0 (mg L^{-1})$ is the initial dve concentration, $C_t (mg L^{-1})$ the dye concentration at any time t, V (L) the volume of the solution

and m (g) is the mass of the adsorbent. In an adsorption study, it is necessary to fit the equilibrium adsorption data using different adsorption isotherm models and kinetic equations in order to analyze and design an adsorption process. Therefore, different theoretical models are applied to experimental data in order to find a model which adequately predicts kinetic and isotherm data. The validity of the models was evaluated by the coefficient of determination (r²) [29].

The regeneration efficiency (RE, %) was calculated according to the following equation:

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

Results and discussion

Sorbent characterization

FT-IR spectrometry

FT-IR spectrometry was used to characterize the structure of the PMMA and methyl methacrylate

/Na-Y- Zeolite composite (Fig. 1a, **1b**). respectively. The FT-IR spectrum of PMMA shows a distinct absorption band from 1147.44 to 1270.86 cm⁻¹, which can be attributed to the C-O-C stretching vibration. The band at 1733.69 cm⁻¹ shows the presence of the acrylate carbonyl group. The band at 1448.28 cm⁻¹ can be attributed to the bending vibration of the C-H bonds of the -CH₃ group. The two bands at 2998.77 and 2952.48 cm⁻ can be assigned to the C-H bond stretching vibrations of the -CH₃ and -CH₂- groups, respectively. The FT-IR spectrum of methyl methacrylate /Na-Y- Zeolite composite shows a shift of the carbonyl band by about 100 cm⁻¹ this behavior is similar to that suggested by Kabanov [29] and Diab et al [30] in polymerization of MMA in the presence of ZnCl₂, AlCl₂ and some transition metal chlorides, respectively.



Figure 1: FT-IR analysis of (a) PMMA and (b) MMA/Na-Y-Zeolite composite





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

X-ray of MMA/Na-Y-Zeolite composite

The X-ray diffraction (XRD) patterns of PMMA/ homopolymer (**Fig.2a**) shows the amorphous phase. The X-ray diffraction (XRD) patterns of MMA/Na-Y-Zeolite composite presented in (**Fig.2b**) shows many diffraction peaks which confirm the polycrystalline phase. The average crystallite size (ξ) and dislocation density (δ) can be calculated from the XRD according to the following equations [31, 32].

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

$$\delta = \frac{1}{\xi^2} \tag{6}$$

Where λ is wavelength of X-ray radiation (1.541874 Å), K is constant taken as 0.95 for organic compounds and $\beta_{1/2}$ is full width at half maximum of the reference diffraction peak measured in radians and θ is the angle of diffraction. The calculated values of ξ are found 470.75, 485.11, 478.92 and 492.515.

Sorption of methyl methacrylate / Na-Y-Zeolite composite

Effect of pH

The pH of the aqueous solution is an important parameter affecting dye adsorption. The effect of pH on the adsorption of Sunfix Blue SF-RL dye on the methyl methacrylate / Na-Y-zeolite composite was investigated in the initial pH range of 2-8. For Sunfix Blue SF-RL dye (Fig. 3). The removal of the tested dye by methyl methacrylate / Na-Y-Zeolite composite at different pH values was studied at initial concentrations of 100 mg/L of the dye, 25 °C and 10 g/L adsorbent dosage. The pH value of the solution was an important

controlling parameter in the adsorption process. methyl methacrylate / Na-Y-Zeolite composite has proved to be an effective adsorbent for the removal of the dye, which was achieved via adsorption from an aqueous solution at pH 2 was achieved (Fig. 3). It shows that the adsorption capacity of tested dye onto methyl methacrylate / Na-Y-Zeolite composite increases significantly with decreasing pH. The maximum removals for contact time 120 min. were carried out at pH 2. As the pH of the adsorption system increases, the number of negatively charged sites increases and the number of positively charged sites decreases. A negatively charged surface site on the adsorbent does not favor the adsorption of dye anions, due to the electrostatic repulsion. Also, lower adsorption of tested dye at alkaline pH is due to the presence of excess hydroxyl ions competing with the dye anions for the adsorption sites [33].



Figure 3: Effect of pH on the adsorption of the dye onto MMA/Na-Y-Z

3.2.2. Kinetic studies

The uptake kinetics of Sunfix Blue SF-RL dye using the MMA- Na-Y-Zeolite composite is shown in (Fig. 4). It can be observed that adsorption process for dye is rapid at initial stage and decreases gradually reaching equilibrium at 55 min. This may be due to the fact that at initial stage there are large number of active sites available for removal of dye, and removal is difficult as time increases because of repulsion between solutes and solid.

Uptake kinetics of dye sorption on the sorbent was analyzed using two models: the so-called pseudo-first order rate equation (PFORE) [34] and pseudo-second order rate equations (PSORE) [35]. These models and their linear forms are reported in **Table 1** where k_1 is the pseudo first order rate constant (min⁻¹) of sorption and q_e and q_t (mg g⁻¹) are the amounts of dye sorbed at equilibrium and time t, respectively, k₂ is the pseudo second order rate constant (g $mg^{-1} min^{-1}$). The validity of each model is checked by the correlation coefficient associated to linear fit. The best models for describing the kinetic data can be selected if R2 is equal to or near 1. Table 2 reports the parameters of the different models for the studied adsorbents. Systematically, the best correlation coefficients were found for the PSORE model; this is confirmed by the plot of experimental data according the linearized forms of these models: (Fig. 4a, 4b) for PFORE and PSORE, respectively, show a best fit of kinetic profiles by PSORE. In addition, the comparison of equilibrium adsorption capacities for the calculated values and the experimental values are only consistent for the PSORE model: the equilibrium sorption capacities are found close to 0.16978, and PSORE modeling gave value of 0.17865, closer from experimental value than PFORE 1.77815. However, the PSORE describes kinetic data through a global approach, and does not take into account the contribution of diffusion mechanisms in the control of the kinetics. Under these conditions, the kinetic parameters should be considered as apparent rate coefficients.

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
0.1697793	-0.09964 1.7		1.7	78151	0.82745	1.956233908		0.178651		0.99553
Table 2: Kinetics models and their linear forms										
Kinetic model	Kinetic model Non-Linear form		Linear form		Plot		Author	References		
Pseudo-First order	q_t	$= q_e \left[1 - e^{-k_1}\right]$	$-e^{-k_1 t} \log (q_e - q_t) = \log q_e$			$\frac{k_1}{2.303}$) t	$\log (q_e - q_t)$	<i>vs</i> . 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]

Table 1: Kinetic parameters for Sunfix Blue SF-RL dye adsorption



Figure 4: Dye uptake kinetics using MMA/Na-Y-Z sorbent

Equilibrium sorption isotherm

The adsorption isotherms reveal the specific relation between the concentration of adsorbate and the adsorption capacity of an adsorbent at a constant temperature. Adsorption isotherms provide some information on how an adsorption system proceeds, and indicate how molecules of adsorbate interact with adsorbent. Several isotherm models have been used to describe experimental data for sorption isotherms. The Langmuir [36] and Freundlich [37] models were used to explain the sorption of the dye on the MMA - Na-Y-Zeolite sorbent. These models and their linear forms are reported in Table 2 (see Supplementary Material Section), where q_e the adsorbed amount of dye at equilibrium concentration (mg g^{-1}), $q_{m,L}$ is the maximum sorption capacity (corresponding to the saturation of the monolayer, mg g^{-1}) and Kl is the Langmuir binding constant which is related to the energy of

sorption (L g^{-1}), C_e is the equilibrium concentration of dye in solution (mgL⁻¹). K_f (mg g^{-1}) (L mg⁻¹)^{1/n} and n are the Freundlich constants related to the sorption capacity and intensity, respectively.

 Table 3: Parameters of the models for adsorption isotherms

	Langmui	ir mode	1	Freundlich model			
$q_{m, exp}$ (mg g ⁻¹)	$\begin{array}{c} q_{m,L} \\ (mg \ g^{-1}) \end{array}$	$\begin{matrix} K_L \\ (L \ g^{-1}) \end{matrix}$	R ²	n	$\begin{array}{c} K_F \\ (mg \ g^{-1}) \\ (L \ mg^{-1})^{1/n} \end{array}$	R ²	



Figure 5: Dye sorption isotherms onto MMA/Na-Y-Z sorbent

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

Table 4: Sorption isotherms and their linear forms

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, 40, 50 and 60 °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. 11) and conventional thermodynamic equation (Eq. 10) for evaluating the thermodynamic constants of the sorbents (i.e., the standard enthalpy change, ΔH° , the standard free Gibbs energy, ΔG° , and the standard entropy change, ΔS°).

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

Where q_e and C_e are equilibrium concentrations of metal ions on the adsorbent and in the solution, respectively.

$$\Delta G^{o} = - RT \ln K_{c}$$

$$\Delta G^{o} = \Delta H^{o} - T\Delta S^{o}$$
(10)

Therefore the van't Hoff equation becomes:

$$\ln K_{\rm C} = \frac{-\Delta {\rm H}^{\circ}}{{\rm RT}} + \frac{\Delta {\rm S}^{\circ}}{{\rm R}}$$
(11)

The values of standard enthalpy change (ΔH°) and standard entropy change (ΔS°) for the adsorption process are determined from the slope and intercept for the plot of $\ln K_c$ versus 1/T (Fig. 6). The values of thermodynamic parameters are reported in **Table 5**. The positive values of ΔH° confirm the endothermic nature of sorption process and the negative values indicate the exothermic reaction. The positive values of ΔG° that sorption reaction indicate the is nonspontaneous and the negative values of ΔG° indicate that the sorption reaction is spontaneous.



Figure 6: Effect of temperature on dye sorption using MMA/Na-Y-Z sorbent.

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

ΔH^{o}	ΔS^{o}	D 2	ΔG^{o} (kJ mol ⁻¹)				
$(kJ mol^{-1})$	$(J mol^{-1} K^{-1})$	K-	298 K	303 K	313 K	323 K	333 K
-0.001473	0.03192576	0.87	-0.0095	-0.0097	-0.0099	-0.01	-0.011

Effect of sorbent dose

The adsorption of dye on the MMA- Na-Y-Zeolite composite was studied by changing the quantity of adsorbent range of (0.05 to 0.25) g, 50 mL with the dye concentration of 100 mg L⁻¹ at \pm 25 °C and pH 2. The results in Fig. 7 show the dye adsorption capacity as a function of adsorbent amount. It has been found that the adsorption capacity decreases from 51 to 8 mg/g when the dose of composite increases from 0.05 to 0.25 g. At low dose of adsorbent, all the sites are exposed entirely and the adsorption on the surface is saturated faster showing a higher adsorption capacity. An increase in the mass of adsorbent leads to a decrease in equilibrium adsorption capacity per unit weight of the adsorbent (qe) because there is excess adsorbent for the limited amount of dye in the solution. According to the result maximum removal efficiency is 84%.



Figure 7: Effect of sorbent dose (SD) on dye sorption using MMA/Na-Y-Z sorbent.

Regeneration

Desorption of dye is generally operated by pH change. In most cases, desorption is performed under basic conditions. Regeneration of the composite was carried by contacting 20 mL of 0.1

N NaOH with composite for 60 min. After regeneration the composite was again carefully washed with distilled water to become ready for the second run of uptake. The regeneration efficiency for each adsorption/desorption cycle was found to be 77%.

Determination of point of zero charge (pHpzc)

The pHpzc gives very significant information about the type of surface active centers. The pH of MMA/Na-Y-Zeolite composite was found to be 7.5. This shows that below this pH, the composite acquires a positive charge due to protonation of functional groups and above this pH, negative charge exists on the surface of composite.

Conclusion

The present study clearly demonstrated that (MMA/Na-Y-Zeolite) composite is an effective adsorbent for the removal of the dye from aqueous solution and polluted water. The prepared sorbents are characterized by efficient and selective sorption towards the dye from aqueous medium at approximately pH 2. Adsorption parameters for Langmuir and Freundlich isotherms were determined and the equilibrium data fit well with Langmuir equation for the adsorption of the dye. The kinetic data tends to fit very well in the pseudo-second-order kinetic model with high correlation coefficients. The thermodynamics of adsorption indicated spontaneous the and endothermic reaction.

Desorption studies were conducted and the results showed that (MMA/Na-Y-Zeolite) composite can be used in adsorption of the dye several times by regeneration process using 0.1 N sodium Finally, hydroxide solution. taking into consideration of the results above, it can be concluded that the (MMA/Na-Y-Zeolite) composite is a suitable adsorbent for the dye from wastewaters in terms of high adsorption capacity, natural and abundant availability and low cost.

References

- T. Kalburc, A. Tabak, N. Ozturk, N. Tuzmen, S. Akgol, B. Caglar, A. Denizli, Adsorption of lysozyme from aqueous solutions by a novel bentonite-tyrptophane (Bent-Trp) microcomposite affinity sorbent, J. Mol. Struct. 1083 (2015) 156.
- L. S. Oliveira, A. S. Franca, T. M. AlvesSônia, D. F. Rocha, Evaluation of untreated coffee husks as

potential biosorbents for treatment of dye contaminated waters, J. Hazard. Mater. 155 (2008) 507.

- R.P.F. Melo, E.L. Barros Neto, M.C.P.A. Moura, T.N. Castro Dantas, A.A. Dantas Neto, H.N.M. Oliveira, Removal of Reactive Blue 19 using nonionic surfactant in cloud point extraction, Sep. Purif. Technol. 138 (2014) 71.
- T. T. Ma, P. R. Chang, P. W. Zheng, F. Zhao, X. F. Ma, Fabrication of ultra-light graphene-based gels and their adsorption of methylene blue, Chem. Eng. J. 240 (2014) 595.
- M. R. Patil and V. S. Shrivastava, Adsorption removal of carcinogenic acid violet19 dye from aqueous solution by polyaniline-Fe₂O₃ magnetic nanocomposite, J. Mater. Environ. Sci. 6(1) (2015) 11.
- M. Ghaedi, H. Khajehsharifi, A. H. Yadkuri, M. Roosta, A. Asghari, Oxidized multiwalled carbon nanotubes as efficient adsorbent for bromothymol blue, Toxicol. Environ. Chem. 94 (2012) 873.
- T.A. Ammar, K.Y. Abid, A.A. El-Bindary, A.Z. El-Sonbati, Chlorine dioxide bulk decay prediction in desalinated drinking water, Desalination 352 (2014) 45.
- A. El-Bindary, M. A. Hussien, M. A. Diab, A. M. Eessa, Adsorption of Acid Yellow 99 by polyacrylonitrile/activated carbon composite: Kinetics, thermodynamics and isotherm studies, J. Mol. Liq. 197 (2014) 236.
- A. A. El-Bindary, M. A. Diab, M. A. Hussien, A. Z. El-Sonbati, A. M. Eessa, Adsorption of Acid Red 57 from aqueous solution onto polyacrylonitrile/activated carbon composite, Spectrochim. Acta A 124 (2014) 70.
- M. Ghaedi, A. Ansari, M. H. Habibi, A. R. Asghari, Removal of malachite green from aqueous solution by zinc oxide nanoparticle loaded on activated carbon: Kinetics and isotherm study, J. Ind. Eng. Chem. 20 (2014) 17.
- M.R. Fathi, A. Asfaram, A. Farhangi, Removal of Direct Red 23 from aqueous solution using corn stalks: Isotherms, kinetics and thermodynamic studies, Spectrochim. Acta A 135 (2015) 364.
- M. S. Sajab, C. H. Chia, S. Zakaria, P. S. Khiew, Cationic and anionic modifications of oil palm empty fruit bunch fibers for the removal of dyes from aqueous solutions, Bioresour. Technol. 128 (2013) 571.
- S. Wang, Y. Boyjoo, A. Choueib, Z.H. Zhu, Removal of dyes from aqueous solution using fly ash and red mud, Water Res. 39 (2005) 129.
- P.C.C Faria, J.J.M Órfão, M.F.R Pereira, Adsorption of anionic and cationic dyes on activated carbons with different surface chemistries, Water Res. 38 (2014) 2043.
- A. A. El-Bindary, A. Z. El-Sonbati, A. A. Al-Sarawy, K. S. Mohamed, M. A. Farid, Adsorption and

thermodynamic studies of hazardous azocoumarin dye from an aqueous solution onto low cost rice straw-based carbons, J. Mol. Liq. 199 (2014) 71.

- M. Roosta, M. Ghaedi, N. Shokri, A. Daneshfar, R. Sahraei, A. Asghari., Removal of malachite green by gold nanoparticles loaded on activated carbon: experimental design, Spectrochim. Acta A 118 (2014) 55.
- S. S. Madaeni, Z. Jamali, N. Islami, Highly efficient and selective transport of methylene blue through a bulk liquid membrane containing Cyanex 301 as carrier, Sep. Purif. Technol., 81(2011), 116.
- Serpone N, Horikoshi S, Emeline AV (2010) Microwaves in advanced oxidation processes for environmental applications. A brief review. J. Coll. Interf. Sci. 430 (2014) 166.
- G.Z. Kyzas, E.A. Deliyanni, N.K. Lazaridis, Magnetic modification of microporous carbon for dye adsorption, J. Coll. Interf. Sci. 430 (2014) 166.
- M. Asgher, H. N. Bhatti, Evaluation of thermodynamics and effect of chemical treatments on sorption potential of citrus waste biomass for removal of anionic dyes from aqueous solutions, Ecol. Eng. 38 (2012) 79.
- S. Yang, M. Gao, Z. Luo, Adsorption of 2-Naphthol on the organo-montmorillonites modified by Gemini surfactants with different spacers, Chem. Eng. J. 256 (2014) 39.
- A. M. Alsabagh, M. Fathy and R. E. Morsi, Preparation and characterization of chitosan/silver nanoparticle/copper nano particle/carbon nanotube multifunctional nano-composite for water treatment: heavy metals removal; kinetics, isotherms and competitive studies, RSC Adv. 5 (2015) 55774.
- K. H. Kima, A. A. Keller, J. K. Yang, Removal of heavy metals from aqueous solution using a novel composite of recycled materials, Colloid. Surface. A. 425 (2013) 6.
- D. Karadag, E. Akgul, S. Tok, F. Erturk, M. A. Kaya, M. Turan, Basic and Reactive dye removal using natural and modified zeolites, J. Chem. Eng. Data, 52 (2007) 2436.
- B. Armagan, O. Ozdemir, M. Turan, M. S. Celik, The removal of reactive azo dyes by natural and modified zeolites, J. Chem. Technol. Biotechnol., 78 (2003) 725.

- G. Amin, D. Dordević, S. Konstantinovic, I. Jordanov, The removal of the textile basic dye from the water solution by using natural zeolite, Advanced technologies, 6(2) (2017) 67.
- A. U. Metin, Synthesis, Physical properties, and application of aminated poly(glycidyl methacrylate)/zeolite composite, polym. Composites, 37(8) (2015) 2313.
- 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 Sympersium on Macromolecular Chemistry, Budapest, p 435-462 (1969).
- M. A.Diab, A. Z.El-sonbati, A. S.Hilali, H. M. Killa, M. M.Ghoneim, Polymer complexes X. Polymerization of methyl methacrylate in presence of some transition metal salts, 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, 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. Prot., 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 lasungen, Z. Phys. Chem., 57 (1906) 385.

الملخص العربى

عنوان البحث: إزالة صبغة صنفكس الزرقاء من محاليلها المائية باستخدام مركب بوليمرات الميثيل ميثاأكريلات- الزيوليت

محمود سالم إبراهيم ، عادل زكى السنباطى ، مصطفى أمين دياب ، تامر يس السعيد ا

ن قسم علوم البيئة - كلية العلوم - جامعة دمياط - دمياط - ج.م.ع
 ن قسم الكيمياء - كلية العلوم - جامعة دمياط - دمياط - ج.م.ع

يتضمن البحث دراسة إمتزاز صبغة صنفكس الزرقاء من محاليلها المائية باستخدام مركب بوليمرات الميثيل ميثاأكريلات- الزيوليت عند أزمنة مختلفة ودراسة تاثير الأس الهيدروجيني ودرجة الحرارة وكمية المادة الممتزة علي كفاءة الامتزاز، كما تم دراسة الخواص الفيزيانية للمركب محل الدراسة باستخدام أطياف الأشعة تحت الحمراء والأشعة السينية. وبتطبيق نموذج لاتجمير فراندليش الايزو ثرمي للامتزاز امكن إثبات أن الرتبة الثانية الكاذبة هي الصيغة السائدة. كما أمكن تعيين ثوابت الديناميكا الحرارية مثل طاقة جبس الحرة والتغير في الانتلابي والتغير في الانتروبي واقترحت ميكانيكية للمركب المتراز.