

SYNERGY OF MAGHEMITE INTERCALATED BENTONITE FOR ENHANCED REMOVAL OF BEMACID RED DYE FROM INDUSTRIAL TEXTILE WASTES

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Abstract— The study of the removal of Bemacid red dye “BR” present in textile industry waste by bentonite intercalated with iron oxide “maghemite $\gamma\text{-Fe}_2\text{O}_3$ ” is carried out by studying several parameters such as: effect of the initial concentration of the dye, the time necessary to reach the equilibrium, effect of the initial pH, effect of the ionic strength and the effect of the temperature.

The results of extractions obtained show that the extraction equilibrium is found after 60 minutes of agitation with a yield higher than 85%. The extraction efficiency reaches the maximum in the range of $\text{pH}_i = 2.5$. The extraction process is described by the Langmuir isotherm and follows pseudo-second order kinetics. The study of the diffusional mechanisms through the exploitation of experimental data of kinetics, highlighted the preponderance of the external diffusion (liquid film). The thermodynamic study showed that dye sorption is a spontaneous and exothermic process. Increasing the temperature causes a decrease in the dye adsorption capacity.

Keywords— Magnetic separation, Bemacid Red, Adsorption, Maghemite, Bentonite.

I. INTRODUCTION

The growth of human activity and the development of science and technology are causing an environmental disorder due to the pollution of waters by a number of pollutants including synthetic dyes, which have a complex molecular structure that makes them more stable and difficult to be biodegraded [1]. There are more than 10,000 commercially available dyes with several thousand tons of dyes that are produced each year in the world, and which are rejected in nature [2]. Following this great environmental threat, several technologies have been developed for dyed wastewater treatment, including oxidation, photocatalytic degradation [3], micellar-enhanced ultrafiltration [4], adsorption/precipitation processes [5], and coagulation. Of all these technologies, adsorption remains among the most widely used techniques and the easiest to implement.

The elimination of dyes from aqueous solutions by adsorption on various solid materials, in particular on natural

materials, has been the subject of much research. An alternative solution would be to use other efficient and more economical adsorbent materials.

Many researchers have considered low cost and effective substitutes, such as waste metals, coconut husks [6], spent tea leaves [7] peanut hulls [8], and surface soil [9]. Our choice was a material that is found in abundance in Algeria, namely clay. Bentonite are clays rich in montmorillonite, which can be effectively used as adsorbents for the retention of many pollutants.

In environmental applications, the use of magnetic composites “Magnetic Bentonite” “M-Bt” for the separation of pollutants in effluents is an innovative technology that is gaining much attention. The technique of magnetic separation has an objective to provide optimal efficiency, less expensive, simplicity; for these reasons, magnetic separation is a promising method, which can be used for rapid removal of pollutants from hazardous waste solutions. Also, it is a technique that respects the rules of the environment “green chemistry” which eliminates the use or generation of substances harmful to the environment.

II. MATERIALS AND METHODS

A. Reagents and instruments

Dye solutions at 50 mg/l were prepared by 0.0125g Red Bemacid dye N-TF ($\lambda_{\text{max}} = 505\text{nm}$, $\text{C}_{24}\text{H}_{20}\text{ClN}_4\text{NaO}_6\text{S}_2$, $M = 583\text{g}\cdot\text{mol}^{-1}$) in 250 mL of distilled water. The initial pH of the sample solution was adjusted by using diluted HCl or NaOH (from sigma-Aldrich).

The separation of dye was studied by the batch process using a stirring vibrator (HAIER model). The pH measurements were performed with a pH meter a combined electrode Adwa (AD1030) instrument. The analyses and the determination of the concentration of the dye “BR” was carried out with a UV-Visible spectrophotometer type SPECORD 210/Plus.

B. Adsorption Procedure

Bemacid Red dye was selected as the model of water pollutants. To do this adsorption studies, bentonite magnetic “M-Bt” were investigated as adsorbents. Typically, 0.01g of adsorbent was used for the adsorption of a 5 ml solution of bemacid red for different concentrations ranging from 1 mg. L⁻¹ to 100 mg.L⁻¹. Effect of pH was studied by adjusting the pH of dye solution using NaOH (0.1M) and HCl (0.1M). Adsorption kinetics were studied by analyzing samples as a function of time. The adsorbents were collected by an external magnet at a different time interval. The residual dye concentration in the solution was determined using UV-Visible spectrophotometer by measuring the absorbance at a wavelength of maximum ($\lambda_{max} = 505 \text{ nm}$) of Bemacid red. The removal efficiency (R%) and adsorption capacity (q) of adsorbent were calculated using Eqs. 1 and 2 respectively.

$$R (\%) = (C_o - C) / C_o \times 100 \dots\dots\dots (1)$$

$$Q = [V \times (C_o - C)] / m \dots\dots\dots (2)$$

Where C_o (mg/L) represents the initial Bemacid Red concentration, C (mg/L) is the Bemacid Red concentration in solution after adsorption, V (L) is the volume of the aqueous solution and m (g) is the mass of adsorbent. The mechanism of adsorption and kinetics were correlated by common adsorption isotherms and kinetic models respectively.

III. RESULTS AND DISCUSSION

A. Effect of contact time

The contact time was studied to determine the optimal time with high BR removal efficiency (shown Fig.1).

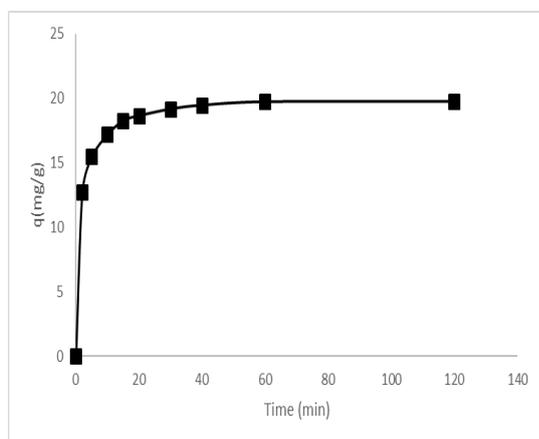


Fig. 1 Adsorption kinetics of Bemacid Red on magnetic bentonite ($[C_o] = 50\text{ppm}$, $m = 0.01\text{g}$, $\Phi = 300 \text{ tpm}$, $V = 5\text{mL}$, $\text{pH} = 2.5$)

It can be seen from Fig.1 that the adsorption process could be divided into two stages. In the first stage, the adsorption rate was rapid and 70% of the adsorption capacity was reached within the first 30 minutes of the adsorption process. This is followed by the second step, the adsorption rate of BR

on the magnetic bentonite was slow and reached equilibrium at about 60 min with 85% of the adsorption capacity of BR. The rapid adsorption in the first 30 minutes of the adsorption process and the strong diffusion of the dye molecules into the outer surface of the magnetic bentonite. At later times, the adsorption sites became fewer, reducing the rate of adsorption and an equilibrium state was achieved.

B. Effect of concentration

The effect of the initial dye concentration was studied by stirring at 300 tpm, one volume of BR dye solution, at the pH of the solution 2.5, mixed with a quantity of the bentonite magnetic (0.01g) during an equilibrium time. During the magnetic bentonite BR dye sorption experiments, for all of the initial dye concentration used, the amount of BR adsorbed increased with increasing initial concentration. The initial concentration provides a driving force to overcome the resistance mass transfer of dye molecules between the liquid phase and the solid phase during adsorption.

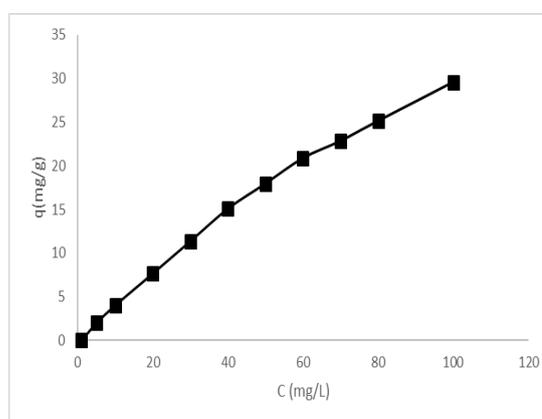


Fig. 2 Evolution of the amount of adsorption on the magnetic bentonite depending on the initial concentrations of Bemacid Red ($V = 5\text{mL}$, $m = 0.01 \text{ g}$, $\Phi = 300 \text{ tpm}$, $\text{pHi} = 2.5.$)

C. Effect of pH

The pH of a dye solution plays an important role in the adsorption process, especially on the adsorption capacity [10]. In general, the initial pH value can increase or decrease the rate of dye absorption and is intercorrelated with changes in adsorbent surface area and dye chemistry [11]. Fig. 3 shows the effect of the initial pH of BR solution (pH: 1–10) on the adsorption capacity of magnetic bentonite. It can be seen that the elimination of the dye is better suited in an acidic medium (pH = 1-3) with a binding capacity of 21 mg/g. When the pH increases from 4 to 10 we notice a big decrease in the adsorbed quantity, until reaching a value of 2 mg/g. This behavior can be explained by the existence of an attraction between the bentonite surface and the BR dye, which also confirms that the industrial dye used is an acidic (anionic) dye. The effect of pH on the adsorption of BR dye observed in this study can be explained by the protonation of the adsorbent surfaces and the electrostatic interactions between the magnetic bentonite and the BR dye.

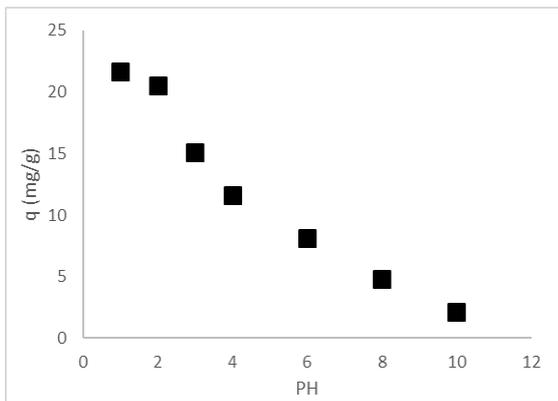


Fig. 3 Influence of pH on the adsorption of BR ($[C_0] = 50\text{mg/L}$; $V = 5\text{mL}$; $m = 0.01\text{g}$; $t = 60\text{min}$)

D. Adsorption isotherms

Isothermal adsorption models are widely used to describe the adsorption process and to study adsorption mechanisms [12]. They described the interaction of adsorbate molecules with the surface of the adsorbent [13]. The isothermal data thus obtained were fitted to Langmuir, Freundlich Isotherm (linear regression) models according to equations (3) and (4) respectively. The Langmuir isotherm assumes a monolayer adsorption on a surface containing a finite number of adsorption sites, using uniform adsorption strategies without transmigration of the adsorbate to the surface plane [14].

The linearization of the Langmuir equation is written as follows:

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{q_m \times K_L} \dots \dots \dots (3)$$

Where C_e (ppm) is the dye concentration at equilibrium, q_e and q_m (mg/g) are the equilibrium and the maximum adsorption capacity of the adsorbents respectively and K_L is the Langmuir isothermal constant [14].

By plotting the line $C_e/q_e = f(C_e)$ and using the slope, we determine the values of the capacity of the monolayer q_m and of the Langmuir parameter K_L (Fig. 4).

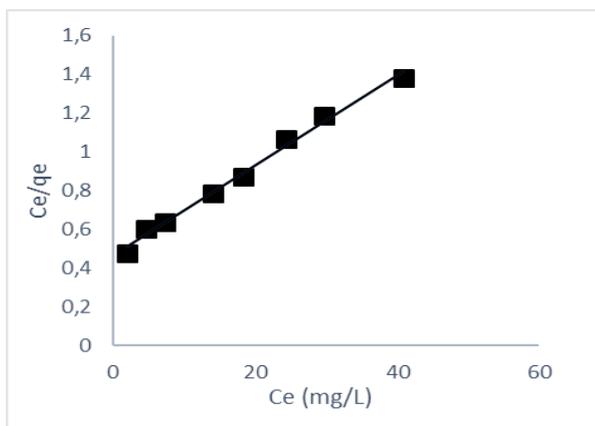


Fig. 4 Langmuir isotherm of adsorption of BR on magnetic bentonite.

If the adsorption is multilayer, it follows the Freundlich isothermal model with a heterogeneous surface on the adsorbent [15]. The following expression allows the isothermal model of Freundlich :

$$\ln(q_e) = \ln k_f + \frac{1}{n} \ln(C_e) \dots \dots \dots (4)$$

k_f et n sont des constantes isothermes de Freundlich et sont associés à l'adsorption maximale de matière et sont déterminées à partir de l'interception et la pente du graphique de $\ln(q_e)$ vs $\ln(C_e)$ respectivement [16] (Fig. 5)

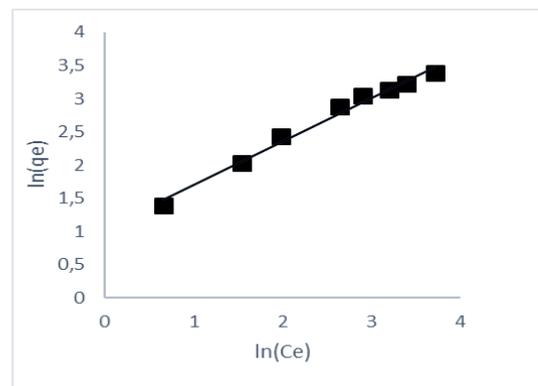


Fig.5 Freundlich isotherm of adsorption of BR on magnetic bentonite.

TABLE I
 ISOTHERM CONSTANTS FOR BR ADSORPTION ON M-Bt

Langmuir			Freundlich		
K_L	$q_m(\text{mg/g})$	R^2	K_F	n_F	R^2
0.049	43.10	0.992	2.861	1.525	0.987

The adsorption of Langmuir and Freundlich isothermal models as shown in the figure 4 and 5. The R^2 values of Langmuir and Freundlich were obtained at 0.992 and 0.987 respectively. This implies that the Langmuir model is better suited than Freundlich model. Therefore, the adsorption of BR on magnetic bentonite could be a single layer covering process. In addition, as shown in Table 1, the modified maximum monolayer adsorption capacity (q_{max}) evaluated value of the Langmuir model was 43.10 mg/g.

E. Adsorption Kinetics:

The analysis of the kinetics of the adsorption process is useful to validate the adsorption mechanism between the adsorbent and the studied solute. In this case, pseudo-first-order [17] and pseudo-second-order [18] kinetic models have been used. The rate expression of the pseudo-first-order model based on the capacity of the adsorbent is the most widely used rate equation for assigning the adsorption rate of wastewater pollutants in different fields and is known as the Lagergren rate equation. It is represented as follows:

$$\ln(q_e - q) = \ln q_e - k_1 t \dots \dots \dots (5)$$

The kinetic expression of the pseudo-second order model was developed by Ho, which demonstrate how the rate depended on the sorption capacity but not on the sorbate concentration. It is expressed as follows:

$$\frac{t}{q} = \frac{1}{q_e^2 k_2} + \frac{t}{q_e} \dots \dots \dots (6)$$

Where q_e and q are the amounts of dye adsorbed (mg/g) at equilibrium and at time t , respectively. k_1 is the rate constant (min^{-1}) and k_2 is the Pseudo-second-order model rate constant ($\text{g mg}^{-1} \text{min}^{-1}$).

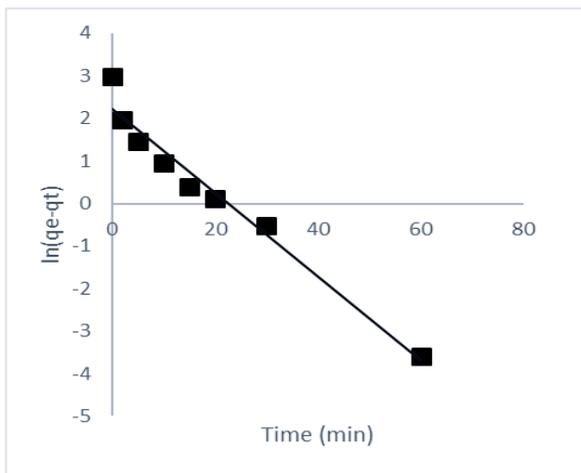


Fig.6 Pseudo-first order for the adsorption of Bemacid Red by M-Bt.

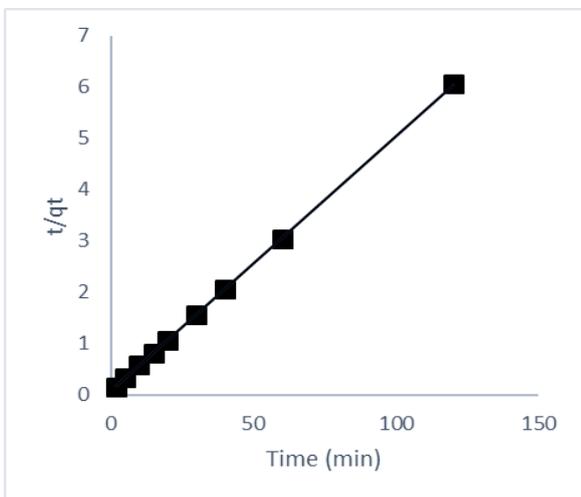


Fig.7 pseudo-second order for the adsorption of Bemacid Red by M-Bt.

The application of the kinetic models (Table II) allows to conclude that the kinetic data obtained follow the pseudo-second order ($R^2 = 0.999$) compared to the pseudo-first order rate model ($R^2 = 0.966$) and the other two models; the pseudo-second order rate model adequately describes the kinetics of sorption.

TABLE III
 KINETIC DATA FOR THE ADSORPTION OF BEMACID RED BY MAGNETIC BENTONITE

models	Parameter	
$Q_c \text{ (exp)}$	19.77 (mg/g)	
Modèle du Pseudo-premier ordre	R^2	0.966
	K_1	0.098
	q_e	9.17
Modèle du Pseudo-second ordre	R^2	0.999
	K_2	0.037
	q_e	20.04

The adsorption capacity (q_e) obtained from the fit to the pseudo-second order rate model (20.04 mg/g) are very close to the experimental values (19.76 mg/g) obtained from the sorption kinetics at equilibrium suggesting that it is applicable to adsorption kinetics and rate constant (k_2) for pseudo-second order sorption, was calculated to be equal to $0.037 \text{g.mg}^{-1} . \text{min}^{-1}$.

F. Thermodynamic studies

The effect of temperature on adsorption capacities was evaluated by performing a series of experiments at 283, 293,298,303,313, and 323 K. This study allows us to determine various thermodynamic parameters such as enthalpy (ΔH), entropy (ΔS) and Gibb free energy (ΔG) of the adsorption of BR by magnetic bentonite.

These thermodynamic quantities allow us to predict the spontaneity of a process. In general, the phenomenon of adsorption is always accompanied by a thermal effect, which can be either exothermic or endothermic. The measurement of heat is the main criterion which makes it possible to differentiate chemisorption from physisorption.

These thermodynamic quantities were calculated using the following equations:

$$\Delta G = \Delta H - T \Delta S \dots \dots \dots (7)$$

$$\Delta G = -RT \ln K_d \dots \dots \dots (8)$$

$$K_d = \frac{(C_1 - C_2)v}{C_e m} \dots \dots \dots (9)$$

$$\ln K_d = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \dots \dots \dots (10)$$

Experimentally from the slope and the interception of the van't Hoff plots, that is to say $\ln K_d$ versus $1/T$ (Fig.8) and the calculated values are presented in Table III.

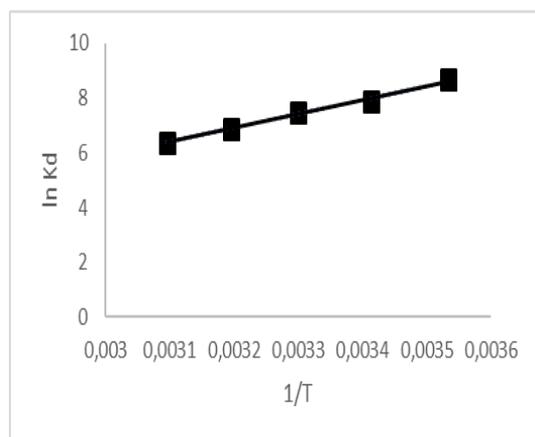


Fig. 8 the evolution of the thermodynamic equation of adsorption of BR by magnetic bentonite. ($[C_0] = 50\text{mg/L}$; $m = 0.01\text{g}$; $\text{pH} = 2.5$; $V = 5\text{mL}$; $t = 60\text{min}$)

TABLE III
 THE THERMODYNAMIC ADSORPTION PARAMETERS OF BR ON
 THE MAGNETIC BENTONITE

T	ΔG (kJ/mol)	ΔH (KJ/mol)	ΔS (J/mol.K)
283	-20.45	-42.69	-79.15
293	-19.17		
303	-18.87		
313	-17.92		
323	-17.13		

The negative value of ΔH suggests that the RB adsorption process is exothermic. The negative value of entropy can be attributed to the fact that the dye molecules lose their randomness when they are adsorbed to the surface of the magnetic bentonite. ΔG values with increasing temperatures indicate that adsorption becomes less favorable at higher temperatures. Negative values of ΔG indicate that the adsorption process is spontaneous.

IV. CONCLUSION

Intercalated with magnetic $\gamma\text{Fe}_2\text{O}_3$ nanoparticles into the bentonite surface generates a porous surface with a large surface area which is suitable for the adsorption of acid dyes like bemacid red. The results of the batch experiments for the removal of Bemacid red showed that the adsorption capacity increases with increasing contact time and initial pH of BR solutions with maximum adsorption capacity at pH 2. The adsorption kinetics data are well adjusted by the pseudo 2nd order kinetic model. The experimental equilibrium data correspond perfectly to the isothermal Langmuir which implies the formation of a monolayer on the surface of the magnetic bentonite. The maximum adsorption capacity was 43 mg/g. Thermodynamic studies have indicated that the adsorption process was exothermic and spontaneous.

REFERENCES

- [1] H.M. Pinheiro, E. Touraud, O. Thomas, "Aromatic amines from azo dye reduction: Status review with emphasis on direct UV spectrophotometric detection in textile industry wastewaters", *Dyes Pigm.* Vol.61, pp. 121–139, 2004.
- [2] S. Chowdhury, R. Mishra, P. Saha, P. Kushwaha, "Adsorption thermodynamics, kinetics and isosteric heat of adsorption of malachite green onto chemically modified rice husk", *Desalination and water Treatment*, vol.265, pp. 159–168, 2011.
- [3] Z. Aksu, "Application of biosorption for the removal of organic pollutants": *A review, Process Biochem.* Vol.40, pp. 997–1026, 2005.
- [4] G. Annadurai, R. Juang, D. Lee, "Use of cellulose based wastes for adsorption of dyes from aqueous solutions", *J. Hazard. Mater.*, vol.92, pp.263–274, 2002.
- [5] V.K. Gupta, Suhas, "Application of low-cost adsorbents for dye removal", *A review, J. Environ. Manage.*, vol.90, pp. 2313–2342, 2009.
- [6] I.A.W. Tan, A.L. Ahmad, B.H. Hameed, "Adsorption of basic dye on high-surface-area activated carbon prepared from coconut husk: Equilibrium, kinetic and thermodynamic studies", *J. Hazard. Mater.*, pp.154 337–346, 2008.
- [7] B.H. Hameed, "Spent tea leaves: A new nonconventional and low-cost adsorbent for removal of basic dye from aqueous solutions", *J. Hazard. Mater.*, vol.161, pp.753–759, 2009.
- [8] R. Gong, M. Li, C. Yang, Y. Sun, J. Chen, "Removal of cationic dyes from aqueous solution by adsorption on peanut hull", *J. Hazard. Mater.* Vol.121, pp. 247–250, 2005.
- [9] B.C. Qu, J.T. Zhou, X.M. Xiang, C.L. Zheng, H.X. Zhao, X.B. Zhou, "Adsorption behavior of Azo Dye C. I. Acid Red 14 in aqueous solution on surface soils", *J. Environ. Sci.* vol.20, pp.704–709, 2008.
- [10] B. Yasemin, A. Haluk, "A kinetics and thermodynamics study of methylene blue adsorption on wheat shells", *Desalination and water Treatment*, vol.194, pp.259–267, 2006.
- [11] K.Y. Foo, B.H. Hameed, "An overview of dye removal via activated carbon adsorption process", *Desalination and Water Treatment*, vol.19, pp. 255–274, 2010.
- [12] Ghania Henini, Ykhlef Laidani & Fatiha Souahi, "Study of the kinetics and thermodynamics of adsorption of Red Bemacid on the cords of *Luffa cylindrica*", *Desalination and Water Treatment*, vol.57, pp.3741–3749, 2016.
- [13] C.C. Wang, L.C. Juang, T.C. Hsu, C.K. Lee, J.F. Lee, "Adsorption of basic dyes onto montmorillonite", *J. Colloid Interface Sci.* vol.273 pp.80–86, 2004.
- [14] Aoopngan, C., Nonkumwong, J., Phumying, S., Promjantuek, W., Maensiri, S., Noisa, P., Pinitsoontorn, S., Ananta, S., Srisombat, L. "Amine-functionalized and hydroxyl-functionalized magnesium ferrite nanoparticles for Congo Red adsorption". *ACS Appl. Nano Mater.* vol. 2, 2019.
- [15] C. Santhosh, P. Kollu, S. Felix, V. Velmurugan, S.K. Jeong, A.N. Grace, "CoFe₂O₄ and NiFe₂O₄@graphene adsorbents for heavy metal ions-kinetic and thermodynamic analysis", *RSC Adv.* vol.5. pp.4-5, 2012.
- [16] Jia, S., Tang, D., Peng, J., Sun, Z., Yang, X, "β-Cyclodextrin modified electrospinning fibers with good regeneration for efficient temperature-enhanced adsorption of crystal violet". *Carbohydr. Polym.* vol.208, pp 486-494, 2019.
- [17] Ho YS, McKay G." Pseudo-second order model for sorption processes". *Process Biochem.* vol.34, pp.451-465, 1999.
- [18] Tian Y, Wang X, Lian L, Lou D, "Study on adsorption of dye orange II with magnetic cetylpyridinium bromide". *Topics in Chemical & Material Engineering*, 2018.