Available online at http://ijcpe.uobaghdad.edu.iq and www.iasj.net
Iraqi Journal of Chemical and Petroleum Engineering
Vol.19 No.4 (December 2018) 1 – 11
EISSN: 2618-0707, PISSN: 1997-4884

Biosorption of Methylene Blue from Aqueous Solution Using Mixed Algae

Aya Abbas Najim and Ahmed A. Mohammed

Environmental Engineering Department, College of Engineering, University of Baghdad

Abstract

A mixture of algae biomass (Chrysophyta, Cyanophyta, and Chlorophyte) has been investigated for its possible adsorption removal of cationic dyes (methylene blue, MB). Effect of pH (1-8), biosorbent dosage (0.2-2 g/100ml), agitated speed (100-300), particle size (1304-89µm), temperature (20-40˚C), initial dye concentration (20-300 mg/L), and sorption–desorption were investigated to assess the algal-dye sorption mechanism. Different pre-treatments, alkali, protonation, and $CaCl_2$ have been experienced in order to enhance the adsorption capacity as well as the stability of the algal biomass. Equilibrium isotherm data were analyzed using Langmuir, Freundlich, and Temkin models. The maximum dye-sorption capacity was 26.65 mg/g at pH= 5, 250 rpm, 89µm, 25˚C, and 50 mg/L as initial concentration. Four kinetic models were tested, pseudo first order, pseudo second order, intra- particle diffusion and Elovich model. Taking into account the analysis of the (SSR and X^2), the data were best fitted to Temkin isotherm model. The pseudo-second order with higher coefficient of determination fitted the data very well. Thermodynamic parameters (ΔG^0, ΔH^0, ΔS^0, E_a and S*) at temperature ranges of 293–313 K demonstrated that biosorption is an endothermic, spontaneous reaction and higher solution temperature favors MB removal by adsorption onto algae biomass. Results show that adsorption- desorption process lasts for five cycle before losing its efficiency and the recovery efficiency increased up to 80.52%.

Keywords: cationic dye, adsorption, desorption, algae, endothermic

Received on 02/10/2018, Accepted on 13/11/2018, published on 30/12/2018

https://doi.org/10.31699/IJCPE.2018.4.1

1- Introduction

Many industries, such as textiles, plastic, leather, dye manufacturing, sugar manufacturing, carpet, pulp, cosmetic and paper use pigments to color their products **[1]**.

Serious pollution of surface waters, ground waters and soil is caused by the colored effluent discharged by these industries. Among the above cited industries, textile and dye manufacturing industries are the main source of dye contamination that on discharge creates serious environmental problems **[2]**.

Synthetic dyes are dangerous toxic organic compounds which have a major negative environmental impact, and cannot degrade completely due to the presence of the atomic rings that afford high thermal, physiochemical, and optical stability **[3]**, **[4]**.

Therefore the present of these dyes in water is unwanted due to inhibiting photosynthetic action, affects the nature of the water so decrease site value for swimming, boating and fishing, even at low concentrations the physio-chemical properties of the ecosystem are changed and prevent light penetration into water, it is hard to be treated by conventional treatment system. Biodegradation or biological treatment of textile industry dyes is ineffective, time-consuming and very difficult because such dyes must have a high photolytic and chemical stability **[5]**.

Methylene Blue (MB) dye has several side effects such as eye burns, dyspnea, a burning feeling while ingestion through the mouth, vomiting, profuse, plentiful sweating, blood problems, nausea, and mental distraction **[5], [6], [7]**.

Various methods for dye contaminant treatment include ozone treatment, photochemical oxidation, cation exchange membranes, ultrafiltration, nano-filtration, electro-chemical degradation, reverse osmosis, and anaerobic degradation **[8]**. Nevertheless, those mentioned treatments have many limitations, such as expensive, corrosion, low efficiency, require sensitive operating conditions, consume large amount of energy and chemical reagents, imperfect removal of colored, and produce huge quantity of sludge **[3]**, **[9]**.

Compared to the above cited methods, adsorption has been proven to be more effective, because it offers many benefits such as simple to design, cost effective, non-sensitivity to toxic materials, and easy to operate. Adsorption has some limitations such as problems faced in segregating sorbent from sorbate in order to be regenerated and spent adsorbent may be considered a hazardous waste.

Adsorption is traditionally done by using activated carbon.

Corresponding Authors: Aya Abbas Najim, Email: ayaaabbas@yahoo.com, Ahmed A. Mohammed, Email: ahmed.abedm@yahoo.com
IJCPE is licensed under a Creative Commons Attribution-NonCommercial 4.0 International License.

Yet, the high cost of the activation processes limits its usage in wastewater treatment processes, ineffectual against disperse and vat dyes moreover, there is regeneration problems, as well as, after adsorption process it is difficult to separate the treated activated carbon from the bulk solutions **[10]**, **[11]**. Adsorption is a multi-step process, comprising of four consecutive elementary steps in the case of biomass; the adsorption of solute from solution by adsorbent with pores, the transport of the moving contaminating ions to the outer surface of the biomass (film diffusion), the movement of the solute from the particle surface into interior site by pore diffusion, and finally the adsorption of the adsorbate that takes place into the active sites inside adsorbent particle. The third phenomenon, between these three processes, is take into consideration to be faster and is not the step that limits organic compounds uptake **[6]**, **[10]**.

Over the last decade, many paths have been done to promote inexpensive and effective adsorbents to remove contaminants from a set of starting materials such as agriculture waste and biological material (bacteria, fungi, yeast, algae, and plants) **[12]**, **[13]**. Algae is one of the most favorable sources of protein supplements, biofuel, biosorbent, and organic fertilizer owing to their advantages like capacity to use fresh, marine or wastewater, reduce greenhouse gas from the environment, do not compete with food yields, and non-requirement of fertile land **[14]**. It is an efficient biosorbent to be used for dyes removal from wastewaters discharges by industrial activities and gainful, due to the functional groups (amino, hydroxyl, sulfate, and carboxyl) located on the cell surface, which play an active role in the biosorption process **[15]**. Maurya et al [14] showed that the De-Oiled Algal Biomass DAB (10 g/ L) removes 86% of the dye (50 mg/ L) in 5 minutes under static condition and nearly 100% in 24-hours with agitation at 150 rpm, which indicates the MB removal by DAB in static conditions is more feasible as it requires lesser energy input. The objective of this work is to examine the ability of mixed algae as an adsorbent for the removal of cationic (basic) dye from simulated wastewater under various pH values, algae dosage, contact times, initial methylene blue dye concentrations, temperature, different shaking speed and different algae particles size. Moreover different substances with different concentration for algae pretreatment, and desorption - recovery process by using different concentration of nitric acid to reuse the biomass was also evaluated. Equilibrium and kinetic models were used to estimate the sorption potential and the rate of reaction respectively.

2- Experimental Work

2.1. Preparation of Biomass and Adsorbate

Mixed algae consist of (80% Chrysophyta, 5% Cyanophyta, 14% Chlorophyte, and 1% Microscopic animals). These algae were collected from the Tigris River, Iraq. After that, the collected algae was washed many times with tap water to get rid of impurities, dirt and other unwanted materials such as (non-vertebrate animals, small worms, crustaceans, bird feathers), then with distilled water twice to ensure clearness. The washed algae was left under the sun for three days to dry and then dried in an oven (Model: F62700, Barnstead Thermolyne, Germany) at 60°C for 3 h to ensure that the sample is dried completely. The dried algal biomass were cut off, crushed in a mechanical mill and sieved, average size of (1304, 500, 177, and 89) **µ**m particle diameters. Thirty grams of dried algae biomass 177 µm diameter were treated with 500 ml of NaOH, $CaCl_2$ and HCl for 1 hr at different concentrations (0.05 M, 0.1 M, and 0.5 M), then put in a shaker at 50 rpm for 1 hr to improve the biosorption capacity to methylene blue.

The mixture was filtered, washed several times with distilled water till the solution pH value reached 7.0 and then the algal biomass dried at 60 ˚C for a period of 4 hr in the oven.

The dye utilized in this study was Methylene Blue (CI 52015; CAS No=7220-79-3; chemical formula: $C_{16}H_{18}ClN_3S.3H_2O$; molecular weight = 373.90 g/mole.; minimum assay=99.0%; HIMEDIA), a cationic thiazine. Synthetic aqueous stock solution 1000 mg/l of methylene blue was prepared by dissolving 1.0 g of MB in 1L of distilled water. For all experiments, the concentration of MB was determined by an UV-visible spectrophotometer (Cary-100 conc., Varian, USA) at a wavelength corresponding to the maximum absorbance of the dye solution (λmax= 662 nm), using 0.1 N of NaOH and HCl to get the desired value of the initial pH. HNO_3 (0.05M and 0.1) M was used for sorbent desorption.

2.2. Batch Experiments

The experiment on the effects of pH was conducted by mix-up 0.5 g adsorbent dosage with 50 ppm of MB solution at different pH (1-8), and then the flasks were shaken at 200 rpm for 2 hr. For studying the influence of various biomass dosages on the MB percentage removal, experiments were conducted by varying the biomass dosage (0.2-2 g/100 ml) with 50 mg/L MB solution.

Shaking speed effects on MB adsorption was investigated by using 50 mg/L solution at various shaking speed (100, 200, and 300 rpm) with best values of biomass dosage and pH.

To investigate whether particle size (1304, 500, 177, and 89 µm) affected the removal of MB, the experiment was carried out using 50 mg/l of MB solution (pH=5, 7g/L adsorbent, 250 rpm shaking speed, and 120 min shaking time).

To study the effect of shaking time and initial MB concentration on the percentage removal, experiments were conducted by mixing 0.7 g/100 ml adsorbent dosage with different MB concentrations (20, 50, 100, 200, and 300 mg/L) for 3 hr. at best conditions obtained from the previous experiment. The impact of the temperature on MB adsorption was studied by changing the temperature (20, 25, 30, 35, and 40) using shaking incubator (ISO 9001, model: LSI-3016A, NO.B110416002, Korea) at the best conditions obtained from the previous tests.

The results from these experiments were used to calculate the associated thermodynamic parameters. Adsorption–desorption experiments were carried for (0.05 M and 0.1 M HNO_3) discretely up to five cycles. A single cycle system is composed of adsorption step (120 min) followed by desorption step (60 min) (pH, 5.0; biosorbent, 0.7g/100 ml; agitation, 250 rpm; dye concentration, 100 mg/l; temperature, 25˚C; adsorption contact time, 120 min; desorption time, 60 min). The dye loaded algal biomass after adsorption, was filtered, dried in air then reintroduced into desorption solvent (0.05 M and 0.1M) HNO_3 (0.7 g/ 100 ml, HNO_3). The biosorption capacity and removal efficiency were calculated as follows **[16]**:

$$q_e = \frac{(ci-ce)V}{m} \quad (1)$$

$$\% \text{ Removal efficiency} = \frac{Ci-Ce}{Ci} * 100 \quad (2)$$

Where C_i and C_e are the initial and equilibrium dyes concentration in the solution (mg/L), V is the volume of solution in (L), and m the quantity of biomass applied in (g).

The eluting efficiencies of the desorbent Ed are expressed as follows **[17]**:

$$E\ (\%) = \frac{md}{mad} \text{x } 100 \quad (3)$$

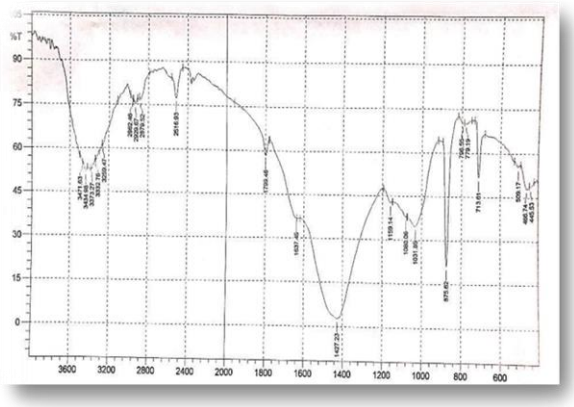
m_{ad}: total adsorbed quantity of MB, mg/l , m_d :the MB mass desorbed, mg/l

3- Results and Discussion

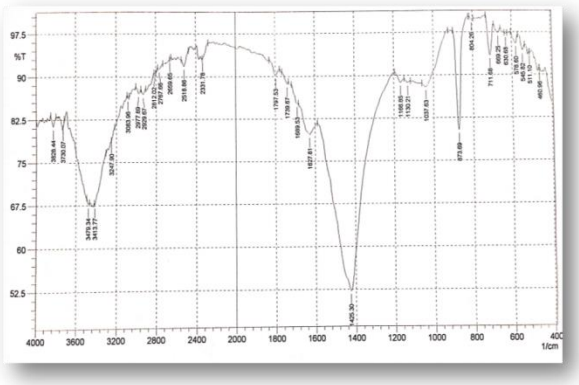
3.1. FT-IR Analysis

The purpose behind the FTIR analysis is to identify the different functional groups found in algae that's responsible for the adsorption process and to pin point the changes that take place in the algae biomass structure **[18]**. **Fig. 1** shows the results of the notice IR absorption frequencies in different regions for algae before and after biosorption of MB. The peaks show in the FTIR spectrum were allocated to several functional groups according to their own wave numbers. The band at 3700-3000 cm^{-1} is O-H and N-H stretching of (alcohols, phenols, and carboxylic acids), and 3400-3200 cm^{-1} is stretching of polymeric compounds; 2962-2853 cm^{-1} interval is stretching vibration of C-H especially alkyl chains, intense band at 2000-2500 cm^{-1} interval for carboxylic acid, 1720-1431 cm^{-1} interval for the presence of amide, carboxylates, sulfonates, and ketone groups.

The C-O, C-C, C-OH stretching vibration referred to peaks in the region of 1359-1041 cm^{-1}, while bands in the fingerprint regions (900–750 cm^{-1}) referred to the aromatic –C–H groups. From Figure 1, we noticed that after biosorption of the dye molecules, a shifting or disappearance of some peaks as well as the emergence of new ones. The reason behind these shifts is the binding process that occurs on the surface of the biomass.



(a)



(b)

Fig. 1. FTIR peaks of transmittance of MB, (A) before adsorption, (B) after adsorption

3.2. Effect of pH

The pH is a significant feature impacting the adsorption studies. This was because pH effects the function groups on the biomass surface and determines dye solubility in the aqueous solution **[19]**.

Dependence of organic and inorganic biosorption on pH is associated to both the ionization state of functional groups of the adsorbent which affects the availability of binding sites and the contaminants chemistry (complexation by organic and/or inorganic ligands, hydrolysis, precipitation and redox reactions) in the solution **[20]**. The effect of solution pH on the sorption of dyes on the sorbent was studied by altering the pH in range (1-8). The increase in pH cause an increase in percentage sorption as depicted in **Fig. 2**. The minimum sorption was observed at low pH (pH= 1.0-4.0) due to the existence of higher H^+ ion concentration which is favored sorption in comparison with other cationic pollutants. At higher concentration of H^+ ions, the biomass surface will be farther positively charged thus reducing the attraction force between adsorbent and cation pollutant **[16]**. At pH values (5–8), the removal percentage of dye was almost constant.

The solute (dye ions) uptake can be related to the chemical structure of the solute in the solution and also to the active sites located at the biomass surface. The removal percentage of methylene blue (MB) reaches maximum at pH 5, no significant altered beyond pH 5 was observed because when pH is high, the adsorbent particles surface may be negatively charged causing the enhancement the cationic dyes through electrostatics forces of attraction.

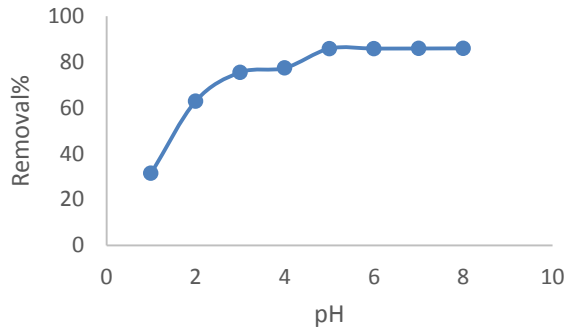


Fig. 2. pH effect on the removal efficiency of MB (m=0.5 g/100 ml, C_i= 50 mg/l, T= 25˚C, 89µm, speed= 200 rpm, and time=120 min)

In general non- treated algal biosorbent has alkali and alkaline earth metals such as Na^+, Mg^{2+}, K^+ and Ca^{2+} which are essentially tied to the acid functional groups of the algae and were attained from sea water [20]. The pH and EC were measured at different time intervals during the agitation process. Fig. **3** shows the increase in the electrical conductivity (EC) and pH values with time. In this case, the cations of light metals were being eluted from the algal biomass during the experiments, while the cationic dyes were being sorbed onto the biomass. It was noticed that the solution final pH was greater than the initial value, attributed to ion exchange mechanisms, hence, the witnessed release light metals well-adjusted the uptake of cation. Accordingly, the light metals released, when algae biomass reacts with the cationic pollutants causing an increase in the pH as a result of formation of light metal alkalis [21].

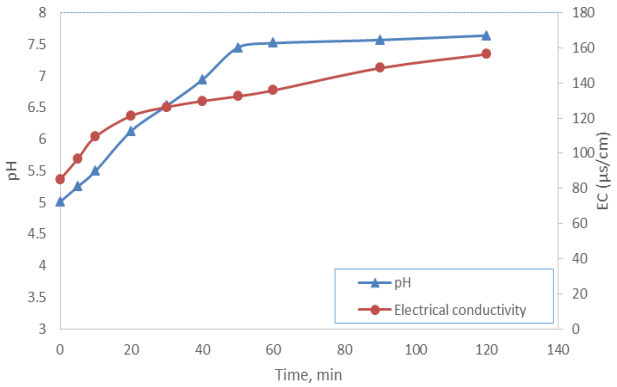


Fig. 3. pH and EC evolution as a function of time dyes biosorption, (m=0.7 g/100 ml, T=25˚C, C_i= 50 mg/l, 89 µm at 200 rpm)

3.3. Effect of Biomass Dosage

The doses (mass) of adsorbent effects on the adsorption of MB are shown in **Fig. 4**. The biomass dosage is an important parameter used to determine the capacity of biosorbent for specific initial concentration **[3]**. In this paper different amount of algae biomass (0.2-2 g/ 100 ml) were used. An increasing amount of algal biomass may be able to fully adsorb the pollutants or reach an equilibrium state when reaching a plateau at a fixed concentration of each pollutant **[3]**, **[11]**. It is obviously noticed that the removal percentage of MB increases from 61.94 to 92.43%, as the algae dosage increases from 0.2 to 0.7 g.

After some point (above 0.7 g), adsorption removal efficiency was steady credited to a screen effect between adsorbent **[21]**, or the observed behavior occurred because at the initial stage there were sufficient binding sites for the complexation of dye molecules and increasing the dose beyond 0.7 g resulted in the establishment of equilibrium between the cationic dyes bounded to biosorbent and those remaining un-adsorbed in the mixture **[12]**, or because high adsorbent amounts are known to cause agglomeration and accordingly reduce the distance between biomass leading to protecting the binding sites from contaminants **[10]**. Increasing biomass concentrations results in increases final bio-removal although it has negative effects on biosorption capacity because fixed initial concentration leads to unsaturated active site on biomass surface and the increase in the biomass concentrations cause particle aggregation **[3]**.

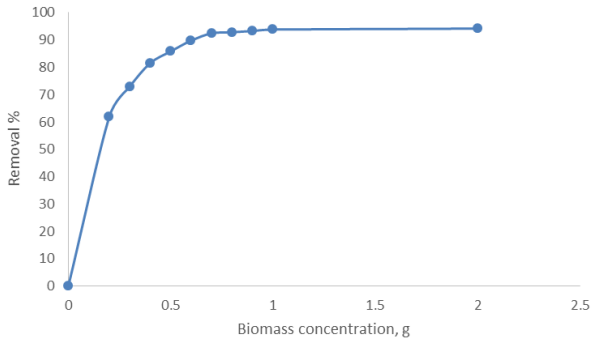


Fig. 4. Effect of sorbent amount on the removal efficiency of MB by algae biomass (pH 5, T= 25˚C, C_i=50 mg/l, 89 µm, speed = 200 rpm and time=120 min)

3.4. Effect of Shaker Speed

With suitable agitation speed, the resistance of mass transfer can be reduced. The solution rate of diffusion (from the bulk liquid to the liquid boundary layer surrounding particles) becomes higher because turbulence improves and the liquid boundary layer thickness is reduced, as a result of increasing the agitation rate **[13]**.

Shaker speed affects the spreading of dye molecules in solution and also disrupts the film resistance surrounding the adsorbent particles by influence the uptake of dye molecules.

When speed of the shaker increased from 100 to 300 rpm, the time required to achieve equilibrium was reduced, so the available biomass surface area increases due to the deficiency of aggregation of the biosorbent that finally leads to rapid adsorption of MB **[14]**.

Furthermore, these results obviously show that 250 rpm is adequate to gain maximum percentage removal of MB as shown in Fig. **5**, no significant altered beyond this point was observed because the solution has reached equilibrium.

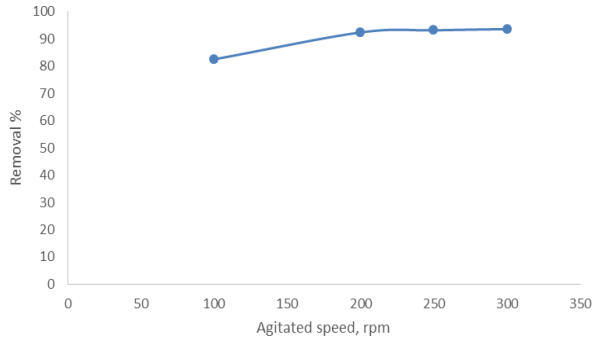


Fig. 5. Effect of shaker speed on the removal efficiency of MB (pH 5, m= 0.7 g/100 ml, T= 25˚C, Ci= 50 mg/l, 89 µm, and time=120 min)

3.5. Effect of Particle Size of Biomass

Surface area of the biomass is a key parameter for sorption. Fig. **6** shows the relationship between the size of sorbent particle and the removal efficiency.

The results show an adverse relation between the removal efficiency and particle size, the former increase with later decrease.

The higher sorption level attained by the smallest sorbents particle size connected to the notation that smaller particle sizes provide large surface areas and exhibit faster adsorption more than that of sorbents with lower surface area.

The removal efficiency decreased from 93.19 to 66.82 % as the particle size increased from 89 to 1304 µm.

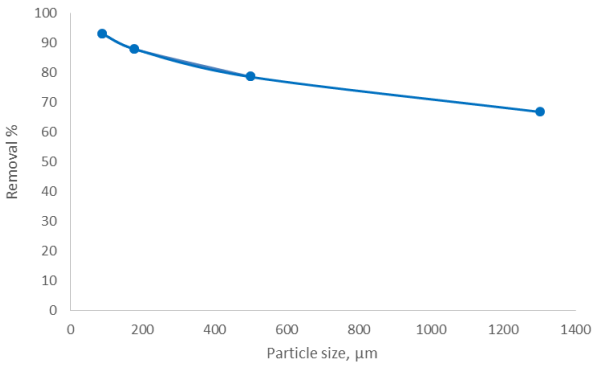


Fig. 6. Effect of particle size diameter of sorbent on the removal effeciency of MB (pH 5, m= 0.7 g, T= 25˚C, speed= 250 rpm, C_i= 50 mg/L, and time=120 min)

The diffusional resistance to mass transfer is greater for large particles, but the smallest size allows very fast removal kinetics if the adsorption is to be primarily a surface phenomenon **[8]**. There is a tendency as fine particles takes lesser time to equilibrium in shorter time.

3.6. Effect of Initial Concentration with Time

The initial concentration of MB affords a main driving force to outweigh all mass transfer resistance between the aqueous and solid phases **[8].** The experiments were performed at distinct initial MB concentrations (20 to 300 mg/L). From Fig. **7** it notes that the percentage removal decreases from: 98.97 to 65.48%, as the initial concentration increased from 20 to 300 mg/L. One of the most essential parameters affecting the biosorption efficiency, modeling and designing the adsorption process in the industry is the contact time. It was inferred that the amount of MB adsorbed was fast for the first 15 min and after that, a slower pace (15–60 min) for the range 20-100 mg/L, (15-120 min) for 200-300 mg/L, and finally reached saturation. The available sites saturation occurs much earlier when the solution contains a higher initial dye concentration, resulting in a solution with high dye content at equilibrium **[14]**. It can be seen that the percentage removal was not altered significantly when the concentration increased from 20-50 mg/L because the dosage of algae may have sufficient sites that can be exchanged for the above mentioned range. However, by increasing concentrations to 100, 200 and 300 mg/L, a sharp reduction in percentage removal was obvious due to insufficient exchangeable sites in the biomass to accumulate these concentrations. Pirbazari et al **[10]** show that 80 min duration is the contact time was needed for MB solutions with initial concentrations of 50–200 mg/L to reach equilibrium.

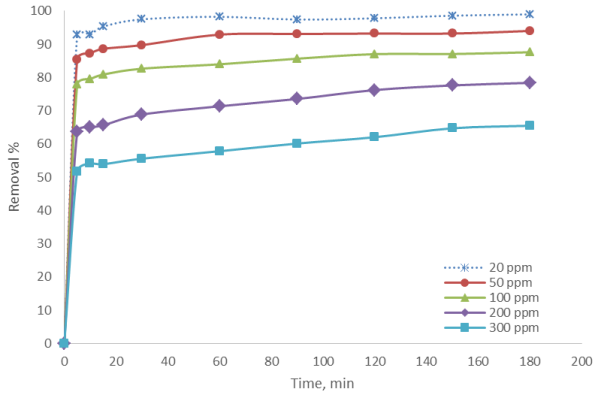


Fig. 7. Effect of initial concentration with time on the removal efficiency of MB (pH 5, m= 0.7 g, 25˚C, speed= 250 rpm, 89 µm, and time=180 min)

3.7. Effect of Temperature and Thermodynamic Parameter:

Temperature has a vigorous influence on adsorption process as it can affect the process by an increase or decrease in the amount of adsorption.

Yu and Luo, **[9]** show that temperature is an essential factor for the real application of MAC as most of the textile dye effluents are produced at relatively high temperature. The results are plotted in Fig. **8** and the values of thermodynamic parameters are tabulated in Table **1** which shows the adsorption efficiency of MB onto algae biomass at five different temperatures of 20, 25, 30, 35, and 40^{o}C. It can be seen that with increasing temperature the percentage removal increases, suggesting that endothermic nature of the process. This effect may be due to the fact that at higher temperature, an increase in active sites occurs due to bond rupture **[10]**, or an increasing of the surface area available for the sorption because pores in algae were enlarged, penetration of contaminants within the pores of algae, diffusion, and the equilibrium capacity of the adsorbent will be modified for a particular adsorbate **[9]**. The removal efficiency increase as temperature increase till it reaches 40˚C. At higher temperature, texture of biomass was changed, as a results damaging and reduce number of functional groups, that's why temperature was limited to 40˚C **[18]**.

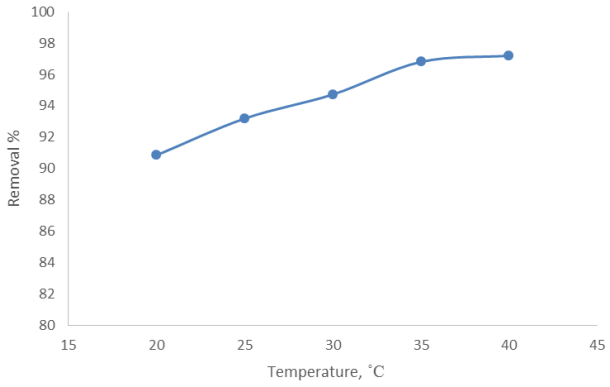


Fig. 8. Effect of temperature on the removal efficiency of MB (pH 5, m= 0.7 g, Ci= 50 mg/l, speed= 250 rpm, 89 µm, and time=120 min)

A linear plot with intercept of ln S*and slope of Ea/R will be observed by plotting (1−θ) against 1/T. The positive values of ΔH° and E_a reveal that: adsorption is endothermic and higher solution temperature favors MB removal by adsorption on algae biomass **[3]**. Similarly, the ΔS° values are positive indicating increasing in randomness at the solid/ solution interface during their sorption. The negative values of ΔG at all temperatures range studied showed that the process is spontaneous with high affinity of MB to dried algae **[3]**. The value of sticking probability S* is found very close to zero indicating that the adsorption process follows chemisorption [10].

$$\ln K_C = \left(\frac{\Delta S^{\circ}}{R}\right) - \left(\frac{\Delta H^{\circ}}{RT}\right) \quad (4)$$

$$\Delta G^{\circ} = \Delta H^{\circ} - \Delta S^{\circ} T \quad (5)$$

$$KC = \frac{Cad}{Ce} \quad (6)$$

$$S^* = (1 - \theta) \exp - \left(\frac{Ea}{RT}\right) \quad (7)$$

$$\theta = \left(1 - \frac{Ce}{Ci}\right) \quad (8)$$

Where: Kc stands for the equilibrium constant, C_{ad} stands for the adsorbed concentration of MB on the adsorbent per liter of the solution at equilibrium (mg.l^{-1}), Ce is the equilibrium concentration of MB in the solution (mg.l^{-1}), ΔH° stands for the biosorption process enthalpy (kJ/mole), R stands for the universal gas constant (8.314 J/mole. K), ΔS° stands for the biosorption process entropy (J/K. mole), ΔG° stands for the Gibbs free energy of biosorption (kJ/mole), T stands for the solution temperature (K), θ is surface coverage, S* is sticking probability, and Ea is activation energy.

Table 1. The thermodynamic parameters for the sorption of MB on algae biomass

T(K)	ΔG^{o} (kJ/mol)	ΔS^{o} (J/mol K)	ΔH^{o} (KJ/mol)	Ea (kJ/mol)	S*
293	-5.558	190.615	50.2922	47.645	2.986E-10
298	-6.511				
303	-7.464				
308	-8.417				
313	-9.370				

3.8. Desorption

The recyclability of an adsorbent is of fundamental importance in industrial practice for pollutant removal from wastewater **[22]**. Desorption of the adsorbed MB from the tested algae biomass were studied in a batch system. The dye adsorbed onto biosorbent was eluted with various concentrations of nitric acid.

More than 80% of the adsorbed MB was desorbed from the biosorbent by using 0.1 M HNO_3 in the first cycle. If desorbent achieves the assigned standards, it is promising to recover the adsorbate in concentrated form and to regenerate the biosorbent in order to use it in another biosorption cycle. In order to show the reusability of algae biomass, adsorption- desorption cycle of pollutants was repeated five times by using the same preparations. The recovery percentages using two concentrations of HNO_3 from algae biomass are calculated from Eq. (3).

Nitric acid was used for this purpose because at acidic condition the adsorbent surface protonate by replacing the adsorbed pollutants on the adsorbent surface leading to desorption of positively charged pollutants or due to the fact that most biosorption exhibit an ion-exchange mechanism for cations and thus increasing the acidity of species loaded algae leads to leaching of cations pollutants from biosorbent **[23]**.

The sorption process of contaminants is not completely reversible due to diffusion of trace contaminants within oxide particles or into micro pores, incorporation of contaminants into oxides, precipitation, re-adsorption, and chemisorptive adsorption of contaminants onto adsorbent hinders the desorption of contaminants from the spent biomass **[24]**.

He et al., **[5]** used acetonitrile to desorbe methylene blue from Nano-crystalline Cellulose, the results show that only 18% of MB was desorbed so acetonitrile was not very effective. Nevertheless, more than 90% removal after 7 desorption cycles was achieved by using ethanol. The results of adsorption- desorption processes are shown in Fig. **9**.

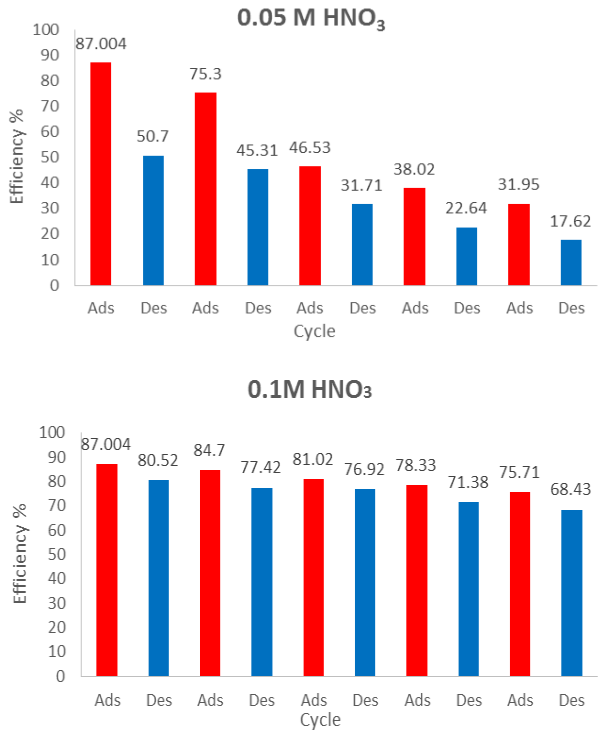


Fig. 9. Five cycle of adsorption- desorption for MB with two different concentration of HNO_3 (pH 5, m= 0.7 g, C_i= 100 mg/l, 89 µm, speed= 200 rpm, T= 25 ˚C, adsorption time=120 min, and desorption time= 60 min)

3.9. Results of Pretreatment

Treated biosorbent generally involves one of two chemical modifications. The first, the biosorbent is interacted with a high concentration of a given ion in aqueous solution consequently, the majority of the sites are occupied by, materials such as calcium, sodium, or potassium.

The second is protonation of the biomass with a strong acid such as HCl, so the proton transfers the light metal ions from the binding sites **[21]**.

The most common algal pretreatments are NaoH, $CaCl_2$, HCl, formaldehyde, and glutaraldehyde **[25]**. In this review, algae biomass was treated with sodium hydroxide (0.05, 0.1, and 0.5) M, calcium chloride (0.05, 0.1, and 0.5) M, and hydrochloric acid (0.05, 0.1, and 0.5) M to improve the biosorption capacities to methylene blue dye.

From Fig. **10**, the modification of algae biomass by chloride calcium has removal efficiency lower than NaOH but better than HCl, the adsorption efficiency decreased with the strength of the acidity.

Alkali treatment with NaOH creates additional basic sites for binding MB cations while acid-treated bleaching earth is a better adsorbent for reactive dyes and acid dyes than for basic dyes **[26]**.

Lignocellulosic materials treatment with sodium hydroxide can cause a decrease in crystallinity, a decrease in the degree of polymerization, swelling which leads to an increase in internal surface area, separation of structural linkage between lignin and carbohydrates, increase in the amount of galactouronic acid groups after hydrolysis of O^- methyl ester groups, removes natural fats and waxes from the cellulose fiber surfaces thus revealing chemically reactive functional groups like ^-OH, and disruption of the lignin structure, the decrease in copper removal at high NaOH concentration, due to the destruction of biomass.

For the adsorption of cationic dyes, the surfaces of biomass must be negatively charged. Pretreatment by chloride calcium causes calcium binding to alginate that plays a significant role in ion exchange.

To increase the contaminants removal efficiency by algae biomass, $CaCl_2$ consider a cost- effective treatment **[25]**. Although acid modification decrease organic content (lignin, and hemicellulose) of adsorbent and increase porosity, positively charged surfaces with hydrogen ions prevented to extra increase of adsorption **[19]**.

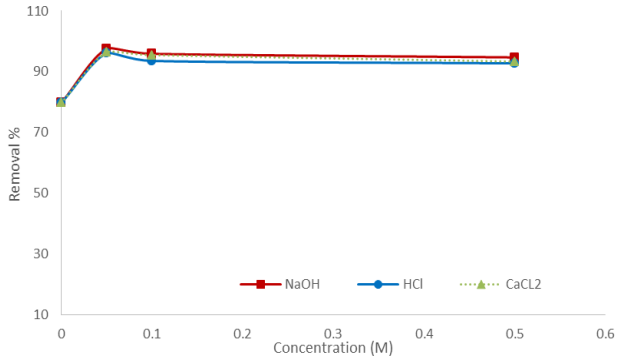


Fig. 10. Modification of algae biomass using different concentrations of NaoH, $CaCl_2$, and HCl to remove dyes from solution (pH 5, m= 0.6 g, Ci= 50 mg/l, 177 µm, speed= 200 rpm, and time=120 min)

4- Biosorption Isotherm and Kinetics Models

A very essential tool for the investigation of sorption process is sorption isotherms. Establish the connection between the amount of adsorbate adsorbed and the equilibrium concentration at a constant temperature by the unit weight of adsorbent. Langmuir**,** Freundlich, and Temkin isotherm models are widely used to study the sorption process.

The model parameters can be construed further, providing understanding of sorption mechanism, surface properties, and an affinity of the sorbent. The Langmuir adsorption has been the most widely used adsorption isotherm for the adsorption of a solute from a liquid solution **[1]**.

The Langmuir model assumes a monolayer adsorption of solutes onto a surface comprised of identical sites with homogeneous biosorption energy **[3]**. The multilayer sorption and the sorption on heterogeneous surfaces model by using the Freundlich equation **[7]**.

Temkin isotherm has a factor that obviously taking into the account of adsorbent–adsorbate interactions.

The model presumed that the heat of adsorption (function of temperature) of all molecules in the layer, by ignoring the extremely low and large values of concentrations, decreases linearly rather than logarithmic with coverage **[27]**.

The experimental data was analyzed by using non-linear isotherm models. The non- linear isotherm model parameters were evaluated by using Microsoft Excel SOLVER software. These models are plotted in Fig. **11**, tabulated in Table **2** and the results are shown in Table 3. It can be seen that Temkin model has the higher coefficient of determination R^2.

The biosorption kinetics is very important to study the removal of contaminants from wastewater, as it offers valued insights into sorption reaction mechanism and the reaction pathways **[28]**.

Pseudo- second- order model better fits the experimental data compared to the pseudo- first- order model, particle diffusion model and Elovich model according to higher value of correlation coefficient (R^2).

This means that biosorption of MB occurs in a monolayer on the surface of adsorbent. The rate limiting step may be chemical sorption according to the second order kinetic model assumption **[5]**. The results are shown in Table **4**, figures not shown.

Table 2. Equations for the sorption isotherm and kinetics models

Model	Equation used	Reference
Langmuir Isotherm	$q_e = \frac{q_m\, b\, Ce}{1+b\, Ce}$	[27]
Freundlich Isotherm	$qe = K\, Ce^{1/n}$	[27]
Temkin isotherm	$qe = BT \ln K_T\, Ce$, $B_T = \frac{RT}{bT}$,	[27]
Pseudo-first-order	$\ln (q_e - q_t) = \ln q_e - k_1 t$	[3]
Pseudo-second-order	$\frac{t}{q_t} = \left(\frac{1}{k_2 q_e^2} + \frac{t}{q_e}\right)$	[3]
Intra- particle diffusion	$qt = kpt^{1/2} + C$	[4]
Elovich model	$q_t = \frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta}\ln(t)$	[29]
Sum square error (SSE)	$\sum (q_{e,calc} - q_{e,meas})^2$	[30]
Nonlinear chi-square test (X^2)	$\sum \frac{(qe,calc - qe,meas)2}{qe,meas}$	[30]

Where, q_e is the sorbed dyes molecules on the adsorbent (mg g^{-1}), q_m is the maximum sorption capacity for monolayer coverage (mg g^{-1}), b is the affinity of the binding site (L mg^{-1}), and C_e is MB concentration in the solution at equilibrium (mg L^{-1}).

K_f = constant indicative of the relative adsorption capacity of the adsorbent (mg/g), 1/n = constant indicative of the intensity of the adsorption. k_T is Temkin sorption potential (L mg^{-1}), and BT & b_T are Temkin constants.

qt is MB uptake capacity (mg/g) at any time t; k_1 is the pseudo-first-order rate constant (1/min); and k_2 is the pseudo-second-order rate constant (g/mg. min), K_p (mg/g $min^{0.5}$) is the intra-particle diffusion rate constant, C is the value of intercept that gives an idea about the boundary layer thickness. α is the chemi- sorption rate (mg/g. min) and β is a coefficient in relation with the extension of covered surface and activation energy of chemi-sorption (g/mg).

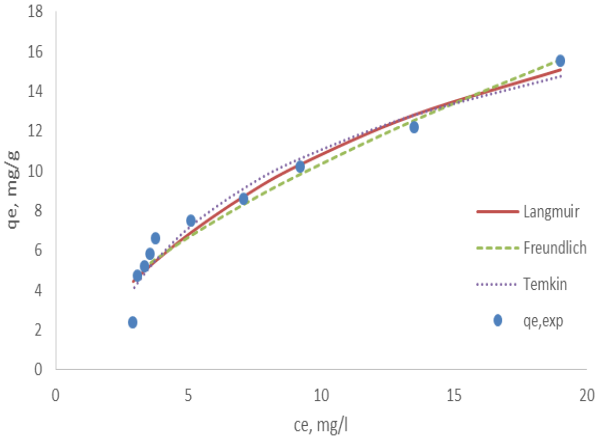


Fig. 11. Isotherm data of MB adsorption onto algae biomass (pH=5; shaking speed=250 rpm, initial dye concentration =50 mg/l, 89 µm, and 25˚C)

Table 3. Parameters of isotherms model for sorption of MB

Type of isotherm	parameters	values
Langmuir	q_m (mg/g)	26.65
	b (l/mg)	0.0685
	R^2	0.9493
	R_L	0.226
	Sum square error SSE	6.908
	X^2	2.1949
Freundlich	K_f	2.388
	n	1.5699
	R^2	0.9429
	Sum square error SSE	7.794
	X^2	2.6931
Temkin	K_T (l/mg)	0.695
	B_T	5.7149
	R^2	0.955
	Sum square error SSE	6.0597
	X^2	1.6221

Table 4. Parameters of kinetic models for sorption of MB

Kinetic models	Parameters	20 ppm	50 ppm	100 ppm	200 ppm	300 ppm
Experimental	q_e	2.8277	6.7134	12.511	22.391	28.063
Pseudo first order	q_e	0.129	0.476	1.447	5.092	6.980
	K_1	0.0153	0.017	0.021	0.02	0.0163
	R^2	0.7154	0.854	0.969	0.9544	0.8804
Pseudo second order	qe	2.827	6.725	12.56	22.57	28.17
	K_2	0.558	0.159	0.051	0.012	8E-3
	R^2	0.9999	1	0.9999	0.999	0.9979
Intra-particle diffusion	C	2.65	6.102	11.02	17.35	21.13
	K_P	0.0144	0.051	0.121	0.39	0.51
	R^2	0.764	0.881	0.959	0.9946	0.9863
Elovich model	α	2.2E21	1.45E14	124.58E9	428679.8	271798.3
	β	20.24	5.875	2.531	0.8118	0.631
	R^2	0.8766	0.9693	0.9933	0.9633	0.9207

5- Conclusions

The results indicated that algae biomass could be used as an efficient biosorbent material for the removal of methylene blue dye molecules from aqueous solution. The higher percentage achieved (98.97%) at pH 5, 0.7 g /100ml biomass dosage, 250 rpm shaking speed, 89 µm particle size, 20 ppm initial dye concentration, and T=25˚C for 120 min. Temkin model fitted the experimental data very well compared to Langmuir and Freundlich models, while the kinetic study well fitted by pseudo second order with very high R^2. The thermodynamic parameters calculated (ΔG°, ΔH° and ΔS°) showed that the biosorption of MB were feasible, spontaneous and endothermic at temperature ranges of 293-313 k. Results show that adsorption- desorption process lasts for five cycle before losing its efficiency and the recovery efficiency increased from 50.7% to 80.52% when the concentration of nitric acid increased from 0.05 to 0.1M. Treated algae with NaOH show the highest removal efficiency compared to $CaCl_2$ and HCl in all its concentrations.

Nomenclature

B: Affinity of the binding site, L/ mg,
B_T & b_T: Temkin constants
C: Value of intercept that gives an idea about the boundary layer thickness, mg/g
C_{ad}: Adsorbed concentration, mg/L
C_e: Concentration at equilibrium, mg/L
C_i: Initial concentration, mg/L
Ea: Activation energy, KJ/ mole
EC: Electrical conductivity, µs/cm
ΔG°: Gibbs free energy, KJ/mole
ΔH°: Enthalpy change, KJ/mole
k_1: Pseudo-first-order rate constant, 1/min
k_2: Pseudo-second-order rate constant, g/mg. min
K_C: Equilibrium constant
K_f: Constant indicative of the relative adsorption capacity of the adsorbent, mg/g
K_p: Intra-particle diffusion rate constant, mg/g $min^{0.5}$
k_T: Temkin sorption potential, L/ mg
m: Mass of adsorbent, g
m_{ad}: Total adsorbed, mg/L
m_d: Desorbed concentration, mg/L
1/n: Constant indicative of the intensity of the adsorption
q_e: Sorbed dyes molecules on the adsorbent, mg/ g
q_m: The maximum sorption capacity for monolayer coverage, mg/ g
q_t: MB uptake capacity, mg/g at any time t
R: Universal gas constant
S*: Sticking probability
ΔS°: Entropy change, J/K. mole
T: Temperature, K
V: Volume, L
Θ: Surface coverage
A: Chemisorption rate, mg/g. min
B: Coefficient in relation with the extension of covered surface and activation energy of chemisorption (g/mg)

References

[1] O. Gulnaz, A. Sahmurova, and S. Kama. "Removal of Reactive Red 198 from aqueous solution by Potamogeton crispus". Chemical Engineering Journal, 174(2-3), 579-585, 2011.
[2] C. C. Ambasana. "Microbial Degradation of Recalcitrant compound". Doctoral dissertation, Saurashtra University, 2006.
[3] R. K. Gautam, A. Mudhoo, and M. C. Chattopadhyaya. "Kinetic, equilibrium, thermodynamic studies and spectroscopic analysis of Alizarin Red S removal by mustard husk". Journal of Environmental Chemical Engineering, Vol. 1, pp.1283-1291, 2013.
[4] H. D. Bouras, A. R. Yeddou, N. Bouras, D. Hellel, M. D. Holtz, N. Sabaou, ... and B. Nadjemi. "Biosorption of Congo red dye by Aspergillus carbonarius M333 and Penicillium glabrum Pg1: Kinetics, equilibrium and thermodynamic studies". Journal of the Taiwan Institute of Chemical Engineers, Vol. 80, pp. 915-923, 2017.
[5] X. He, K. B. Male, P. N. Nesterenko, D. Brabazon, B. Paull, , and J. H. Luong. "Adsorption and desorption of methylene blue on porous carbon monoliths and nanocrystalline cellulose". ACS Applied Materials & Interfaces, Vol. 5, pp. 8796-8804, 2013.

[6] B. H. Hameed, A. M. Din, and A. L. Ahmad. "Adsorption of methylene blue onto bamboo-based activated carbon: kinetics and equilibrium studies". Journal of hazardous materials, Vol. 141, pp. 819-825, 2007.

[7] M. Rafatullah, O. Sulaiman, R. Hashim and A. Ahmad. "Adsorption of methylene blue on low-cost adsorbents: a review". Journal of hazardous materials, Vol. 177, pp. 70-80, 2010.

[8] O. Gulnaz, A. Sahmurova and S. Kama."Removal of Reactive Red 198 from aqueous solution by Potamogeton crispus". Chemical Engineering Journal, Vol. 174, pp. 579-585, 2011.

[9] L. Yu, and Y. M. Luo. "The adsorption mechanism of anionic and cationic dyes by Jerusalem artichoke stalk-based mesoporous activated carbon". Journal of Environmental Chemical Engineering, Vol. 2, pp. 220-229, 2014.

[10] A. E. Pirbazari, E. Saberikhah, M. Badrouh, and M. S. Emami. "Alkali treated Foumanat tea waste as an efficient adsorbent for methylene blue adsorption from aqueous solution". Water Resources and Industry, Vol. 6, pp. 64-80, 2014.

[11] S. Chowdhury, M. Yasin, M. T. Uddin, and M. A. Islam. "Batch and Continuous (fixed bed column) Adsorption of Methylene Blue by Rubber Leaf Powder". International Journal of Integrated Sciences & Technology, Vol. 2, pp. 24-28, 2016.

[12] E. Rubin, P. Rodriguez, R. Herrero, J. Cremades, I. Barbara, and M. E. Sastre de Vicente. "Removal of methylene blue from aqueous solutions using as biosorbent Sargassum muticum: an invasive macroalga in Europe". Journal of Chemical Technology & Biotechnology: International Research in Process, Environmental & Clean Technology, Vol. 80, pp. 291-298, 2005.

[13] M. A. Hossain, H. H. Ngo, W. S. Guo, and T. Setiadi. "Adsorption and desorption of copper (II) ions onto garden grass". Bioresource Technology, Vol. 121, pp. 386-395, 2012.

[14] R. Maurya, T. Ghosh, C. Paliwal, A. Shrivastav, K. Chokshi, I. Pancha,... and S. Mishra. "Biosorption of methylene blue by de-oiled algal biomass: equilibrium, kinetics and artificial neural network modelling". PloS one, Vol. 9, pp. e109545, 2014.

[15] H. Shao, Y. Li, L. Zheng, T. Chen, and J. Liu. "Removal of methylene blue by chemically modified defatted brown algae Laminaria japonica". Journal of the Taiwan Institute of Chemical Engineers, Vol. 80, pp. 525-532, 2017.

[16] G. Annadurai, R. S. Juang, and D. J. Lee. "Use of cellulose-based wastes for adsorption of dyes from aqueous solutions". Journal of hazardous materials, Vol. 92, pp. 263-274, 2002.

[17] S. R. Pilli, V. V. Goud, and K. Mohanty. "Biosorption of Cr (VI) on immobilized Hydrilla verticillata in a continuous up-flow packed bed: prediction of kinetic parameters and breakthrough curves". Desalination and Water Treatment, Vol. 50, pp. 115-124, 2012.

[18] D. Bulgariu, and L. Bulgariu. "Potential use of alkaline treated algae waste biomass as sustainable biosorbent for clean recovery of cadmium (II) from aqueous media: batch and column studies". Journal of Cleaner Production, Vol. 112, pp. 4525-4533, 2016.

[19] M. J. Puchana-Rosero, E. C. Lima, S. Ortiz-Monsalve, B. Mella, D. da Costa, E. Poll, and M. Gutterres. "Fungal biomass as biosorbent for the removal of Acid Blue 161 dye in aqueous solution". Environmental Science and Pollution Research, Vol. 24, pp. 4200-4209, 2017.

[20] A. H. Sulaymon, A. A. Mohammed, and T. J. Al-Musawi. "Comparative study of removal of cadmium (II) and chromium (III) ions from aqueous solution using low-cost biosorbent". International Journal of Chemical Reactor Engineering, Vol. 12, pp. 477-486, 2014.

[21] T. A. Davis, B. Volesky, and A. Mucci, "A review of the biochemistry of heavy metal biosorption by brown algae". Water research, Vol. 37, pp. 4311-4330, 2003.

[22] N. Feng, X. Guo, S. Liang, Y. Zhu, and J. Liu. "Biosorption of heavy metals from aqueous solutions by chemically modified orange peel". Journal of hazardous materials, Vol. 185, pp. 49-54, 2011.

[23] Z. Kariuki, J. Kiptoo, and D. Onyancha. "Biosorption studies of lead and copper using rogers mushroom biomass 'Lepiota hystrix'". South african journal of chemical engineering, Vol. 23,pp. 62-70, 2017.

[24] A. G. El-Said, N. A. Badawy, and S. E. Garamon. "Adsorption of cadmium (II) and mercury (II) onto natural adsorbent rice husk ash (RHA) from aqueous solutions: study in single and binary system". J Am Sci, Vol. 6, pp. 400-409, 2010.

[25] A. K. Zeraatkar, H. Ahmadzadeh, A. F. Talebi, N. R. Moheimani, and M. P. McHenry. "Potential use of algae for heavy metal bioremediation, a critical review". Journal of environmental management, Vol. 181, pp. 817-831, 2016.

[26] G. Hisarli. "The effects of acid and alkali modification on the adsorption performance of fuller's earth for basic dye". Journal of colloid and interface science, Vol. 281, pp. 18-26, 2005.

[27] A. O. Dada, A. P. Olalekan. A. M. Olatunya, and O. Dada. "Langmuir, Freundlich, Temkin and Dubinin–Radushkevich isotherms studies of equilibrium sorption of Zn2+ unto phosphoric acid modified rice husk". IOSR Journal of Applied Chemistry, Vol. 3, pp. 38-45, 2012.

[28] A. H. Sulaymon, A. A. Mohammed, and T. J. Al-Musawi. "Removal of lead, cadmium, copper, and arsenic ions using biosorption: equilibrium and kinetic studies". Desalination and Water Treatment, Vol. 51, pp. 4424-4434, 2013.

[29] K. D. Belaid, S. Kacha, M. Kameche, and Z. Derriche. "Adsorption kinetics of some textile dyes onto granular activated carbon". Journal of Environmental Chemical Engineering, Vol. 1, pp. 496-503, 2013.

[30] K. Y. Foo, and B. H. Hameed. Insights into the modeling of adsorption isotherm systems. Chemical engineering journal, Vol. 156, pp. 2-10, 2010.

امتزاز صبغه المثيل الزرقاء من المحلول المائي باستخدام الطحالب المختلطة

الخلاصة

تم استخدام خليط من الكتلة الحيوية للطحالب (Chrysophyta، Cyanophyta ، و Chlorophyte) لازاله (الصبغه الزرقاء ، MB). تم دراسة تأثير الأس الهيدروجيني (1–8) ، كمية المادة المازة (0.2–2 جم / 100 مل) ، سرعة التحريك (100–300) ، حجم الجسيمات (1304–89 ميكرو متر) ، درجة الحرارة (20–40°C) ، تركيز الصبغة الأولي (20 –300 ملغم / لتر) ، وتمت دراسة امتصاص الامتصاص لتقييم آلية امتصاص صبغة الطحالب. وقد تم تجربة مختلف المعالجات، القلويات ، والبروتونات ، و $CaCl_2$ من أجل تعزيز قدرة الامتزاز وكذلك استقرار الكتلة الحيوية للطحالب. تم تحليل بيانات متساوي الحرارة باستخدام نماذج Langmuir و Freundlich و Temkin. كانت السعة القصوى لامتصاص الأصباغ 26.65 ملغ / غم عند الرقم الهيدروجيني = 5 ، و 250 دورة في الدقيقة ، و 89 ميكرو متر ، و 25 درجة مئوية ، و 50 ملغم / لتر كتركيز أولي. تم اختبار أربعة نماذج حركية ، من الدرجة الأولى الزائفة ، والنظام الثاني الزائف ، وانتشار داخل الجزيئة والنموذج Elovich. مع الأخذ بعين الاعتبار تحليل (SSR و X^2) ، كانت البيانات الأفضل ملائمة لنموذج Temkin isotherm. اضهرت النتائج ان البيانات تخضع لمودبل الزائف من الدرجة الثانية.

أظهرت المعلمات الديناميكية الحرارية (ΔG^0، ΔH^0، ΔS^0، Ea و S *) عند درجات حرارة تتراوح بين 293–313 K أن الإمتصاص هو تفاعل ماص للحرارة ، وتفاعل تلقائي ، ودرجة حرارة أعلى للحل تدعم إزالة الصبغة الزرقاء بالامتزاز على الكتلة الحيوية للطحالب. تظهر النتائج أن عملية الامتزاز– الاسترجاع تستمر لمدة خمس دورات قبل أن تفقد كفاءتها وزيادة كفاءة الاسترداد إلى 80.52 ٪.