Available online at http://ijcpe.uobaghdad.edu.iq and www.iasj.net
Iraqi Journal of Chemical and Petroleum Engineering
Vol.21 No.4 (December 2020) 21 – 32
EISSN: 2618-0707, PISSN: 1997-4884

Elimination of Congo Red Dyes From Aqueous Solution Using Eichhornia Crassipes

Hamza Qassim Ali and Ahmed A. Mohammed

Environmental Engineering Department, College of Engineering, University of Baghdad

Abstract

Water hyacinth (Eichhornia crassipes) is a free-floating plant, growing plentifully in the tropical water bodies. It is being speculated that the large biomass can be used in wastewater treatment, heavy steel and dye remediation, as a substrate for bioethanol and biogas production, electrical energy generation, industrial uses, human food and antioxidants, medicines, feed, agriculture, and sustainable improvement. In this work, the adsorption of Congo Red (CR) from aqueous solution onto EC biomass was investigated through a series of batch experiments. The effects of operating parameters such as pH (3-9), dosage (0.1-0.9 g. /100 ml), agitated velocity (100-300), size particle (88-353μm), temperature (10-50˚C), initial dye concentration (50-500) mg/l, and sorption–desorption were investigated to assess the efficiency of EC-elimination from aqueous solution. Different pre-treatments, alkali, and acid were achieved to increase the adsorption uptake. The optimum conditions for maximum removal of CR from an aqueous solution of 50 mg/L were as follows: pH (6), particle size (88 μm), stirring speed (200 rpm), and dose (0.3 g). The experimental isotherms data were analyzed using Langmuir, Freundlich, and Temkin isotherm equations and the results indicated that the Langmuir isotherm showed a better fit for CR adsorption with a higher adsorption uptake of 92.263mg/g, and the kinetic data were fitted well with pseudo-second-order kinetic model. Thermodynamic parameters were calculated from Van't Hoff plot, confirming that the adsorption process was spontaneous and endothermic. Data show that the adsorption-desorption process lasts for four cycles before losing its efficiency and the recovery efficiency increased up to 76.63%.

Keywords: anionic dye, adsorption, desorption, Eichhornia crassipes, endothermic

Received on 22/11/2019, Accepted on 05/09/2020, published on 30/12/2020

https://doi.org/10.31699/IJCPE.2020.4.3

1- Introduction

Organic pollution is the term used when large amounts of organic compounds consist of wastewater. It originates from domestic sewage, city run-off, industrial effluents, and agricultural wastewater. Sewage cure plant life and industry which includes meals processing, pulp and paper making, agriculture and aquaculture Organic pollution include pesticides, fertilizers, hydrocarbons, phenols, plasticizers, biphenyls, detergents, oils, greases, pharmaceuticals, proteins, carbohydrates and dye [1].
In brief, over 100 000 types of dyes have been used for industrial applications in textile, pulp, and paper, pharmaceuticals, tannery [2]. Dye wastewater from textile dyeing and dye manufacturing industries cause serious pollution problems. The dye effluents discharged into water bodies like lakes, rivers, etc. [3]. Consequently, the removal of dyes from such wastewaters is an important environmental problem and complete dye removal is needed because dyes are visible even at low concentrations [4].

Generally, dyes are classified into three categories: (a) anionic: direct, acid, and reactive dyes; (b) cationic: basic dyes; and (c) nonionic: disperse dyes [5].

Congo red is an anionic acidic dye, used in the analysis of amyloidosis and medicine as a biological stain. Congo pink acts as an indicator with the aid of changing to red-brown coloration in alkaline medium and to blue color in acidic medium. It is additionally used as a gamma-ray Congo red is an anionic acidic dye, used in the analysis of amyloidosis and two as a biological stain in medicine.

Congo red acts as an indicator by using changing to red-brown color in alkaline medium and to blue color in acidic medium. Congo purple was used as a gamma-ray Dosimeter because its coloration decays with the intensity of irradiation. The Congo red poses enormous poisoning in the direction of and animals human beings.

Both, short time or extended contacts of the CR with and pores and skin eyes cause sharp irritation. On ingestion, it produces gastrointestinal irritation with vomiting, nausea, and diarrhea. It is carcinogenic and prolongs use of the Congo red dye outcomes into tumor formation amongsthumans [6]. Congo red one of important dye that found in the wastewater have higher solubility in the water about 1 g/30 ml. In general physical, chemical and biological remedy techniques can be used for the elimination of dyes from water.

Corresponding Authors: Name: Hamza Qassim Ali, Email: hamzaashter@gmail.com, Name: Ahmed A. Mohammed, Email: ahmed.abd@coeng.uobaghdad.edu.iq

The individual methods vary in their effectivity to eliminate or degrade the dyes and additionally in the cost required for the remedy of the related volumes of polluted water [7]. Dyes can't be easily eliminated through traditional cure due to their complex structure and artificial origin. At present, several methods have been employed for the elimination of dye contaminants from wastewater, which encompass ultrasound irradiation, photocatalytic technology, coagulation-flocculation, Oxidation, Ozonation, Membrane separation, biological remedies [8], Adsorption, reverse osmosis, ion-exchange, electrochemical destruction[9,10].

At present, adsorption among the numerous techniques reported for the treatment of dye-containing wastewater is considered as one of the most promising methods due to its simplicity, effectiveness, and low cost [11]. Hence, in the latest years interests are increasing in the use of alternative non-classical waste materials [12]. So many researchers have proved the capability of agricultural solid wastes as adsorbents to remove many types of pollutants including dyes [13].

This work aims to study the process of purification wastewater through the removal of selective toxic contaminants using water hyacinth (*Eichhornia Crassipes*) because it is available in abundance, inexpensive, easy manipulation, non-polluting, relatively simple recovery of metal contaminant for recycling, and are not a source of secondary waste.

2- Experimental Work

2.1. Preparation of Biomass and Adsorbate

Water hyacinth (Eichhornia crassipes) was collected from Tiger River in the Aldora district of Baghdad. Step one collected the water hyacinth from the site thoroughly washed it to take the sludge off and dirt and other unwanted materials by tap water from the surfaces of EC. Step two, water hyacinths were separated into stems, leaves, and roots. Step three, washed several times with distilled water to make its clean then the biomass were dried in the sun for five days ground into, and then washed several times with distilled water before drying in an oven at 105°C for two hoursto ensure that the sample dried completely.

Step four, the samples are crushed by the electric grinder. The dried pulverized biomass adsorbent material was sieved through standard sieves to obtain particle sizes between (63-125 **µ**m;125-250 **µ**m; 250-500 **µ**m) and storied in a desiccator at room temperature under dry conditions untilused[14,15,16]. A Congo Red dye (1.0 g) was dissolved per one liter of distilled water to prepare (1000) mg/L of CR stock solution, and the concentration of CR used to experiment (5,10,15,20,30,40,50,100,200,300,400 and 500 mg/L) were obtain by dilution of the stock solution. . 0.1 M of hydrochloric acid or sodium hydroxide base was added to regulate the solution pH to the desired value.

Congo red dye was the sodium salt of 3,.3´{[1,1'-Biiphenyl]-4,4´-diylbis(azo)}bis(4-amino-1-naphthalene sulfonic acid disodium salt) with a formula ($C_{32}H_{22}N_6Na_2O_6S_2$), has a molecular weight of 696.66 was obtained from sigmae Aldrich with, 99.99% purity and its chemical structure is showin in Fig. **1**.[17,18].

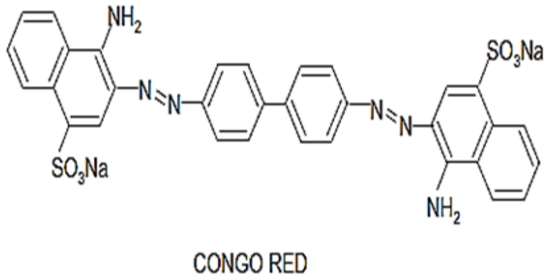


Fig. 1. The chemical formula of Congo red

2.2. Batch Experiments

The study of batch experiments was limited to six steps to identify the circumstances for the maximum dye removal efficiency. The influence of pH, dosage of adsorbent, rpm, and particle size, initial concentration with time, and temperature on the removal of CR were also examined using Eichhornia crassipes. The effect of pH on the Congo red adsorption by EC was investigated at pH range from 3 to 9, dosage (0.1-0.9g/100ml), 50 ppm, 200 rpm. Agitation speed effects were investigated by using different agitation speeds (100,150, 200,250, and 300 rpm) with 50 mg/l dye solution and the optimum values of dosage and pH. To investigate whether particle size (88, 176, and 353 μm) affected the removal efficiency of Congo Red, the experiment was applied using 50 mg/l of Congo Red solution with the optimum values of dosage, pH, and agitation speed. The variance initial concentration of contaminant (50, 100, 200,300,400, and 500 mg/l) with the optimum values of dosage, pH, particle size, and agitation speed to study the effect of initial concentration on removal efficiency. The impact of temperature on the adsorption of Congo red dye was studied within the range of temperatures (10, 20, 30, 40, and 50 °C) and the best condition value of previous tests.

The associated thermodynamic parameters were calculated from the results of temperature experiments. The studies of desorption help to explain the mechanism of adsorption and recovery of the adsorbate and adsorbent so that makes the treatment process economical, the adsorption-desorption experiments were carried for (0.05 and 0.1 M NaOH) discretely up to four cycles. The time of a single cycle system is composed of adsorption phase (120 min) followed by desorption phase (60 min) and the conditions (pH=6, dosage 0.3g/100 ml; speed, 200 rpm; CR concentration, 50 mg/l; temperature, 25˚C), Calculated the uptake removal efficiency and eluting efficiencies of the desorbent Ed was from the equations below [19]:

$$q_e = \frac{(C_i - C_e)V}{m} \quad (1)$$

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

Where:
Ci — Initial conc. of CR (mg/l)
Ce —Conc. of CR at time t (mg/l)
m — Mass of the EC (g).

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

Where:
m_d — the mass desorbed of CR, mg/l
m_{ad} —the total adsorbed quantity of CR (mg/l)

3- Results and Discussion

3.1. FT-IR Analysis

Fourier Transform Infrared Spectroscopy (FTIR) was used to examine the difference in the functional group of water hyacinth (Eichhornia crassipes) and acid treated adsorbents before and after sorption of Congo Red. Analysis of (FTIR) was performed using Perkin-Elmer FTIR, (FTIR spectrum RX1) [20]. The functional groups are important in the adsorption process and act on the control of the adsorption mechanism. The study was carried out within the range of wave-number of (400–4000, cm^{-1}) [21]. Fig. **2**, shows the FTIR spectrum of water hyacinth (Eichhornia crassipes) biomass before and after sorption of Congo red dye. The peak around free water hyacinth (Eichhornia crassipes) at 3379.28,2922.18, 1649.13 and 1039.22 cm^{-1} are due to –OH,–CH, C=O, and C-O stretching vibration respectively[20]. Reduce the intensity of acute peaks concluded that Congo red has been functionalized by the adsorbent. But The peak around modified water hyacinth (Eichhornia crassipes) at 3383.25, 2910.14, 1651.06, and 1050.41 are due to –OH, -CH, C=O, and alcoholic hydroxyl stretching vibration respectively[22].

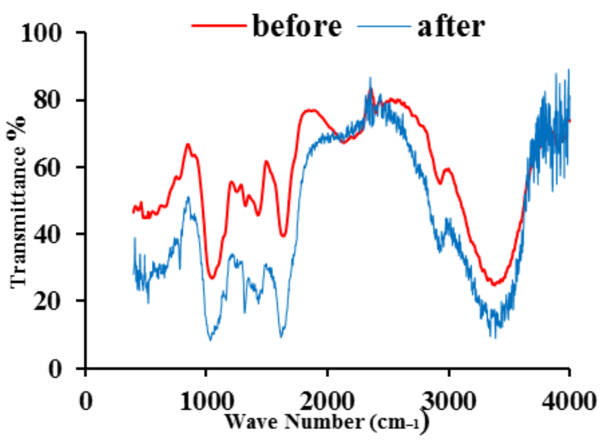


Fig. 2. Before adsorption (free EC) and after adsorption of CR

3.2. Effect of pH

The removal of pollutants from water and wastewater by adsorption is greatly influenced by the pH of the solution which affects the nature of the surface charge of the adsorbent as-well-as the extent of ionization and speciation of the aqueous adsorbate species and consequently the rate of adsorption [23].

A change of pH affects the adsorptive process during the charge on the surface of the adsorbent, the degree of ionization of the adsorptive molecule, and the extent of dissociation of the functional groups on the active sites of the adsorbent [24, 25].

The main red color of CR was found over the pH range of (6–10), and the solution relatively changed its color from red to dark blue when the pH ranges of (3–5).

Also, the red color of the solution for pH values more than ten used to be various from its major red color. Also, Congo red was a little soluble in water when the pH value below 2 [26, 27].

The impact of pH on Congo red adsorption was studied at 25 C° with 50 mg/l of Congo red solution, 0.3 g/L dose of adsorbent, 180 min of contact time, 200 rpm agitation speed, and 88μm particle size adsorbent, when the pH value has increased the adsorption of the dye on the surface of the adsorbent increased until the pH reaches 6 and then the adsorption decreases with increasing pH as shown in Fig. **3**.

The Amplify in the extent of adsorption with increase in pH is due to the neutralization of the charges at the surface of the adsorbents.

It can be safely assumed that through increasing the pH of the solution desire of the poor facilities (SO_3) of the dye for the active websites of the adsorbents increases, which in turn facilitates the adsorption procedure as the pH value of the system rise, the quantity of negatively charged sites increases and the range of positively charged web sites decreases.

At higher pH, the highly negatively charged adsorbent floor sites do not choose the adsorption of deprotonated CR due to electro-static repulsion.

Also, minimize adsorption of CR at alkaline pH is because of the presence of extra [OH^{-1}] ions competing with the dye anions for the adsorption sites. Similar data have been stated for the adsorption of CR on activated carbon and waste orange peels [28].

Therefore, the best pH value should be set to 6, when using Nile flower to remove the Congo red dye, because the electrical interaction between negative charge of CR and positive charge of positive absorption surface is enhanced [8].

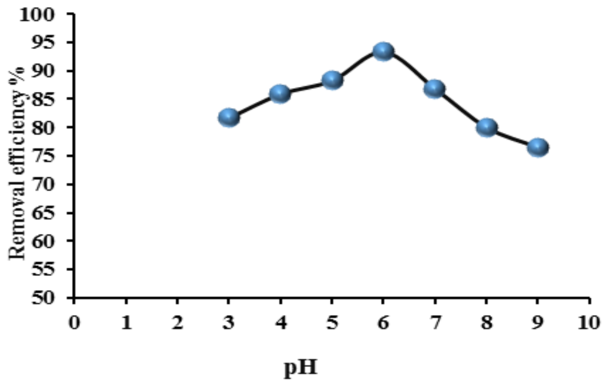


Fig. 3. Effect of pH solution on the removal efficiency (m = 0.3 g / 100 ml, 25˚C, Ci = 50 mg / L for CR, speed = 200 rpm, 88 µm, and time = 120 min).

3.3. Effect of Biomass Dosage

The dose of Water Hyacinth (Eichornia crassipes) is an important parameter to determine the capacity of the sorbent–sorbate equilibrium in the system for a given the best amount of the adsorbent and predict the cost of adsorbent per unit of dye solution [29].

Fig. **4** presents that the percentage removal efficiency of Congo red increases from 86% to 93.95% with an increase in the dose from 0.1 to 0.3 g/100ml while increasing adsorbent dosage more than 0.3g/100ml resulted in a decrease in the removal efficiency. The initial increase in the adsorbent dosage is related to an increased in the surface area and the higher number of available adsorption sites so that increases removal efficiency.

However, the higher dosage will cause the agglomeration of adsorbent particles that can also lead to a decrease in the surface place and increasing the diffusional path length and therefore so that the unsaturation of adsorption sites can also lead to a drop in dye removal percentage. Hence, the adsorption sites remain unsaturated during the process as they are not accessible [30, 31, and 32].

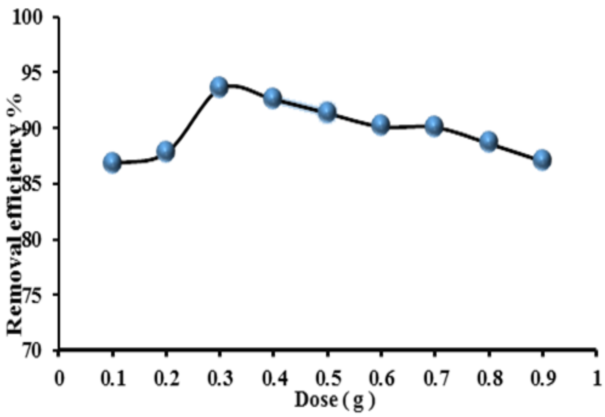


Fig. 4. Effect of adsorbents dosage on the removal of CR dye (Co=50 mg/L, pH=6, agitation speed =200 rpm, D=88µm, time=120 min)

3.4 Effect of agitated speed

Agitation rate carries out an important position in the adsorption technique and affecting the distribution of the solute in bulk media and the formation of the external-boundary layer.

Increasing shaking speed decreases the thickness of the boundary film surrounding adsorbent particles and constrict the resistance offered by film diffusion, finally effect on the adsorption capacity [33, 34, and 35].

The effect of agitation speed on the adsorption capacity of Water Hyacinth (Eichornia crassipes) was studied by varying the shaking speeds range five value (100, 150, 200, 250, and 300 rpm) using an orbital shaker maintained at 25 C^0.

As shown in Fig. **5,** were kept constant. The removal efficiency percent of Congo red increased from 88.39 to 95.03% as the agitation velocity increased from 100 to 300 rpm. The increase in removal efficiency with the increase of rate is due to the proper distribution of adsorbent throughout the bulk solution [36].

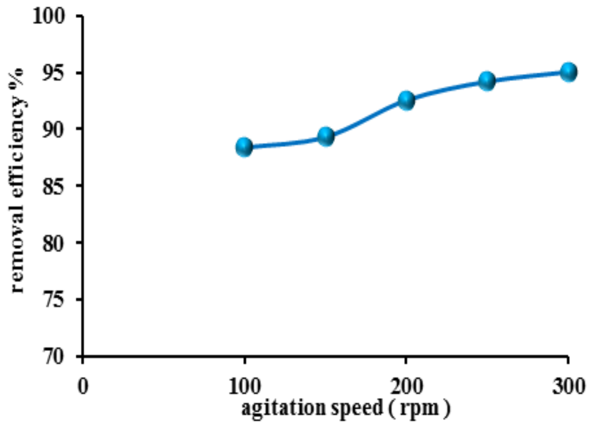


Fig. 5. Effect of agitation speed on removal of Congo red dye by adsorbents (Co=50 mg/L, pH=6, dosage= 0.3g/100ml, D=88µm, time=120 min)

3.5. Effect of Biomass Particle Size

The adsorbent particle size adsorbent plays an important parameter in adsorption. The increase in removal efficiency is because that the smaller adsorbent particles have shortened diffusion paths and increased total surface area, and therefore, the capability to penetrate all internal pore structures of adsorbent is very high[37,38,39].

The process of adsorption was carried out using three different ranges of particle size as fine, medium, and coarse (88, 176, and 353) µm, while other parameters were constant.

Fig. **6** shows that the percentage removal of Congo red decreased from 92.91% to 82.39% as the particle size increased.

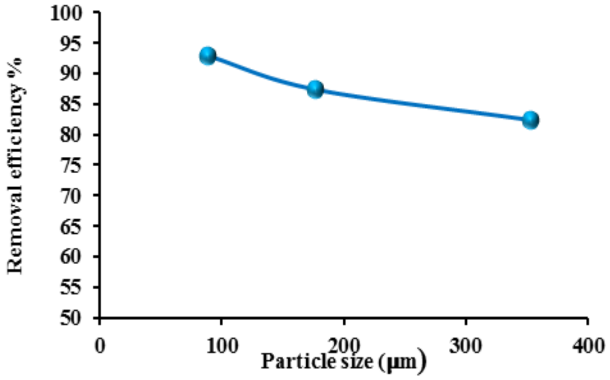


Fig. 6. Effect of particle size on removal of CR (Co=50 mg/L, pH=6, dosage=0.3g/100ml, time=120min, agitation speed=200 rpm)

3.6. Effect of Initial Concentration with Time

Initial Congo red concentration is a significant role in the sorption process. The effect of the concentration on the removal of Congo Red dye was carried out at various initial dye concentration (50, 100, 200, 300, 400, and 500) mg/l shown in Fig. **7**, while other parameters were constant (contact time 120 min, pH 6, dose 0.3 g / L and temperature 25 C^0). The efficiency value decreased from 91.87 to 35.45%, when increasing the initial concentration from 50 to 500 mg/L.

The initial dye concentration supplies the needful driving force to outdo the resistance to the mass transfer of Congo red between the solid phase and aqueous phase [40]. The lowering of removal efficiency of Congo Red dye with the increase of its initial concentration can be explained as follows: because the mass of Water Hyacinth (Eichornia crassipes) is constant for all six concentrations, while the Congo Red molecules must compete for sites onto which they can adsorb and the relative number of function group cites decreases with increasing dye concentration on the surface of the adsorbent. [41].

The higher initial concentration of Congo red in solution leads to saturation of the available, sites much earlier which results in a higher Congo red content in the solution at equilibrium [42]. On the other side, the increase in initial Congo red dye concentration will cause an increase in the uptake of the adsorbent because of the high driving force for mass transfer at a high initial dye concentration [43].

It is shown in Fig. **8** that the Congo red adsorption capacity of adsorbent increased from 15.49 to 65.76 mg/g when the concentration of dye increased from 50 to 500 mg/ L. The effect of contact time on the percentage removal of the Congo red dyes was investigated at initial dye concentration ranging from 50 to 500 mg/L as shown in Fig. **9**.

The contact time is one of the significant parameters for the adsorption operation and the optimization of contact time in the adsorption operation is necessary to improve cost effectiveness [44].

The removal efficiency of Congo red onto Water Hyacinth (Eichornia crassipes) by adsorption was rapid in the first 25 min due to the larger surface area of Water Hyacinth (Eichornia crassipes) available, then slowly arrive equilibrium after 40 min and hold constant until 120 min.

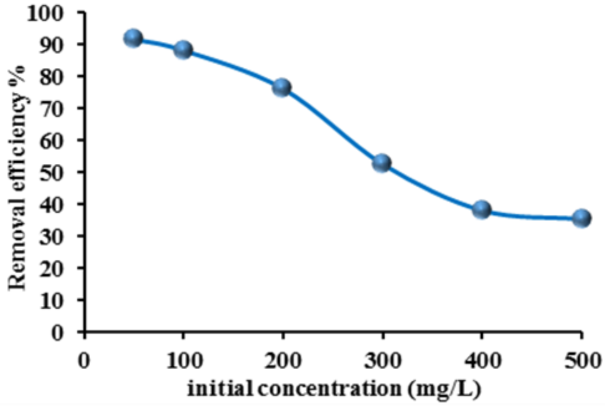


Fig. 7. Effect of agitation speed on removal of Congo Red dye by adsorbents (Co=50 mg/L, pH=6, dosage= 0.3g/100ml, D=88μm, time=120 min)

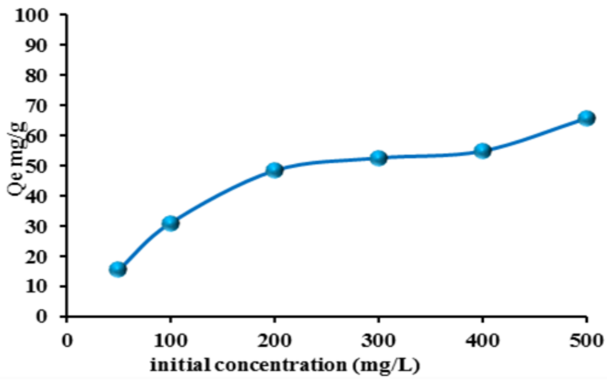


Fig. 8. Effect of initial concentration on adsorption uptake of biosorbent (pH 6, m= 0.3 g, 25˚C, speed= 200 rpm, 88 μm and time=120 min)

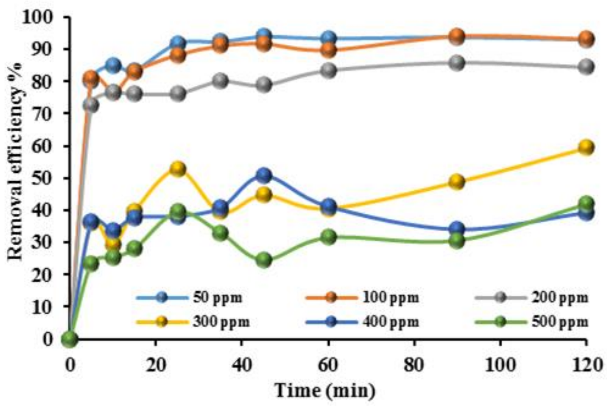


Fig. 9. Effect of initial concentration with time on the removal efficiency of CR (pH 6, m= 0.3 g, 25˚C, speed= 200 rpm, 88 μm, and time=120 min)

3.7. Effect of Temperature and Thermodynamic study

It is well known that temperature plays an important role in the adsorption process. The result of this effect of temperature range from 10 C^0 to 50 C^0 on the adsorption efficiency is shown in **fig. 10** while other parameters were kept constant. With increasing temperature, the results show that the removal efficiency was increased from 81.71% to 93.24%.

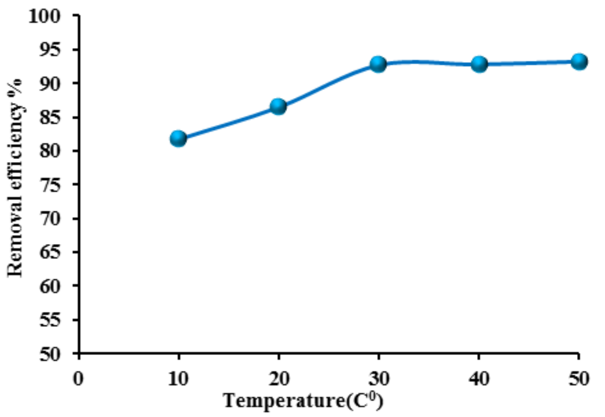


Fig. 10. Effect of temperature on the removal efficiency of CR (pH 6, m= 0.3 g, Ci= 50 mg/L, speed= 200 rpm, 88 µm, and time =120 min)

The sorption thermodynamics is beneficial to look into whether the method is spontaneous or not and additionally to acquire an insight into the sorption conduct. The values of enthalpy and entropy were achieved from the slope and intercept of ln Kc versus 1/T. Calculate parameters including the Gibbs free energy change of adsorption (ΔG^o), enthalpy (ΔH^o), and entropy (ΔS^o) these parameters and the values describing are calculated according to Eqs (4-7) and tabulated in Table **1**. The values of the change in enthalpy indicated that the adsorption process is physical in nature. Also the positive value of ΔH° further confirms the endothermic nature of the adsorption process. The negative value of ΔG^o indicates the feasibility and spontaneity of the adsorption process.

The positive value of ΔS° indicates the perfect affinity of CR towards adsorbent and increased randomness at the Water Hyacinth (Eichornia crassipes) solution surface [45]. The parameter S* indicates the measure of the potential of an adsorbate to remain on the adsorbent [46]. The activation energy (Ea) indicates the type of adsorption which is mainly physical or chemical, so that the activation energy shown in Table **1**, has a value corresponding to chemisorption[12].

$$LnK_c = \left(\frac{\Delta S}{R}\right) - \left(\frac{\Delta H}{R\,T}\right) \tag{4}$$

$$\Delta G^O = \Delta H^O - \Delta S^O\,T \tag{5}$$

$$K_C = \left(\frac{Cad}{Ce}\right) \tag{6}$$

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

Where: Kc the equilibrium constant, Cad the adsorbed concentration of RC on the adsorbent per liter of the solution at equilibrium (mg/L), Ce is the equilibrium concentration of RC in the solution (mg/L), ΔH° change of enthalpy (kJ/mole), R the universal gas constant (8.314 J/mole. K), ΔS° change of entropy (J/K. mole), ΔG^o change of the Gibbs free energy of (kJ/mole), T temperature of the solution (K), θ is surface coverage, S* is sticking probability and Ea is the activation energy.

Table 1. The thermodynamic parameters for the sorption of Congo red on Eichornia crassipes

T (k)	ΔG (kJ/mol)	ΔS (J/mol.k)	ΔH (kJ/mol)	Ea (kJ/mol)	S*
273	-3.544				
293	-4.744				
303	-5.945	120	30.283	43.771	1.52E-09
313	-7.146				
323	-8.346				

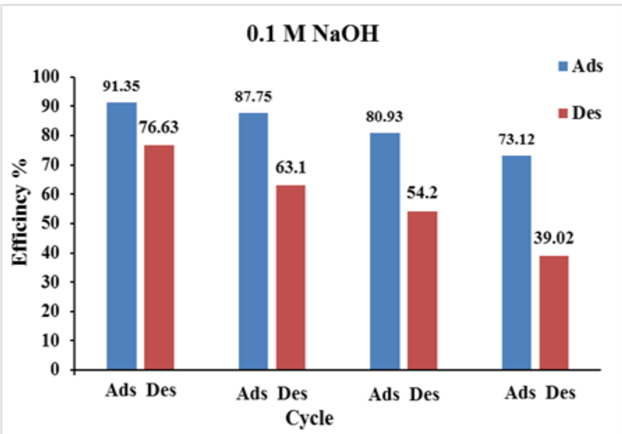
3.8. Desorption

The desirable reusability is essentially important for practical application therapy due to the fact it will decrease the overall fee. The Congo red adsorbed onto adsorbent was recovered by different concentrations of NaOH.

From the de-sorption study, it used to be determined that for increasing in molarity of NaOH, de-sorption increased and greater than (76.63 %) of CR was once desorbed from EC the usage of (0.1 M) NaOH solution. Desorption of Congo red was increased to 81.63% with an increase in the concentration to (0.1 M) NaOH solution. The results show that the biomass can be repeated four times under the same condition. Equation (3) was used to calculate the recovery percentage of 0.05 and 0.1M NaOH concentration.

The strong base inability to completely desorb the Congo red is because the portion of sorbate can be complex formation between the Congo red molecules and the active sites on EC. Fig. **11** shows the results of the desorption process

This desorption is found to be a better solution as it decreases the process cost and also the dependency of the process on a continuous supply of the biosorbent.



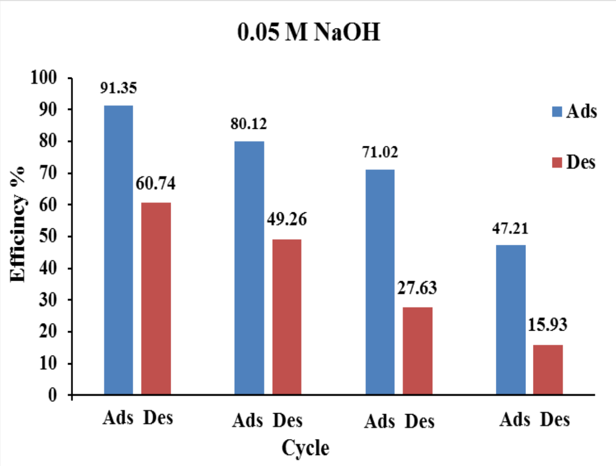


Fig. 11. Regeneration efficiency at various concentration of NaOH

3.9. Pretreatment of biomass

Pretreatment of EC was done using NaOH and /or HCL to raise its efficiency in the removal of dyes from aqueous solution.

The water hyacinth (EC) biomass was modify with (0.05, 0.1, and 0.5) M NaOH and (0.05, 0.1, and 0.5) M HCL

The results plotted in **fig. 12**, showed EC treated by HCL has high efficiency compared with that treated by NaOH.

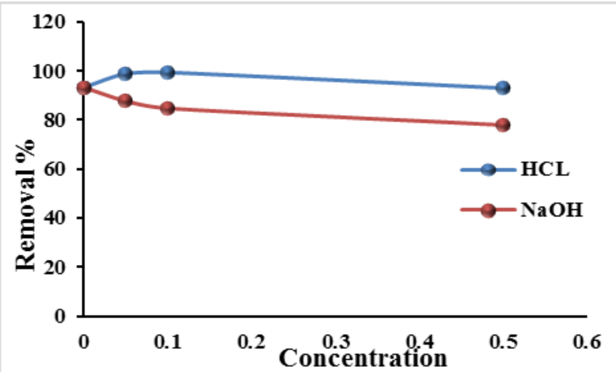


Fig. 12. Modification of algae biomass using different concentrations of NaoH and HCl to remove dyes from solution (pH 6, m= 0.3 g, Ci= 50 mg/l, 88 μm, speed= 200 rpm, and time=120 min)

4- Biosorption Isotherm and Kinetics Models

Adsorption isotherms learn about are essential for the description of how molecules or ions of adsorbate interact with adsorbent surface sites and additionally are indispensable in optimizing the use of adsorbent.

The correlation of equilibrium data the usage of either a theoretical or empirical equation is essential for the adsorption interpretation and prediction of the extent of adsorption. Various theoretical and empirical models were established and studied to characterize the different types of adsorption isotherms. The Langmuir, Freundlich, and Temkin isotherms were among the most frequently used [47, 48].

Table 2. Models to the kinetics and isotherm

Model	Equation	Reference
Langmuir Isotherm	$q_e = \frac{qm\ b\ Ce}{1+b\ Ce}$	[19]
Freundlich Isotherm	$q_e = K\ C_e^{1/n}$	[18]
Temkin isotherm	$qe = BT \ln K_T Ce$ $BT = \frac{R\ T}{bt}$	[19]
Pseudo-first-order	$\ln (q_e - q_t) = \ln q_e - k_1 t$	[53]
Pseudo-second-order	$\frac{t}{qt} = \frac{1}{K2\ qe2} + \frac{t}{qe}$	[54]
Intra- particle diffusion	$qt = k_p t^{1/2} + C$	[53]
Elovich model	$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln(t)$	[19]
Sum square error (SSE)	$\Sigma(q_{e,calc} - q_{e,meas})^2$	[19]
Nonlinear chi-square test (X2)	$\Sigma \frac{(qe,calc-qe,meas)2}{qe,meas}$	[19]

The Freundlich model is to describe heterogeneous surface adsorption and multilayer adsorption beneath different non-ideal conditions. Temkin isotherm assumes the heat of adsorption of all molecules in the layer decreases linearly with coverage and uniform distribution of binding energies [49]. The Langmuir isotherm is prevalently applied to describe the monolayer adsorption befell on the homogeneous surface of adsorbent [50].

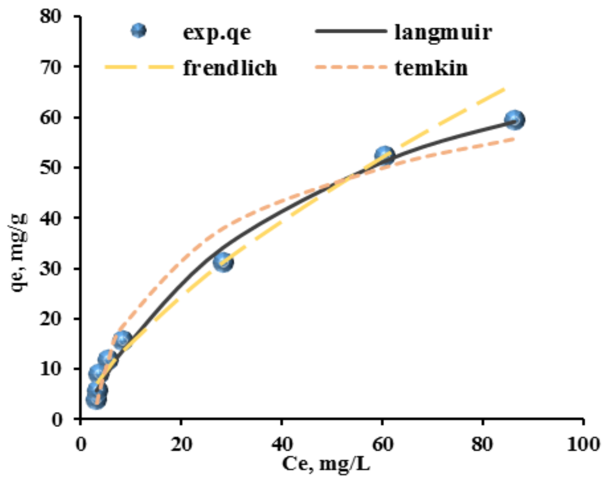


Fig. 13. Isotherm model for sorption of CR dye on EC biomass

The Microsoft Excel SOLVER software was used to analyze of non-linear isotherm model tabulated in Table **2**.

The results of these models were obtained by drawing by Congo red uptake (q_e) versus Congo red concentration (Ce) as showed in Fig. **13**, and values of the parameters were tabulated in Table **3**.

The Langmuir adsorption model was found to fit the experimental data sufficiently in corresponding with the non-linear correlation coefficients (R^2) and the value decrease of the chi-square test statistic (χ^2) and sum square error (SSE) was favorable. The value of RL shows that the isotherm is favorable. Freundlich's value of adsorption intensity (n >1) suggests that the isotherm sorption is favorable [51].

The pseudo-second-order kinetic is greater fitted for this study which is evident with nearly similar values of experimental and calculated values of qe with the high range degree of correlation R2 from (0.99 - 1) as shown in Table **4**.

So that the pseudo 2nd order model is assumed the rate-limiting step can also be chemical phenomena [52]. The values of the kinetic models are tabulated Table **4**.

Table 3. Parameters of isotherms for sorption of Congo red

Type of isotherm	parameters	values
Langmuir	q_{max} (mg/g)	92.263
	b (l/mg)	0.021
	R^2	0.983
	RL	0.432
	Sum square error SSE	10.990
	X^2	1.394
Freundlich	K_f (mg/g)	3.195
	n	1.467
	R^2	0.811
	Sum square error SSE	17.713
	X^2	4.111
Temkin	K_T (l/mg)	0.383
	B_T	15.939
	b_T	155.439
	R^2	0.978
	Sum square error SSE	14.187
	X^2	1.651

Table 4. Parameters of kinetic models for the sorption of CR

Kinetics models	Parameters	50 Ppm	100 ppm	300 ppm	400 ppm	500 ppm
Experimental	q_e	15.499	29.059	58.295	61.525	70.435
Pseudo first order	q_e	8.399	15.016	33.151	41.048	50.522
	K_1	0.048	0.028	0.010	0.0062	0.001
	R^2	0.761	0.659	0.863	0.713	0.825
Pseudo second order	q_e	15.760	29.981	58.987	62.026	71.798
	K_2	0.533	0.453	0.261	0.164	0.064
	R^2	1	1	1	0.988	0.979
Intra-particle diffusion	C	13.463	25.299	51.062	55.041	63.339
	K_P	0.260	0.609	0.676	0.688	0.765
	R^2	0.609	0.722	0.883	0.812	0.751
Elovich model	α	3.64E+15	1.56E+13	3.86E+12	1.64E+08	2.07E+04
	β	2.639	1.166	0.579	0.358	0.171
	R^2	0.829	0.884	0.966	0.936	0.925

5- Conclusions

The results show that Water Hyacinth (Eichornia crassipes) biomass could be used as an efficient biosorbent material for the removal of Congo red dye from aqueous solution.

The maximum value of removal efficiency approximately (93%) at pH 6, 0.3 g /100ml dosage, 200 rpm agitation speed, 88 µm particle size, 50 ppm initial CR concentration, and 25˚C temperature for 120 min. Langmuir model fitted well the experimental data compared to Freundlich and Temkin models. the kinetic study showed that the pseudo-second-order model was very well simulated experimental data.

The values of (ΔG°, ΔH°, and ΔS°) for the thermodynamic study indicated that the biosorption of CR was the feasibility, spontaneity and endothermic at the ranges (293-323 k) of temperature.

The value of adsorption-desorption process showed that the EC can be used for four cycles with nearly the same efficiency. Modify the EC with HCL show the highest removal efficiency compared to NaOH in all its concentrations.

Nomenclature

EC: Eichornia crassipes
CR: Congo red
B: Affinity of the binding site, L/ mg,
B_T & b_T: Temkin constants
C: Value of intercept that offers an notion about the boundary layer thickness, mg/g
C_{ad}: Adsorbed concentration, mg/L
Ce: Concentration at equilibrium, mg/L
Ci: Initial concentration, mg/
Ea: Activation energy, KJ/ mole
ΔG^O: Gibbs free energy, KJ/mole
ΔH^O: Enthalpy change, KJ/mole
k_1: Pseudo-first-order rate constant, min^{-1}
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
Kp: Intra-particle diffusion rate constant, mg/g min0.5
k_T: Temkin sorption potential, L/ mg
m: Mass of adsorbent, g
1/n: Constant indicative of the intensity of the adsorption
qe: Sorbed dyes molecules on the adsorbent, mg/ g
q_m: The maximum sorption capacity for monolayer coverage, mg/ g
q_t: CR uptake capacity, mg/g at any time t
R: Universal gas constant
S*: Sticking probability
ΔS^O: Entropy change, J/K. mole
T: Temperature, K
V: Volume, L
ϴ: Surface coverage

References

[1] M. N. Rashed. "Adsorption Technique for the Removal of Organic Pollutants from Water and Wastewater". Organic Pollutants - Monitoring, Risk and Treatment, 2013.

[2] N. Buvaneswari, and C. Kannan. "Plant toxic and non-toxic nature of organic dyes through adsorption mechanism on cellulose surface". Journal of Hazardous Materials, 189, 294–300, 2011.

[3] O¨. Go¨k, A. S. O¨zcan, A. O¨zcan. "Adsorption behavior of a textile dye of Reactive Blue 19 from aqueous solutions onto modified bentonite'. Applied Surface Science, 256, 5439–5443, 2010.

[4] X. He, K. B. Male, P. N. Nesterenko, D. Brabazon, B. Paull, and J. H.T. Luong. "Adsorption and Desorption of Methylene Blue on Porous Carbon Monoliths and Nanocrystalline Cellulose". American Chemical Society, 5, 8796−8804, 2013.

[5] M. Foroughi-Dahr, H. Abolghasemi, M. Esmaili, A. Shojamoradi, and H. Fatoorehchi. "Adsorption Characteristics of Congo Red from Aqueous Solution onto Tea Waste". Chemical Engineering Communications, 202, 181–193, 2015.

[6] A. Mittal, V. Thakur, J. Mittal, and H. Vardhan. "Process development for the removal of hazardous anionic azo dye Congo red from wastewater by using hen feather as potential adsorbent". Desalination and Water Treatment, 1944-3986, 2013.

[7] N. Rajamohan. "Equilibrium studies on sorption of an anionic dye onto acid activated water hyacinth roots". African Journal of Environmental Science and Technology, Vol. 3 (11), 399-404, 2009.

[8] V. S. Munagapati, and D. Kim. "Adsorption of anionic azo dye Congo Red from aqueous solution by Cationic Modified Orange Peel Powder". Journal of Molecular Liquids, 220, 540–548, 2016.

[9] J. M. Salman1, A. R. Amrin, F. M. Hassan, and S. A. Jouda. "Removal of Congo red dye from aqueous solution by using natural materials". Mesopotamia Environmental Journal, Vol.1, 82-89, 2015.

[10] A. Srinivasan, T. Viraraghavan. "Decolorization of dye wastewaters by biosorbents: A review". Journal of Environmental Management, 91, 1915-1929, 2010.

[11] X. Li, Z. Wang, J. Ning, M. Gao, W. Jiang, Z. Zhou, and G. Li. "Preparation and characterization of a novel polyethyleneimine cationmodified persimmon tannin bioadsorbent for anionic dye adsorption". Journal of Environmental Management, 217, 305-314, 2018.

[12] M. Arulkumar, P. Sathishkumar, and T. Palvannan. "Optimization of Orange G dye adsorption by activated carbon of Thespesia populnea pods using response surface methodology". Journal of Hazardous Materials, 186, 827–834, 2011.

[13] M. A. Mohd Salleh, D. K. Mahmoud, W. A. Wan Abdul Karim, A. Idris. "Cationic and anionic dye adsorption by agricultural solid wastes: A comprehensive review". Desalination, 280, 1–13, 2011.

[14] W. C. Wanyonyi, J. M. Onyari, and P. M. Shiundu. "Adsorption of Methylene Blue Dye from Aqueous Solutions Using Eichhornia crassipes". Bull Environ Contam Toxicol, 2013.

[15] I. Wauton, and S. E. Ogbeide. "Characterization of pyrolytic bio-oil from water hyacinth (Eichhornia crassipes) pyrolysis in a fixed bed reactor'. Biofuels, 2019.

[16] Q. Li, B. Chen, P. lin, J. Zhou, J. Zhan, Q. Shen, and X. Pan. "Adsorption of heavy metal from aqueous solution by dehydrated root powder of Long-root Eichhornia crassipes". International Journal of Phytoremediation, 2014.

[17] A. Mittal, J. Mittal, A. Malviya, and V.K. Gupta. "Adsorptive removal of hazardous anionic dye ''Congo red'' from wastewater using waste materials and recovery by desorption". Journal of Colloid and Interface Science, 340, 16–26, 2009.

[18] 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.

[19] A. A. Najim, and A.A. Mohammed. " Biosorption of Methylene Blue from Aqueous Solution Using Mixed Algae". Iraqi Journal of Chemical and Petroleum Engineering, Vol.19 No.4, 1 – 11, 2018.

[20] T. K. Roy, and N. K. Mondal. "Biosorption of Congo Red from aqueous solution onto burned root of Eichhornia crassipes biomass". Appl Water Sci, 2017.

[21] M. Arulkumar, P. Sathishkumar, and T. Palvannan. "Optimization of Orange G dye adsorption by activated carbon of Thespesia populnea pods using response surface methodology". Journal of Hazardous Materials, 186, 827–834, 2011.

[22] Sumanjit, Seema, R. K. Mahajan, and V. K. Gupta. "Modification of surface behaviour of Eichhornia crassipes using surface active agent: An adsorption study". Journal of Industrial and Engineering Chemistry, 2014.

[23] A. A. Mohammed. "Biosorption of lead , cadmium and zinc onto sunflower shell equilibrium, kinetic and thermodynamic studies". Iraqi Journal of chemical and petroleum Engineering, 16, 1, 2015.

[24] S.D. Khattria, and M.K. Singhb. "Removal of malachite green from dye wastewater using neem sawdust by adsorption". Journal of Hazardous Materials, 167, 1089–1094, 2009.

[25] B.K. Nandi, A. Goswami, and M. K. Purkait. "Removal of cationic dyes from aqueous solutions by kaolin: Kinetic and equilibrium studies". Applied Clay Science, 42, 583–590, 2009.

[26] M. Foroughi-Dahr, H. Abolghasemi, M. Esmaili, A. Shojamoradi, and H. Fatoorehchi. "Adsorption Characteristics of Congo Red from Aqueous Solution onto Tea Waste". Chemical Engineering Communications, 202:2, 181-193, 2015.

[27] V. S.Munagapati, and D. Kim. "Adsorption of anionic azo dye Congo Red from aqueous solution by Cationic Modified Orange Peel Powder". Journal of Molecular Liquids, 220, 540–548, 2016.

[28] A. Mittal, J. Mittal, A. Malviya, and V.K. Gupta. "Adsorptive removal of hazardous anionic dye ‘‘Congo red” from wastewater using waste materials and recovery by desorption". Journal of Colloid and Interface Science, 340, 16–26, 2009.

[29] M. T. Yagub, T. K. Sen, S. Afroze, and H.M. Ang. "Dye and its removal from aqueous solution by adsorption: A review". Advances in Colloid and Interface Science, 209, 172–184, 2014.

[30] N. P. de Moraes, F. N. Silva, M. L. C. P. da Silva, T. M. B. Campos, G. P. Thim, and L. A. Rodrigues. "Methylene blue photodegradation employing hexagonal prismshaped niobium oxide as heterogeneous catalyst: Effect of catalyst dosage, dye concentration, and radiation source". Materials Chemistry and Physics, 214, 95-106, 2018.

[31] R. Araga, S. Soni, and C. S. Sharma. "Fluoride Adsorption from Aqueous Solution using Activated Carbon Obtained from KOH-treated Jamun (Syzygium cumini) Seed". Journal of Environmental Chemical Engineering, 2017.

[32] J. Abdi, M. Vossoughi, N. M. Mahmoodi, and I. Alemzadeh. "Synthesis of metal-organic framework hybrid nanocomposites based on GO and CNT with high adsorption capacity for dye removal". Chemical Engineering Journal, 2017.

[33] A. Alahabadi, A. Hosseini-Bandegharaei, G. Moussavi, B. Amin, A. Rastegar, H. Karimi- Sani, M. Fattahi, and M. Miri. "Comparing adsorption properties of NH4Cl-modified activated carbon towards chlortetracycline antibiotic with those of commercial activated carbon". Journal of Molecular Liquids, 2017.

[34] A. Kumar, and H. M. Jena. "Adsorption of Cr(VI) from aqueous solution by prepared high surface area activated carbon from Fox nutshell by chemical activation with H3PO4". Journal of Environmental Chemical Engineering, 2017.

[35] A. A. Oladipo, M. Gazi, and S. Saber-Samandari. "Adsorption of anthraquinone dye onto eco-friendly semi-IPN biocomposite hydrogel: Equilibrium isotherms, kinetic studies and optimization". Journal of the Taiwan Institute of Chemical Engineers, 2013.

[36] P. Kumar, and M.S. Chauhan. "Adsorption of chromium (VI) from the synthetic aqueous solution using chemically modified dried water hyacinth roots". Journal of Environmental Chemical Engineering, 7, 103218, 2019.

[37] V. K. Gupta, A. Mittal, A. Malviya, and J. Mittal. "Adsorption of carmoisine A from wastewater using waste materials—Bottom ash and deoiled soya". Journal of Colloid and Interface Science, 335, 24–33, 2009.

[38] M. C. Menkitil, C. O. Aniagor, C. M. Agu, and V. I. Ugonabo. "Effective Adsorption of Crystal Violet Dye from an Aqueous Solution Using Lignin-Rich Isolate from Elephant Grass". Water Conservation Science and Engineering, 3, 33–46, 2018.

[39] S. Shakoor, and A. Nasar. "Adsorptive decontamination of synthetic wastewater containing crystal violet dye by employing Terminalia arjuna sawdust waste". Groundwater for Sustainable Development, 2018.

[40] P. S. Kumar, S. Ramalingam, C. Senthamarai, M. Niranjanaa, P. Vijayalakshmi, and S. Sivanesan. "Adsorption of dye from aqueous solution by cashew nut shell: Studies on equilibrium isotherm, kinetics and thermodynamics of interactions". Desalination, 261, 52–60, 2010.

[41] G. Moussavi, and R. Khosravi. "The removal of cationic dyes from aqueous solutions by adsorption onto pistachio hull waste". chemical engineering research and design, 89, 2182–2189, 2011.

[42] R. Maurya, T. Ghosh, C. Paliwal, A. Shrivast, K. Chokshi, I. Pancha, A. Ghosh, and S.Mishra. "Biosorption of Methylene Blue by De-Oiled Algal Biomass: Equilibrium, Kinetics and Artificial Neural Network Modelling". Kinetic Study of Cationic Dye Biosorption by De-Oiled Algal Biomass, Volume 9, 2014.

[43] M. A. M. Salleh, D. K. Mahmoud, W. A. W. Abdul Karim, and A. Idris. "Cationic and anionic dye adsorption by agricultural solid wastes:A comprehensive review". Desalination, 280, 1–13, 2011.

[44] T. Maneerung, J. Liew, Y. Dai, S. Kawi, C. Chong, and C. Wang. "Activated carbon derived from carbon residue from biomass gasification and its application for dye adsorption: kinetics, isotherms and thermodynamic studies". Bioresource Technology, 2015.

[45] P. S. Kumar, S. Ramalingam, C. Senthamarai, M. Niranjanaa, P. Vijayalakshmi, and S. Sivanesan. "Adsorption of dye from aqueous solution by cashew nut shell: Studies on equilibrium isotherm, kinetics and thermodynamics of interactions". Desalination, 261, 52–60, 2010.

[46] G. Moussavi, and R. Khosravi. "The removal of cationic dyes from aqueous solutions by adsorption onto pistachio hull waste". chemical engineering research and design, 89, 2182–2189, 2011.

[47] T. Maneerung, J. Liew, Y. Dai, S. Kawi, C. Chong, and C. Wang. "Activated carbon derived from carbon residue from biomass gasification and its application for dye adsorption: kinetics, isotherms and thermodynamic studies". Bioresource Technology, 2015.

[48] F. Zhang, B.Ma, X. Jianga, and Y. Ji. "Dual function magnetic hydroxyapatite nanopowder for removal of malachite green and Congo red from aqueous solution". Powder Technology, 302, 207–214, 2016.

[49] E. S. Priya,and P. S. Selvan. "Water hyacinth (Eichhornia crassipes) – An efficient and economic adsorbent for textile effluent treatment – A review". Arabian Journal of Chemistry, 2014.

[50] H. Demiral, and C. Güng. "Adsorption of copper(II) from aqueous solutions on activated carbon prepared from grape bagasse". Journal of Cleaner Production, 124, 103e113, 2016.

[51] V. V. Gedam1, P. Raut, A. Chahande, and P. Pathak. "Kinetic, thermodynamics and equilibrium studies on the removal of Congo red dye using activated teak leaf powder". Applied Water Science, 2019.

[52] F. Zhang, J. Lan, Y. Yang, T. Wei, R. Tan, W.J. Song, Adsorption behavior and mechanism of methyl blue on zinc oxide nanoparticles, J. Nanopart. Res. 15, 1–10, 2013.

[53] D.P. Li, Y.R. Zhang, X.X. Zhao, B.X. Zhao, Magnetic nanoparticles coated byaminoguanidine for selective adsorption of acid dyes from aqueous solution, Chem. Eng. J. 232, 425–433, 2013.

[54] N. Ertugay, and E. Malkoc. "Adsorption Isotherm, Kinetic, and Thermodynamic Studies for Methylene Blue from Aqueous Solution by Needles of Pinus Sylvestris L". Pol. J. Environ. Stud, Vol. 23, No. 6, 2014.

أزالة صبغة الكونغو الحمراء من المحلول المائي بأستخدام زهرة النيل

حمزة قاسم علي و احمد عبد محمد

جامعة بغداد/كلية الهندسة/قسم الهندسة البيئية

الخلاصة

صفير الماء (Eichhornia crassipes) نبات عائم ينمو بكثافة في المسطحات المائية الاستوائية. يتم التكهن بأن الكتلة الحيوية يمكن استخدامها في معالجة مياه الصرف الصحي ,المعادن الثقيلة والاصباغ , ركيزة لانتاج الايثانول والغاز الحيوي, توليد الكهرباء, استخدامات صناعية, الغذاء البشري ومضادات الاكسدة, الادوية, الاعلاف, الزراعة والتنمية المستدامة. في هذه الدراسة تم تجربة ازالة صبغة الكنغو الحمراء بأستخدام نبات زهرة النيل(صفير الماء) من خلال سلسلة من التجارب الدفعية. تم دراسة تأثير مدى الاس الهيدروجيني (9–3), سرعة التحريك (300–100), كمية المادة المازة (0.9–0.1 غم/100مل), حجم الجيسمات(353–88 ميكرومتر), التركيز الاولي للصبغة(500–50 ملغم/لتر), درجة الحرارة(50–10 سيليزية), امتصاص الامتصاص لتقييم كفائة ازالة صبغة زهرة لنيل من المحلول المائي. وقد تم تجربة معالجات مختلفة بواسطة القلويات والاحماض من أجل تعزيز قدرة االامتزاز وكذلك استقرار الكتلة الحيوية لزهرة النيل. كانت الظروف المثلى للإزالة القصوى لـ CR من محلول مائي قدره 50 مجم / لتر كما يلي: درجة الحموضة (6) ، حجم الجسيمات (88 ميكرون) ، سرعة التحريك (200 دورة في الدقيقة) والجرعة (0.3 جم). تم تحليل بيانات الايزوثيرم التجريبية بواسطة استخدام نماذج Langmuir, Freundlich و Temkin.

كان نموذج(Langmuir)اكثر ملائمة بأعلى امتصاصية لصبغة الكونغو الحمراء 92.263 ملغم/غم عند الرقم الهيدروجيني = 6، 200 دورة في الدقيقة ، 88 ميكرو متر ، كمية المادة المازة 0.3 غم, 30 درجة مئوية و 50 ملغم/لتر كتركيز أولي. كذلك اظهر النموذج (pseudo–second order kinetic model) الذي تم حسابه من (Van't Hoff plot) اكثر ملائمة وان عملية الامتزاز تحدث بصورة تقائية ون التفاعل ماص للحرارة. تظهر النتائج أن عملية االامتزاز– االاسترجاع تستمر لاربع دورات قبل أن تفقد كفاءتها وزيادة كفاءة االسترداد إلى 76.63٪.

الكلمت الدالة: صبغة أنيونية ، امتزاز ، امتصاص, ماص للحرارة