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Development of a Novel Hydrogel Adsorbent for Removal of Reactive Dyes from Textile Effluents .

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ABSTRACT

A hydrogel composed of chitosan-grafted acrylamide-co-acrylic acid monomers has been synthesized using ceric ammonium nitrate as an initiator. The prepared hydrogel samples have been characterized using FTIR and SEM. The aim of this work is to use the prepared hydrogel in the reactive dyes adsorption from real wastewater sample collected from a textile factory. Effect of preparing four hydrogel samples using different cross-linker weight ratios in adsorption of Reactive Red RSS and Blue HB dyes have been studied. Effects of contact time (2 to 6 hours) and initial solution pH (2–6) on dye adsorption has been investigated. The best obtained results of COD and TDS have been achieved when applying 3 hours contact time and pH 6. The adsorption parameters were determined based on Langmuir and Freundlich isotherms obtained from the equilibrium adsorption data for the direct dye, Also, it was noticed that the prepared hydrogel shows good ability to uptake textile dyes from wastewater.

Keywords: Adsorption rate, Blue HB, Red RSS, Chitosan, Dye removal, Hydrogel

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INTRODUCTION

Nowadays, contaminated colored effluents are the reason of a huge environmental problem [1], therefore colored wastewater cannot be discharged without an adequate treatment. Wastewater treatment difficulties is faced when Synthetic dye is used because of its complex aromatic structures, which increase both stability and biodegradability [2-5]. Different procedures have been applied for removing dyes from wastewater such as coagulation [6], filtration [7], ozonation [8], absorption [9], membrane processes [10], advanced oxidation processes [11] and adsorption [12].

Among the mentioned methods for dye removal, adsorption is an effective, economical and simply applied methods used in the removal of textile dyes [13-15]. Many different adsorbents were used to lower dye concentrations in the contaminated wastewater [16-18]. Recently, much attention has been paid to polysaccharide adsorbent known as "hydrogel" for dyes removal.

Hydrogels are 3D cross-linked polymers, which have the ability of swelling and retaining a huge amount of water. Hydrogels have many applications, which help in solving some environmental problems [19-20]. Nowadays, some studies have dealt with the removal of dyes using natural polysaccharides hydrogel especially using chitosan. Due to the anionic properties of chitosan polysaccharide hydrogel it has the capability of adsorbing cationic dyes from aqueous solutions via the electrostatic attraction force.

In case of anionic dyes, chitosan-based hydrogel is an appropriate solution due to the presence of the amino groups which are protonated and hence positively charged in acidic solutions [21]. Chitosan has been investigated by several researchers as a biopolymer adsorbent for the dye removal from aqueous solutions [22].

Chitosan has a potential as an efficient adsorbent for almost all classes of dyes, except basic dyes that can be related to its natural cationic properties [23]. George & Nikolaos [24] studied reactive and basic dyes removing methods from aqueous solutions using cross-linked chitosan derivatives as sorbents; Hemalatha & Sudha [25] Studied the effect of polymerization variables including initiator and cross-linker concentration on the dye adsorption capacity on N-maleilated chitosan-g- (methyl methacrylate) co-polymer hydrogel.

Mousa et. al., [26] synthesized biopolymer adsorbent composed of chitosan-ethyl acrylate (Ch-g-Ea) and applied it for the removal of Basic Blue 41 (BB41) and Basic Red 18 (BR18) from colored solutions. Lazaridis et al. [27] induced a free radical initiated polymerization for grafting chitosan by poly (acrylic acid) and poly (acrylamide) through persulfate processes, maximum adsorption equals to 1.068 mmol/g.

The aim of the present study is to describe the synthesis and characterization of a grafted chitosan using different cross-linker weight ratios. The grafting process has been confirmed using FTIR and SEM. Swelling water ratio for the obtained hydrogels have been studied. The adsorption behavior of Reactive two reactive dye Blue HB towards chitosan has been studied. The influence of some factors, such as pH, contact time on chitosan adsorption capacity for mentioned dyes, has been investigated. The adsorption kinetics parameters that characterize the adsorption processes were estimated.

MATERIALS AND METHODS

Materials

Chitosan (Ch) industrial grade degree of acetylation >70% (Sigma Aldrich Chemical Company Ltd.). Acrylamide (Am) [Baker Chemical Co., USA] were used after crystallization in acetone (El-Naser Pharmaceutical Chemical Co.). Acrylic acid (AA) (Merck, Germany) was stored below 4°C. All other chemicals were analytical grade and used without any purifications.

Hydrogel Preparation

The grafting procedure has been carried out after the procedure described by Souror et al. [28] with some modifications. Hydrogel samples have been prepared, where 4g of chitosan has been dissolved in 140 mL. Then, 1 g of ceric ammonium nitrate (CAN), 16 g of acrylamide (Am) and 4 ml acrylic acid (AA) mixtures

have been added. Four different weights of MBA (0.1, 0.3, 0.5 & 0.7 g) has been added, samples named from 1 to 4, respectively.

The resulted hydrogel samples have been adjusted to pH 8 then, washed with ethanol solution, filtered and dried at 70°C until constant weight has been achieved [1,9,28]. A base hydrolysis process has been adopted with about 5.0 g of the hydrogel added to 250 ml of 1N NaOH. The hydrolysis carried-out at 90°C for 60 min. After completion of the hydrolysis, the product is washed thoroughly with 70% ethanol and dried at 80°C until achieving constant weight [29].

Characterization and Analysis

FTIR

FTIR spectra of the grafted hydrogel products were determined using FT/IR-6100 type A Jasco-Japan TGS detector with the absorbance technique wavelength ranging from 500 to 4000 cm^{-1} with scanning speed of 2 mm/s.

SEM

Hydrogel samples were hydrated with de-ionized water, frozen in liquid nitrogen overnight. Dried. SEM instrument model JEOL: JXA-840A has been used. All samples were gold coated prior to measurement.

Swelling water ratio (SWR)

Swelling behavior of the produced hydrogel samples have been evaluated. The dry hydrogel (0.1g) has been soaked in 100 ml distilled water for period up to 24 hr at room temperature. After this time, swollen samples have been removed from the water, the surface water has been removed using filter paper after 10 min then the samples were weighted. SWR has been calculated using the following equation [30]:

$$SWR (g/g) = \frac{(W_s - W_d)}{W_d} \quad (1)$$

Where: W_s and W_d represent the weight of the wet and the dry hydrogel, respectively.

Adsorption kinetics

Adsorption kinetics experiment has been carried-out using batch technique; 100 mg hydrogel has been immersed in 50 ml dye solutions at room temperature. The effect of contact time on dye removal of both dye types has been done using shaker at a constant stirring speed of 120 rpm. Adsorption experiments have been carried-out at 2, 4 and 6 hr contact time, 2, 4 and 6 pH and 100-500 mg/L initial dye concentration. The corresponding absorbance dye concentration left in the solution was measured using spectrophotometer at 532 nm for Reactive Red RSS and 400 nm for Reactive Blue HB.

The wastewater characterization is shown in Table (1). The dye adsorbed quantities have been calculated from the difference between the starting and ending solution concentrations. The amount (mg) of adsorbed dye per unit mass (g) of the hydrogels have been calculated by using the following equation:

$$Q_t = \frac{(C_i - C_e) \cdot V_s}{m} \quad (2)$$

Where:

Q_t : amount of dye absorbed per unit mass of the hydrogel (mg dye/g hydrogel), C_i and C_e are the concentration of the dye in the initial solution and the equilibrium solution, respectively, (mg/dm^3), V_s is the dye solution volume (dm^3), and m (g) is the weight of dry hydrogel.

Equilibrium Studies

The adsorption equilibrium was obtained by employing 0.15 g of chitosan and 100 mL aqueous solution of dye with various concentrations at room temperature. The solutions were stirred until reaching adsorption equilibrium and then the same steps as mentioned in section 2.3.4. The adsorption capacity of the prepared hydrogel has been evaluated via calculating the amount of dye adsorbed at equilibrium using equation (2).

Table (1) Wastewater Effluent and Dye Characteristics

Wastewater Effluent Characteristics		
Parameter	Sample 1	Sample 2
Initial dye concentration, mg/L	350	300
pH	11	9.8
COD, mg/L	1440	1279
TDS, mg/L	12500	10450
Dyes Characteristics		
Parameter	Dye 1	Dye 2
Name	Reactive Red RSS	Reactive Blue HB
Molecular Formula	$C_{52}H_{30}Cl_2N_{14}Na_6O_{20}S_6$	$C_{29}H_{17}ClN_7Na_3O_{11}S_3$
Molecular Weight	1752.11	840.097
Color	Red	Blue

RESULT AND DISCUSSION

Hydrogel Characterization

FTIR

FTIR for chitosan, acrylamide and the produced hydrogel samples are presented in Figure (1). The IR spectrum for raw chitosan has strong peaks around 3455 cm^{-1} (O–H stretch vibration and inter hydrogen bonds), 2879 cm^{-1} (C–H stretch), 1600 cm^{-1} (N–H bend), 1327 cm^{-1} (C–N stretch) and 1092 cm^{-1} (C–O stretch). For the three grafted chitosan samples, the peak at 3416 cm^{-1} is of quite a reduced intensity and broad (due to overlapping of O–H stretching of chitosan and N–H stretching of amide groups at Am). Reduced intensity of this peak with respect to chitosan, shows that appreciable amounts of O–H and N–H of chitosan have been grafted with polyacrylamide chains.

Amide (I) (C=O) and amide (II) (NH₂) bands are seen at 1583 cm^{-1} as one sharp peak in spite of being separated into two peaks at 1671 cm^{-1} and 1630 cm^{-1} in the IR spectra of raw Am. Peak around 1432 cm^{-1} (C–N stretching) in graft copolymer further supports grafting, these data showed characteristic peaks which are in close agreement with the reported data. Occurrence of the nitrogen-hydrogen and carbon-oxygen stretching vibrations in the tested hydrogel confirms the signal of grafting process [31, 32].

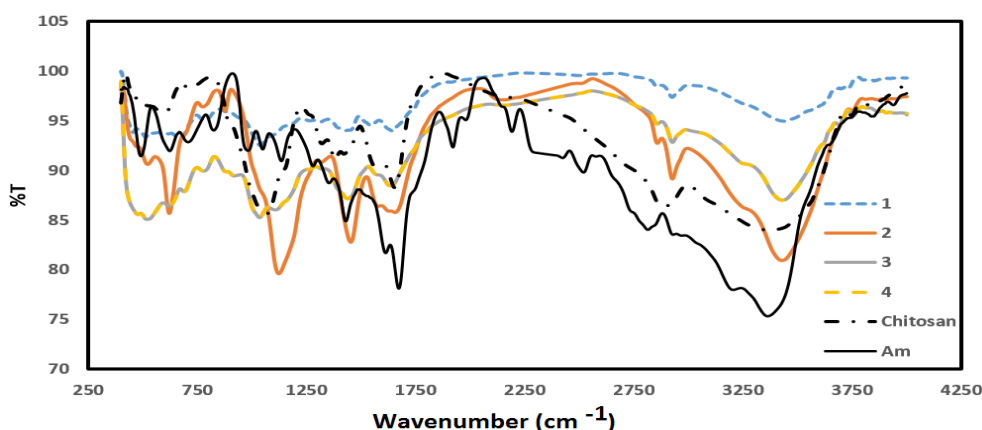


Figure (1) FTIR for chitosan, Am and the grafted hydrogel samples

SEM

SEM for pure chitosan, acrylamide and grafted hydrogel samples are presented in Figure (2). Pure chitosan shows flaky nature with irregular shape and porous surface according to the chitosan nature [33], while Acrylamide has an oval shape. For the grafted chitosan samples (1,2,3 & 4), obviously observed difference in the surface morphology due to the absence of either oval shaped particles or the flaky shape and the presence of more number of pores. It provides direct evidence that phase separation occurred in chitosan grafted hydrogel [34].

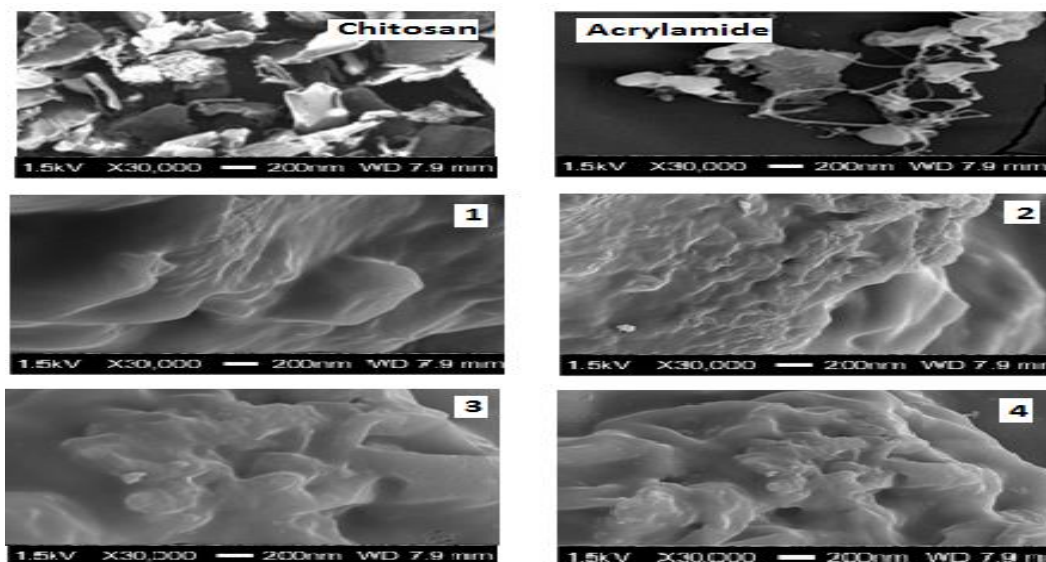


Figure (2) SEM for chitosan, Am and grafted hydrogel samples (1, 2, 3 & 4) with different MBA weight ratios.

Swelling Water Ratio (SWR)

SWR over a period of 24 hr has been studied for the prepared hydrogel samples and presented in Figure (3). For all samples, it's noticed that SWR has been increased gradually during the first five hours, after that the hydrogel weight began to slightly increase till the water uptake almost stopped. The maximum SWR values were 54, 51.86 and 38.8 g/g for samples 2,3 and 4, respectively. There was an initial increase in the swelling at the beginning, which may be due to the presence of more number of monomer molecules in the vicinity of the propagated chain sites of hydrogel chain. Upon starting the swelling process, the hydrogel has a high hydrophilicity that causes a stronger ability for increasing the water absorption. The reduction in water absorbency by increasing of cross-linker content, can be attributed to the fact that cross linker increases the degree of chain attaching and hence decrease the availability of absorbing water [35].

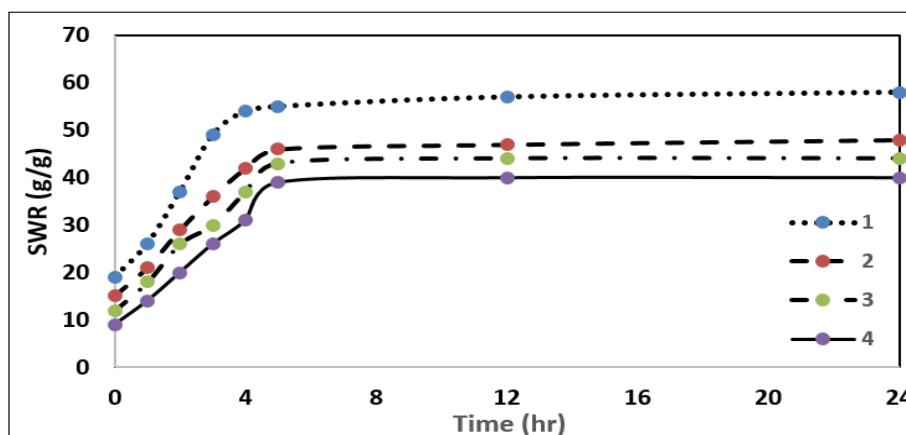


Figure (3) SWR in distilled water during 24 hr

COD, TDS and Dyes Adsorption

Effect of contact time on adsorption of COD and TDS

The effect of contact time on COD and TDS values using the grafted chitosan hydrogel has been studied. As shown in Figures (4 & 5), the investigation has been done on two different types of reactive dyes (Red RSS and Blue HB) at pH 6.2 with the contact time ranged from 3 to 24 hours under constant shaking speed. It was found that increasing the contact time up to 24 hours does not affect the COD removal or TDS reduction. The best results have been achieved applying contact time (3-6 hours). When comparing the results achieved using the four-hydrogel samples, it was found that sample 1 did not achieve good results. Wastewater containing red dye RSS is excluded due to low response towards the COD and TDS with different hydrogel types.

It can be observed by increasing the cross-linker weight ratio to 0.7 g, the adsorption capacity was promoted, while the composite hydrogels containing 0.1 g show low adsorption capacity. It can be observed that by increasing the cross-linker weight ratio to 0.7 g the adsorption capacity was elevated. This result may be attributed to the fact that the physical crosslinking degree increases, leading to the increase in the polymer molecular weight and hence increase the number of functional groups which will lead to trapping more molecules to a definite limit. From the previous results, it can be concluded that during the second phase of the experiments only wastewater containing blue HB dye sample will be tested. The contact time adopted was between 3-6 hours.

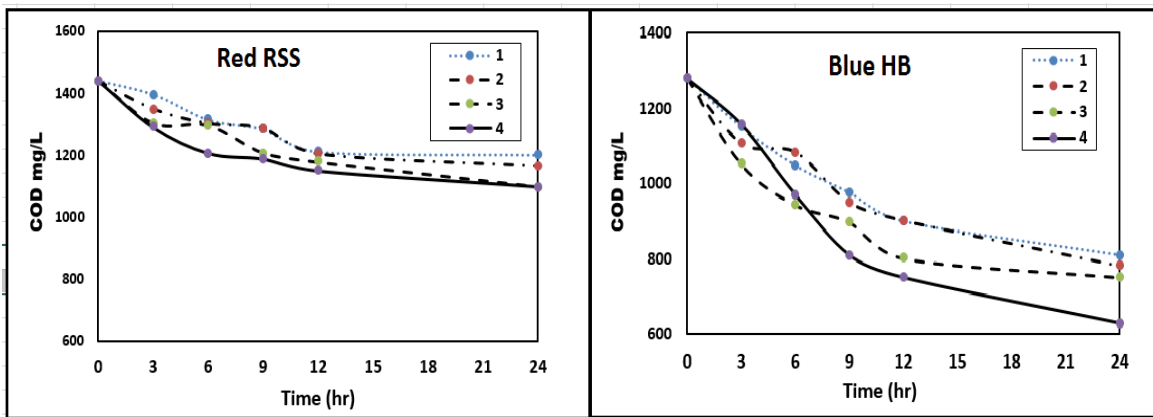


Figure (4) Effect of contact time on COD for Red RSS and Blue HB dyes using the four Hydrogel Samples

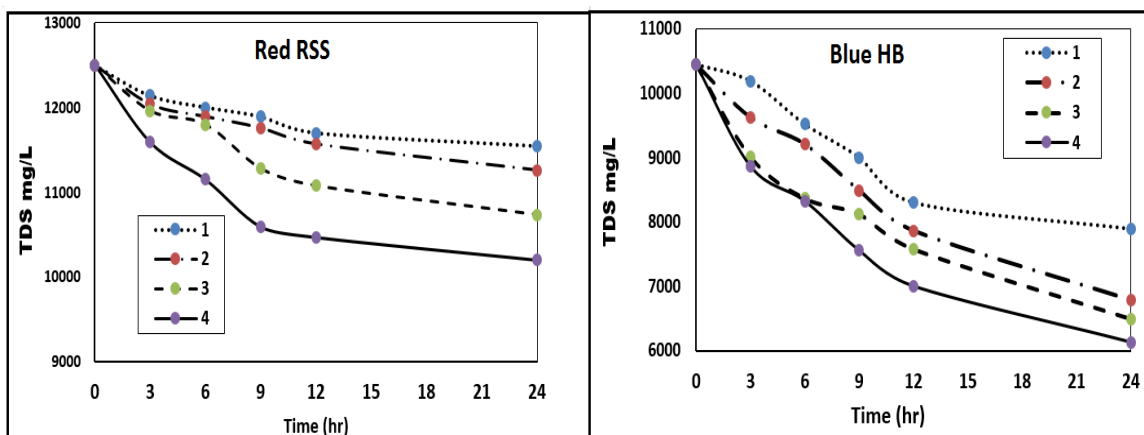


Figure (5) Effect of contact time on TDS for Red RSS and Blue HB dyes using the four Hydrogel Samples

Effect of Initial Ph

Dye Adsorption

The results of Blue HB dye adsorption with initial concentration of 300 mg/g, using 3 hr. contact time and different pH values ranging from 2 to 6 have been studied and the results have been indicated in Figure (6). For Blue HB dye, the hydrogel adsorption capacities increased with increasing pH to a certain limit. This result may be attributed to the occurrence of ionized group in the hydrogel structure, because of the change in ionization degree at low acidic conditions. The carboxyl groups occurred in non-ionized form and no interaction can take place between the carboxyl groups in the adsorbent and the dye molecules. The optimum pH reported for chitosan in the case of Reactive Blue dye was 6.0. [36]

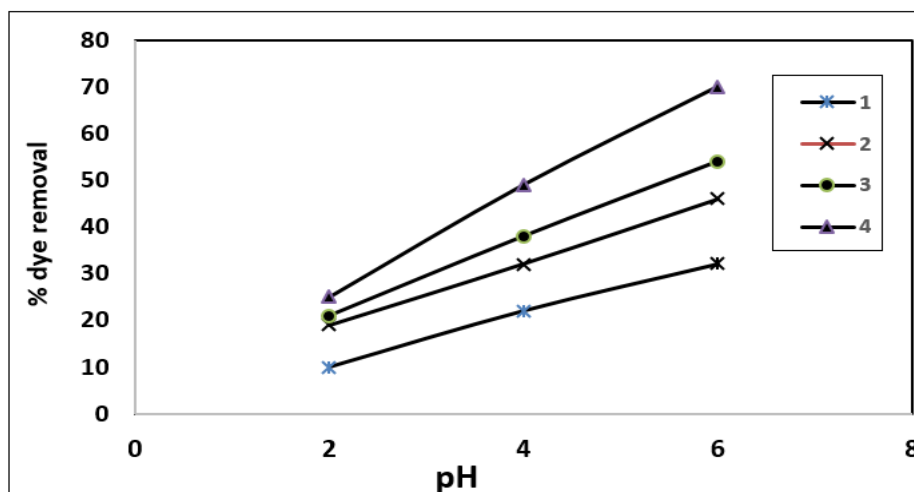


Figure (6) Effect of initial pH on Blue HB dye adsorption ($C_0= 300 \text{ mg/g}$, $w= 0.02 \text{ g}$, $V=0.25 \text{ L}$, $T=25 \text{ }^\circ\text{C}$)

COD and TDS Adsorption

To study the effect of pH on COD and TDS values, experiments have been performed at pH range 2-6 as shown in Table (2). The pH of the solution has a significant effect on the efficiency of dye removing process, as it influence the adsorbent surface charge, the ionization degree for the material present in the solution, the dissociation of functional groups on the active sites of the used hydrogel and the chemistry of dye solution [37].

To determine the effects of pH on the adsorption capacity, a series of experiments have been adopted at different pH values from 2 to 6 at 3-hour contact time. During the hydrolysis process, most of the hydroxyl groups presented in the polymer matrix are converted to carboxylic acid group. Therefore, a constant adsorption capacity is observed at initial pH 2.0. Also, it was observed that for a pH of 2, there were a lot of fine particles suspended in the solution, this may be the reason for low adsorption capacity at this pH [38]. Nevertheless, at pH "4 and 6", all carboxylate groups are transformed to carboxylic groups, causing that the electrostatic attraction force between adsorbent and adsorbent to increase. Therefore, the adsorption capacity shows a remarkable decrease in the stronger acidic range. The prepared hydrogel may be used in acidic pH, signifying its promising potential as an excellent adsorbent material for the dye removal in wastewater treatment [39]. Hence, the reduction of both COD and TDS were observed to be pH dependent. Results showed that the adsorption capacity increased to attain its maximum weight at pH 6.

Table (2) Effect of pH on the COD & TDS values

Sample	Effluent	pH		
		2	4	6
1	COD = 1063 mg/L	974	851	784
2		842	702	635
3		713	490	428
4		634	429	394
Sample	Effluent	pH		
		2	4	6
1	TDS = 11970 mg/L	10200	9490	8908
2		9230	7476	7397
3		8935	5735	5414
4		6390	3554	2736

Kinetic Models

The kinetic analysis of blue HB adsorption onto chitosan grafted hydrogel samples was performed using the pseudo-first-order model proposed by Lagergreen, [25] pseudo-second-order model proposed by Ho and McKay. [40]

The adsorption dynamics can be indicated by determining the adsorption rate constant using a linear form of the Lagergreen equation (4).

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} \cdot t \quad (4)$$

Where: q_e and q_t are the amounts of dye adsorbed (mg/g) at equilibrium and at time t , respectively, and k_1 is the rate constant.

The pseudo-first-order kinetics constant k_1 (min⁻¹) values have been evaluated from the slopes of the linear plot of $\log(q_e - q_t)$ versus t and q_e corresponding model (q_{ec}) from intercept (Figure 7 a and b). The linear form of the equation that describes the adsorption kinetics corresponding to the pseudo-second-order model is the following:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (5)$$

Where: k_2 is the rate constant of pseudo-second order (g /mg. min) and can be calculated from the linear plot of t/q_t versus t , and (q_e) corresponding model (q_{ec}) from intercept. Also, the initial adsorption rate h (mg/g.min) may be calculated using the following equation (6):

$$h = k_2 q_e^2 \quad (6)$$

Table (3), shows that the values of R^2 of the pseudo-second-order model are all higher than those of the first-order model. The experimental data follow the linear relationship of pseudo-second-order adsorption model. By comparing the equilibrium concentration values determined experimentally (q_e) with those calculated (q_{ec}), but there are great differences for all concentrations of Blue HB dye. The rate constants (k_2) decreased with the increase in the initial dye concentration. For the smaller concentration of the dyes, maximum k_2 values of 0.0016. By comparing the obtained equilibrium concentration values with those determined experimentally by Maurusa-Elena et al. [41], a good agreement has been observed.

Table (3) Kinetic Parameters for Blue HB Dye Adsorption

C ₀	q _e	Pseudo-first-order kinetic model			Pseudo-second-order kinetic model			
		q _{ec}	K ₁	R ²	q _{ec}	K ₂	h	R ²
mg/L	mg/g	mg/g	min ⁻¹		mg/g	g/mg·min	mg/g·min	
100	64.00	3.405	0.0272	0.758	1.051	0.0016	6.55	0.997
200	60.00	2.1488	0.0299	0.822	1.043	0.0091	32.76	0.993
300	52.67	1.211	0.272	0.853	1.1371	0.0073	20.25	0.987
400	38.00	2.13	0.0299	0.822	1.2782	0.0078	11.26	0.946
500	26.67	3.81	0.0268	0.754	1.0846	0.0046	3.27	0.992

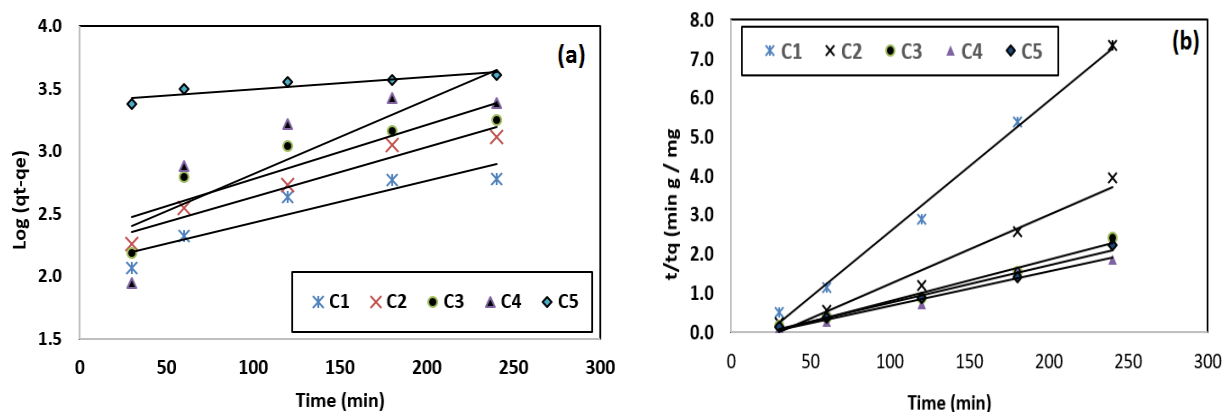


Figure (7) Pseudo first order kinetics (a) and pseudo-second-order kinetics (b) for Blue HB dye removal (C₁=100 mg/L, C₂=200 mg/L, C₃=300 mg/L, C₄=400 mg/L)

CONCLUSION

Hydrogel adsorbent has been successfully prepared using chitosan polymer grafted acrylamide-co-acrylic acid mixture conventionally. FTIR spectrum showed the presence of nitrogen-hydrogen and carbon-oxygen peaks; which proved the presence of acrylamide and acrylic acid monomers in the produced hydrogel backbone. SEM displayed the surface morphology of hydrogel with changed porosity; which affects the swelling and adsorption degree. Hydrogel; which have high porosity shows high swelling degree and hence high adsorption capacity for dye. For swelling test, the three prepared samples swelled in distilled water over 24 hours, it was noticed that after 6 hours the swelling process slightly increased. Hydrogel could efficiently adsorb the dyes under low acidic medium (pH =6) with optimum contact time of 3 hours. The adsorption of Blue HB in 3 h contact time as shown in sample 4, was able to absorb more dye compared to samples 1. The experiments indicate that Ch-g-Am-co-AA hydrogel has a promising potential to remove some kinds of dyes In view of that, the prepared hydrogel is technically achievable, with acceptable efficiency and a cost effective adsorbent. According to the experimental data, the adsorption process follows a pseudo-second-order model for reactive blue HB. From our work, it may be recommended to use in an integrated treatment system to increase the dye removal efficiency.

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