



# Adsorption of crude oil from aqueous solution by hydrogel of chitosan based polyacrylamide prepared by radiation induced graft polymerization

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## ABSTRACT

The adsorption of crude oil (initial concentration 0.5–30 g/L) from aqueous solution using hydrogel of chitosan based polyacrylamide (PAM) prepared by radiation induced graft polymerization has been investigated. The prepared hydrogel was characterized by FTIR and SEM micrographs. The experiments were carried out as a function of different initial concentrations of oil residue, acrylamide concentration, contact time and pH to determine the optimum condition for the adsorption of residue oil from aqueous solution and sea water. The results obtained showed that the hydrogel prepared at concentration of 40% acrylamide (AAM) and at a radiation dose of 5 kGy has high removal efficiency of crude oil 2.3 g/g at pH 3. Equilibrium studies have been carried out to determine the capacity of the hydrogel for adsorption of crude oil, Langmuir and Freundlich adsorption models were applied to describe the experimental isotherms and isotherms constants. Equilibrium data were found to fit very well with both Freundlich and Langmuir models. Also the adsorption of oil onto the hydrogel behaves as a pseudo-second-order kinetic models rather than the pseudo-first-order kinetic model.

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## 1. Introduction

Over the recent years there has been an increasing concern for environmental risk of industrial activities associated with extraction, hydrocarbons, food processing, transportation and refining processes. These industries have increased the threats of oil pollution to the environment and their discharges to the natural environment create a major ecological problem throughout the world [1]. The concentration of oil in effluents from different industrial sources is found to be as high as 40,000 mg/L [2]. Unlike free or floating oil spilled in the sea, lakes or rivers, most of industrial wastewaters contain oil-in-water emulsion among their basic contaminants. Emulsified oil wastewater can lead to severe problems in the different treatment stages. Oil in wastewater has to be removed in order to:

(1) Prevent interfaces in water treatment units; (2) reduce fouling in process equipment; (3) avoid problems in biological treatment stages; and (4) comply with water discharge requirements. Hence the removal of residue oil from process or waste effluent becomes environmentally important.

Among several chemical and physical methods, adsorption process is one of the effective methods widely used in wastewater systems. Adsorption of waste oil using natural adsorbents such as peat [3,4], bentonite organically [5,6], attapugite [7] and activated carbon [8] have been done.

Nevertheless, these systems require a preliminary treatment using physicochemical and microbiological treatment to enhance the adsorption. Polysaccharides such as chitosan are interesting as potentially natural polymers, which could provide advantages in terms of flocculation efficiency or reductions in the life cycle environmental burdens associated with synthetic flocculants. However, as the majority of commodity polysaccharides are of limited charges, and flocculation, for many applications, requires molar charge density above 50%, means to increase the charges on polysaccharides are of interest. Therefore, in order to simplify the adsorption process it is necessary to develop a more efficient and environmental friendly adsorbent to remove crude oil from aqueous solution. Among various modification techniques for chitosan, grafting is recognized as the most promising one, because the abundant amino groups and hydrogel groups in chitosan backbone could react with vinyl monomers under mild conditions. So far, much work has been carried out to perform grafting copolymerization of chitosan and vinyl monomers [9–11]. The grafted copolymers generally possess the main properties of both initial components. They are usually biodegradable to some extent because of the pres-

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ence of polysaccharide backbone. They are also reasonably stable under shearing conditions attributed to the attachment of flexible synthetic polymers onto rigid polysaccharide back bones.

A flexible polyacrylamide grafted onto rigid polysaccharide backbones increases the probability for the flocculant to approach the contaminant particles, and thus improves the flocculant ability of poly-saccharide [12–15]. Therefore, in this study chitosan-g-P(AAm) hydrogel was prepared by grafting method using gamma irradiation. A series of adsorption experiments were conducted to evaluate the possibility of the use of the prepared hydrogel as adsorbent for crude oil from aqueous solution. Adsorption was carried out through a series of batch adsorptions. Several of the physico-chemical parameters of adsorption were evaluated at the dynamic and equilibrium conditions. The isotherm kinetic models were used to describe the experimental data. This information will be useful in further application in treatments of practical oil waste effluents.

## 2. Materials and methods

### 2.1. Materials

Samples of crude oil were collected from the oil Company, El-Seweis, Egypt (Table 1). Before the samples were dispersed in batch system; they were left to stand for sedimentation and removal of the total solid. Chitosan, powder was supplied by Fluka chemical company, acetylation degree 14%, average molecular weight 70,000 kDa. Acrylamide was purchased from fluka chemical company.

### 2.2. Graft copolymerization of acrylamide onto 1% chitosan

Chitosan solution was prepared with 1% acetic acid and its concentration was kept constant, while acrylamide concentration was varied from 20 to 50%. Prior to irradiation, acrylamide was mixed carefully with chitosan solution in pyrex glass vessels and deoxygenated by nitrogen bubbling for 7 min at least for each vessel then the solutions were irradiated with  $^{60}\text{Co}$ - $\gamma$ -ray at different irradiation doses 5, 10 and 15 kGy. The grafted copolymer was then dried at 50 °C and then grinded to mesh size 300  $\mu\text{m}$ .

### 2.3. Swelling measurement

The pre-weight ( $W_d$ ) dry hydrogels of different compositions were placed into a double distilled water and left to reach equilibrium for 24 h at room temperature and at pH 7. The swollen hydrogels were then removed from water, whipped with filter paper and then weighed as soon as possible.

The swelling percent ( $S$  %) was calculated from the following equation:

$$S (\%) = \left( \frac{W_s - W_d}{W_d} \right) \times 100 \quad (1)$$

where  $W_d$  and  $W_s$  represent the dry and swollen hydrogel respectively.

### 2.4. Adsorption studies

Crude oil of different concentrations (0.5–30 g/L) were placed in series of 250 mL beakers containing 100 mL water. After adding 1 g of the prepared hydrogel into the suspension, then left to contact time (1–6 h). pH adjustment (3–9) was done to obtain the best condition for removal of crude oil from the aqueous solution. The optimum conditions obtained from this preliminary analysis were then applied to study the equilibrium and rate adsorption experiment at various initial oil concentrations.

#### 2.4.1. Adsorption equilibrium studies

Adsorption equilibrium studies were conducted using the optimized contact time at pH 3, 7 and 9, respectively. Isotherm studies were conducted with a constant hydrogel weight and varying the initial concentration of crude oil in the range (0.5–30 g/L). The amount of adsorption at equilibrium  $x/m$  was calculated by the following mass balance equation:

$$\frac{X}{m} = (C_o - C_e) \frac{V}{W} \quad (2)$$

where  $x/m$  (g/g) and  $C_e$  (g/L) are the adsorbent phase crude oil and sample phase oil concentration at equilibrium, respectively,  $C_o$  (mg/L), the initial crude oil concentration;  $V$  (L), the sample volume, and  $W$  (g), is the mass of adsorbent.

#### 2.4.2. Effect of initial oil concentration and contact time

In order to study the effect of crude oil initial concentration and contact time on the adsorption uptake, 100 mL of crude oil solution with initial concentration (0.5–30 g/L) were prepared in a series of 250 mL Erlenmeyer flask covered with glass stopper and the flasks were then left to stand at room temperature until equilibrium point was reached. In this case, the solution pH was kept without any adjustment.

#### 2.4.3. Batch kinetic studies

The procedure of kinetic adsorption tests was identical to that of batch equilibrium tests. However the aqueous samples were taken at time intervals. The concentrations of crude oil were similarly measured. The oil uptake at any time,  $q_t$  (g/g), was calculated by Eq. (3).

$$q_t = \frac{(C_o - C_t)v}{W} \quad (3)$$

where  $C_t$  (g/L) is the liquid-phase concentration of oil at time,  $t$  (h).  $C_o$  (g/L), the initial crude oil concentration;  $v$  (L), the sample volume, and  $W$  (g), is the mass of adsorbent.

#### 2.4.4. Analysis techniques

The oil residue content was measured using the oil and grease method recommended by APHA, AWWA, WPeE (1992) standard method of examination of water and wastewater, with methylene chloride being used as oil-extraction solvent. The oil content in the suspension was determined for each sample both before and after experiment. Three replicates of each test run were undertaken with the mean value obtained for residual oil content calculated from the replicates. All tests were carried out at ambient temperature (25–30 °C).

### 2.5. FTIR Measurement

The molecular structure of ungrafted and grafted chitosan with acrylamide was studied using Mattson-1000 FTIR spectrophotometer, Unicam (England).

### 2.6. Scanning electron microscopy (SEM)

SEM images of the dry and oil-loaded hydrogel were recorded using JEOL-SEM-25 (Japan) at a suitable magnification.

### 2.7. Differential scanning calorimetry (DSC)

DSC thermograms of pure chitosan and PAAm were recorded by using Shimadzu DSC system of type DSC-50, with heating rate of 10 °C/min from ambient temperature up to 600 °C.

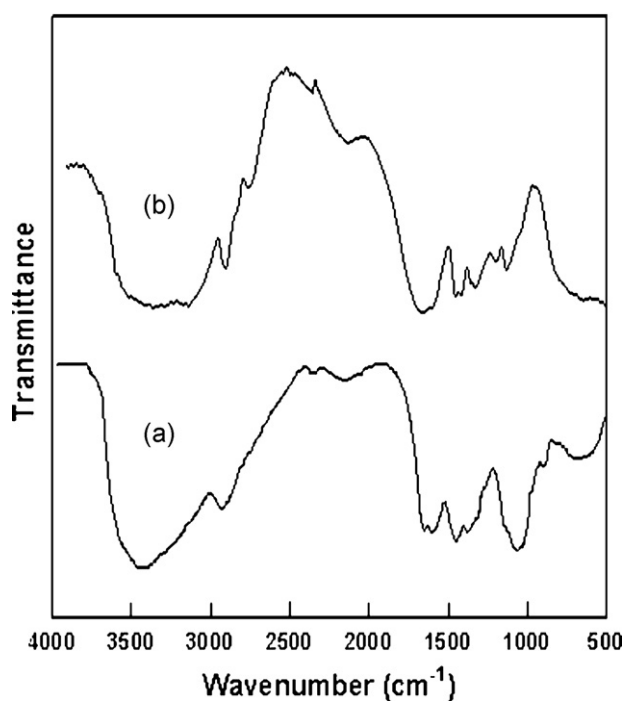


Fig. 1. FTIR Spectra of chitosan (a) and chitosan grafted AM (b).

### 3. Results and discussion

#### 3.1. Characterization of the graft copolymer

##### 3.1.1. FTIR studies

Infrared spectroscopy is a useful tool to confirm the occurrence of graft copolymerization. As shown in Fig. 1a the IR spectrum of the chitosan showed strong bands at 1030, 1081, and 1381  $\text{cm}^{-1}$ , characteristic of saccharide structure (due to O–H bending, C–O stretching, and C–N stretching). The strong band at 3434  $\text{cm}^{-1}$  could be assigned to the stretching vibration of O–H, the extension vibration of N–H, and interhydrogen bonds of the polysaccharide. The FTIR spectrum of the synthesized chitosan-g-P(AAm) showed additional bands at 1664  $\text{cm}^{-1}$  (amide I) and 1641  $\text{cm}^{-1}$  (amide II) due to grafted P(AAm) chains onto chitosan, while a combined band of O–H and N–H stretching in the grafted chitosan is seen at 3414  $\text{cm}^{-1}$  as shown in Fig. 1b. These spectra demonstrate that acrylamide was successfully grafted onto chitosan backbone.

##### 3.1.2. Thermal properties

The graft copolymers prepared in these studies were of natural/synthetic stimuli responsive material. Thermal properties, in particular the melt temperature ( $T_m$ ), of the graft copolymers are interesting in view of the structure–property relationship and for practical applications. The graft copolymers showed inflection points in the DSC profile suggesting the occurrence of structural phase transition. DSC measurements performed on chitosan-g-PAAm and chitosan are presented in Table 2. In the range of temperature scanned, only one endothermic change of the thermal heat capacity is observed that corresponds to the melt temperature ( $T_m$ ). From the table, it is possible to determine the domain of temperature in which the melt transition occurs. The value of  $T_m$  (taken at the mid-point of transition are 228.2 and 86.8  $^{\circ}\text{C}$  chitosan-g-PAAm and chitosan, respectively. This evidence affirms the formation of chitosan-g-PAAm-copolymer.

Table 1  
Basic crude oil analysis.

Experiment	Method	Result
Total acid number, mg KOH/gm	ASTM D-2896	0.133
Total basenumber, mg KOH/gm	ASTM D-974	2.061
Kinematic viscosity, cSt, @ 40 $^{\circ}\text{C}$	ASTM D-445	2.25
PourPoint, $^{\circ}\text{C}$	ASTM D-97	-39
Hydrogen sulfide, ppm	ASTM D-3227	Nil
Mercapten, ppm	ASTM D-3227	Nil
Residual sulfur, ppm	ASTM D-3227	80.37
Total sulfur, wt%	ASTM D-4294	0.59
Nitrogen content, wt%	ASTM D-3228	0.048
Asphalten content, wt%	IP-143	0.16
Wax content, wt%	UOP-64	0.12
BS&W, vol%	ASTM D-96	0.4
Ash content, wt%	ASTM D-482	0.034
Water content, ppm	ASTM D-1744	264.3
Carbon residue, wt%	ASTM D-189	1.096
Molecular weight		160.65
Copper corrosion	ASTM D-130	1a
Flash point, $^{\circ}\text{C}$	ASTM D-93	-15
Salt content, Ptb	ASTM D-3230	36.24
Calorific value	ASTM D-224	45,783

Table 2  
 $T_m$  of Chitosan and 40% AAm grafted chitosan.

Polymer	Chitosan	40% AAm grafted chitosan
$T_m$ $^{\circ}\text{C}$	86.6	228.2

##### 3.1.3. Swelling studies

Fig. 2 shows the swelling behavior of the prepared hydrogels at different AAm concentration and at different irradiation doses. It can be seen that the swelling increases at low AAm concentration (20–30%) and then, decreases with a further increase in the amount of AAm (30, 40%). Also, the swelling decreases with the increase of radiation doses. The initial increment in swelling values can be attributed to the higher hydrophilicity of the hydrogel and the greater availability of AAm molecules in the vicinity of the chitosan macroradicals. The swelling loss at maximum concentration of AAm may be originated from: (a) the increased chance of chain transfer to AAm molecules; (b) increase in the viscosities of the reaction which restricts the movement of the reactants and deactivates the macroradical growing chains soon after their formation, and (c) enhanced homopolymerization reaction over graft copolymerization. Similar conclusions were reported by other investigators [16–19]. With respect to the decrease in the swelling % at high radiation doses. It is well known that at high radiation doses the crosslinking of the prepared hydrogel increases resulting in appreciable decrease in swelling capacity [20].

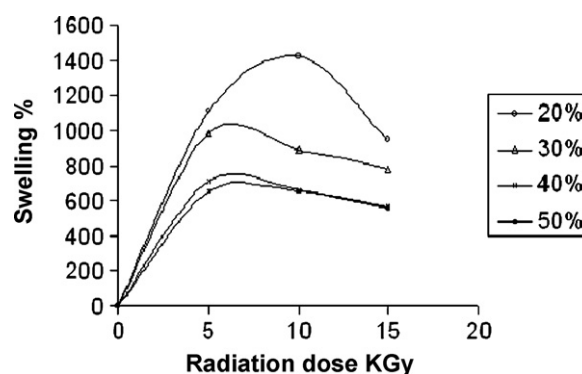


Fig. 2. Relationship between radiation dose and swelling percentage of prepared hydrogel at different acrylamide concentration.

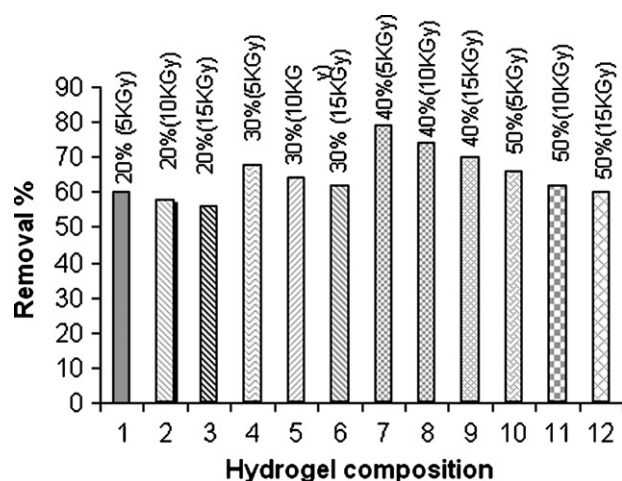


Fig. 3. Removal percentage of crude oil onto prepared hydrogel with different concentration of AM and different radiation doses.

In fact, more crosslinking concentration cause a higher crosslinking density which causes a decrease in the spaces between the copolymer chains and consequently, the resulting highly crosslinked rigid structure cannot be expanded and hold large quantity of water [21,22].

#### 3.1.4. Adsorption of oil onto the prepared hydrogel

Fig. 3 shows the removal percentage of crude oil of initial concentration (30 g/L) after adsorption onto 1 g of the hydrogels prepared at different AAm concentrations (20–50%) and at different radiation doses (5–15 kGy). The results showed that at relatively low AAm concentration (20, 30%) the removal percentage is high compared with that at 50% AAm concentration. The removal percent decreased at high AAm concentration (50%). This may be due to the fact that in dilute suspension, particles may undergo several collisions with other particles before acquiring a sufficient amount of adsorbed polymer to be able to form stable aggregates. With increasing charge density, less polymer is required to neutralize the particle charge. The adsorption time needed to achieve a certain degree of destabilization is less for polymer of higher charge density.

In addition, a combination of factors, such as high molecular mass and very high charge density can contribute to relatively high flocculation activity of cationic polyacrylamide, whereas the attraction between oppositely charged polymer and particles may be stronger for polymer of high charge density because the number of charge per polymer molecule will be higher. As a result, the loops and tails of the flattened adsorbed polymer molecules become too

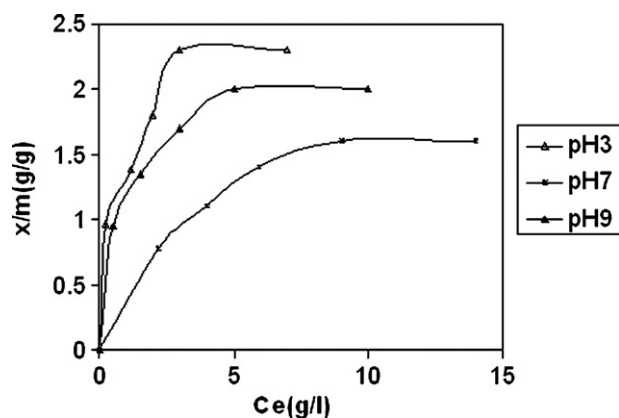


Fig. 5. Equilibrium isotherm of the adsorption of crude oil onto the prepared hydrogel (40% AM at radiation dose 5 kGy).

short to bridge the gap between colliding particle. The decrease in removal percent at 50% AM concentration may be due to the fact that, the possibility of the colliding particles to repeal each other, because of the excess positive charge of the adsorbed is higher with a higher charge density polymer [23].

To further confirm the crude oil adsorption by the prepared hydrogel, SEM micrograph were taken before and after adsorption as shown in Fig. 4. The prepared hydrogel Fig. 4(a) shows a very clear and bumpy layer of pores which are arranged homogeneously. Also the surface is covered with homopolymer resulting from grafting of PAM onto chitosan. However, Fig. 4(b) shows a significant change of the structure and appearance of the prepared hydrogel. The SEM photographs revealed that, most of the hydrogel areas were covered with muddy-line substance which is the adsorbed oil residue. The surface of the hydrogel was spread and covered with a muddy-line or rough surface with crater-line pores due to the oil molecules which cover the hydrogel. These images prove that, oil was adsorbed by hydrogel into its pores and developed a layer of oily substance on the surface.

#### 3.1.5. Effect of initial concentration

The initial concentration study is very important because the initial concentration of the oil residue in solute can strongly affect the adsorption kinetics and more specifically, the mechanism that controls the overall kinetic coefficient. Fig. 5 shows the residual oil removal by hydrogel prepared at 5 kGy and at different pH values as a function of initial concentration. The plots show that the adsorption of oil increases with increasing the initial oil concentration up to a certain value and then tends to reach equilibrium. Certainly, at high initial concentration, the gradient between the solution sample and the center of particle enhances oil residue dif-

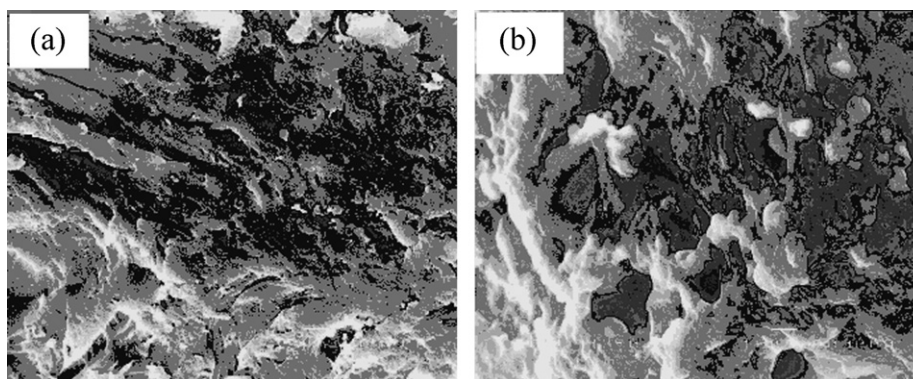


Fig. 4. SEM of prepared hydrogel before oil adsorption (a) and after oil adsorption (b).

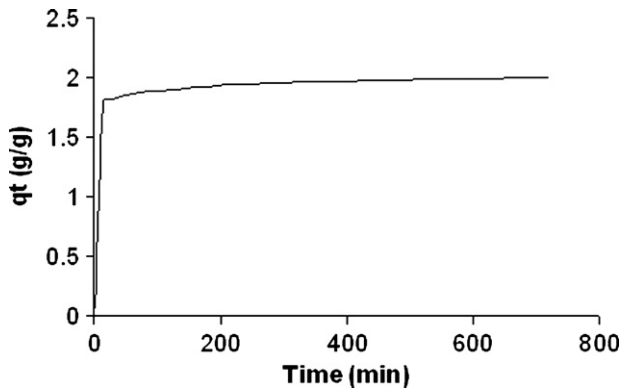


Fig. 6. Effect of contact time on adsorption capacity of crude oil onto prepared hydrogel.

fusion through the film surrounding the particle and in the porous network of the prepared hydrogel [1]. Eventually, when the time goes by, the adsorbed oil residue starts to clog the pores near the outer surface so oil residue can no longer diffuse to the active sites deep within the interior surface.

### 3.1.6. Effect of pH

Emulsion breaking is usually brought about by changing the sample pH value or inorganic coagulants [24]. Therefore, pH adjustments were also done to study the effect of adsorption of crude oil onto the prepared hydrogel. Fig. 5 shows the effect of pH (3, 7 and 9) on the adsorption of crude oil onto the prepared hydrogel. The results showed that the adsorption of crude oil is higher (2.4 g/g) at pH 3, whereas the adsorption is 2 g/g at alkaline medium (pH=9) and the lowest degree of adsorption was shown at pH = 7 (1.6 g/g). Hence it can be concluded that strong acidic conditions aggravates oil to form unstable folk, where chitosan provokes a physico-chemical effect apparently serving to demulsify and increase the droplet size and enhance the adsorption of oil. This acidic condition acts as a catalyst for the reaction between the oil molecules and the adsorption site of hydrogel ( $-\text{NH}_2$  group).

### 3.1.7. Effect of contact time

Fig. 6 shows the effect of contact time on the crude oil uptake on the prepared hydrogel at 25 °C and at pH = 9. The plots show that the adsorption of crude oil increases with time and then reaches a constant value beyond which no more oil was further removed from the solutions. The adsorption curves are single smooth and continuous leading to saturation. At the equilibrium point, the amount of oil desorbed from the prepared hydrogel was in a state of dynamic equilibrium with the amount of oil being adsorbed on the hydrogel. The results revealed that the oil adsorption was fast at the initial stages of the contact period, and thereafter it become slower near the equilibrium. This phenomenon was due to the fact that a large number of vacant surface sites were available for adsorption during the initial stage, and after a lapse of time, the remaining vacant surface sites were difficult to be occupied due to repulsive forces between the solute molecules on the solid and bulk phases.

### 3.1.8. Adsorption isotherms

Adsorption isotherm is important in describing how solute interrelate with the adsorbent and so is critical in optimizing the use of adsorbents. Correlation of isotherm data by empirical or theoretical equations is thus essential for the operating of adsorption systems and practical design. The well-known Freundlich and Langmuir isotherms were used to analyze the adsorption isotherm

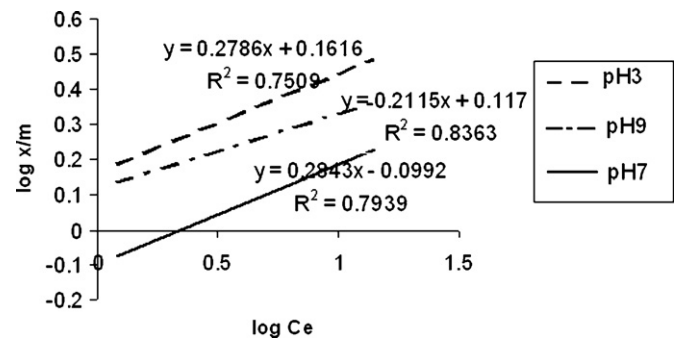


Fig. 7. Freundlich isotherm of adsorption of crude oil onto prepared hydrogel.

results [25] as shown in Figs. 7 and 8. Freundlich isotherm is expressed as:

$$\frac{x}{m} = K_f C_e^{1/n} \quad (4)$$

whereby, this isotherm is usually used in special cases of heterogeneous surface energy which is characterized by the heterogeneity factor  $1/n$  where  $x/m$ , is solid phase sorbate concentration at equilibrium (g/g),  $C_e$  is the liquid phase sorbate concentration at equilibrium (g/L),  $K_f$  is Freundlich constant. Freundlich expression can be obtained in a linear form by taking logarithms of Eq. (5).

$$\text{Log} \frac{x}{m} = \log K_f + \left(\frac{1}{n}\right) \log C_e \quad (5)$$

Therefore, a plot of linearized  $\log x/m$  vs.  $\log C_e$  enables the constant  $K_f$  and exponent  $1/n$  to be determined. The calculated results are listed in Table 3. Langmuir isotherm is expressed as

$$\frac{C_e}{q_e} = \left(\frac{1}{K_L Q_0}\right) + \left(\frac{1}{Q_0}\right) C_e \quad (6)$$

where  $Q_0$  (g/g) is the maximum amount of adsorption corresponding to complete monolayer coverage and  $K_L$  is the Langmuir constant. A linearized plot of  $(C_e/Q_0)$  vs.  $C_e$  gives  $K_L$  and  $Q_0$ .

The essential features of Langmuir isotherm can be expressed in terms of dimensionless constant separation factor,  $R_L$  [26], which is expressed by Eq. (7).

$$R_L = \frac{1}{(1 + bC_0)} \quad (7)$$

where  $C_0$  is the initial concentration of oil residue (g/L);  $b$  (L/g) is Langmuir constant. This parameter shows the shape of isotherm as shown in Table 4.

From Tables 3–5, it can be shown that the magnitude of the exponent  $1/n$  gives an indication of the favorability of adsorption for the prepared hydrogel under the concentration range studied correlation coefficient  $R^2$  were calculated to be 0.7509. The value of  $R_L$  given in Tables 3 and 4 shows that favorable adsorption of oil on hydrogel takes place; therefore, the prepared hydrogel is favorable adsorbents. The mechanism of adsorption may involve three steps;

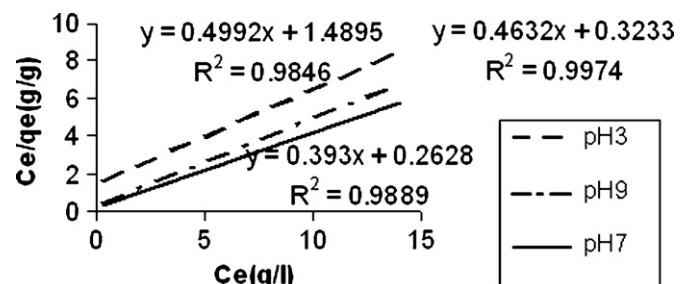


Fig. 8. Langmuir isotherm for adsorption of crude oil onto prepared hydrogel.

**Table 3**  
Langmuir and Freundlich isotherm model constants and correlation coefficient.

Isotherm	Temp (°C)	PH	Constant				R <sup>2</sup>
			Q <sub>e</sub> (g/g)	a <sub>L</sub> (L/g)	K <sub>L</sub> (L/g)	B (L/g)	
Langmuir	25	9	2	2.98	5.96	2.98	0.9846
Isotherm	Temp (°C)	PH	Constant		R <sup>2</sup>		
			K <sub>F</sub> (g/g(L/g) <sup>1/n</sup> )	1/n			
Freundlich	25	9	1.4	0.27	0.7509		

**Table 4**  
The parameter R<sub>L</sub> indicates the shape of isotherm as follows.

Value of R <sub>L</sub>	Type of isotherm
R <sub>L</sub> > 1	Unfavorable
R <sub>L</sub> = 1	Linear
0 < R <sub>L</sub> < 1	Favorable
R <sub>L</sub> = 0	Irreversible

**Table 5**  
R<sub>L</sub> values based on Langmuir equation of oil on hydrogel composite at 25 °C.

Initial concentration, g/L	R <sub>L</sub> values
10	0.03
15	0.02
20	0.016
25	0.014
30	0.011

(I) diffusion of ions residue to the external surface of adsorbent; (II) diffusion into the pores of adsorbent; (III) adsorption of the residue on the internal surface of adsorbent. The first part of adsorption could be affected by the initial concentration and contact time. The final step of the adsorption is considered as a rate-determining step and as a relatively rapid process.

### 3.1.9. Adsorption kinetic studies

In order to examine the controlling mechanism of adsorption such as mass transfer and chemical reaction, several kinetic models are used to test the experimental data.

The rate of adsorption of oil by hydrogel was determined using two simple kinetic analysis. The first one is 1 pseudo-first-order Lagergren's [27] and defined as shown in equation:

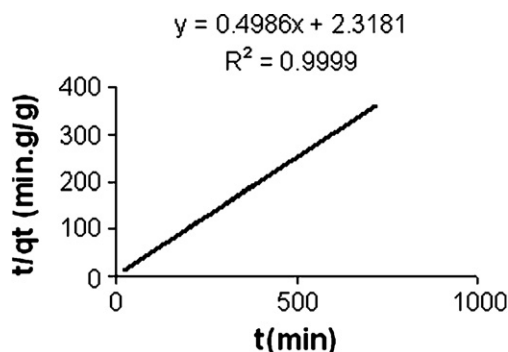
$$\log(q_e - q_t) = \log q_e - \frac{K_1 t}{2.303} \quad (8)$$

where  $q_e$  and  $q_t$  (mg/g) are the amount of adsorbate, adsorbed at equilibrium and at any time,  $t$  (h), respectively and  $k_t$  (1/h) is the adsorption rate constant. The plot of  $\log(q_e - q_t)$  vs.  $t$  (figure is not shown) gave the slope of  $K_t$  and intercept of  $\log q_e$ .

The pseudo-second-order [28] is based on the adsorption equilibrium capacity and expressed as in Eq. (9):

$$\frac{t}{q_t} = \frac{1}{K_2} q_e^2 + \frac{t}{q_e} \quad (9)$$

where  $K_2$  (g/g h) is the rate constant of second-order adsorption. The linear plot of  $t/q_t$  vs.  $t$  gave  $1/q_e$  as the slope and  $1/K_2 q_e^2$  as the intercept as shown in Fig. 9. Normally, pseudo-first-order equation

**Fig. 9.** Pseudo-second order reaction of crude oil onto prepared hydrogel.

is expressed in the range of reaction only and does not fit well with the whole range of contact time and is generally applicable over the initial stage of the adsorption processes, although it has been effectively used to describe adsorption reactions.

The outputs of these models were listed in Table 5. It was found that the correlation coefficient ( $R^2$ ) for the first-order reaction was lower than 1.0. This suggests that the adsorption of oil onto hydrogel is not of first-order. While for pseudo-second-order equation a two-step linear relationship was obtained. Whereby this equation is based on the adsorption capacity, it predicts the behavior over the whole range of studies supporting the validity, and is in agreement with chemisorptions being the rate-controlling process. The straight linear line in plot  $t/q_t$  vs.  $t$  proves a good agreement of experimental data with the second-order kinetic model.

Table 6 shows that the correlation coefficient ( $R^2$ ) for the second-order kinetic model is almost equal to 1.0.

Furthermore, the calculated  $q_e$  value obtained agrees very well with the  $q_e$  of the experimental data. On the contrary, the first-order kinetic model does not give reasonable values and the values are low compared to the actual experimental values. The first- and second-order equations are based on the adsorption capacity. They only predict the behavior over the whole range of studies supporting the validity, and is in agreement with chemisorption being the rate control. Thus, these findings remain uncertain about the adsorption mechanism. Therefore, the intraparticle diffusion model was integrated. This can be described as shown in Eq. (10):

$$q_t = K_t t^{1/2} \quad (10)$$

where  $K_t$  is the intraparticle diffusion rate constant (g/min<sup>1/2</sup>),  $K_t$  is the slope of straight-line portions of plot  $q_t$  vs.  $t^{1/2}$ . The initial

**Table 6**  
Comparison of first- and second-order adsorption rate constants, and calculated and experimental  $q_0$  values for prepared hydrogel.

First-order kinetic				Second-order kinetic			
K <sub>1</sub>	R <sup>2</sup>	q <sub>e</sub> (exp)	q <sub>e</sub> (cal.)	K <sub>2</sub>	R <sup>2</sup>	q <sub>e</sub> (exp)	q <sub>e</sub> (cal.)
3.2 × 10 <sup>-5</sup>	0.8145	2.3	1.16	2.3 × 10 <sup>-5</sup>	0.9999	2.3	2

**Table 7**

Rate parameters of intraparticle diffusion for residue oil adsorption on prepared hydrogel.

Rate parameter, $K_{pi}$ ( $i=1-3$ )		
$K_{p1}$	$K_{p2}$	$K_{p3}$
0.1592	0.0413	0.0059

rates of intraparticle diffusion are obtained by linearization of the curve  $q_t = (t^{1/2})$ .

Previous work showed that such plot may present a multi-linearity [29], which means that two or more stages occur. The slope of each stage is termed as the rate parameter  $K_{pi}$  ( $i=1-3$ ). Table 7 listed rate parameters for hydrogel. It is clearly seen that the first rate is higher compared to the second and third stages because this is the instantaneous adsorption stage. The second one, which is the gradual adsorption, is the stage where the intraparticle diffusion is controlled and the third one is the final equilibrium stage, where the intraparticle starts to slow down due to extremely low oil residue concentration. A good correlation of rate data in this model justifies the adsorption mechanism.

### 3.1.10. Adsorption of crude oil from sea water

The prepared hydrogel was applied for the removal of crude oil (initial concentration (30 g/L) from sea water. The results showed that the removal of crude oil from sea water is 1.8 g/g. This decrease in oil removal than that obtained in aqueous solution at pH = 3 and 9 may be due to the effect of various cations present in sea water, where the water absorbency decreases with increasing the concentration of various alkali metals. This result is attribute to the fact that the osmotic pressure difference between the polymeric network and the external salt solution decreases as the salt solution increases. From the aforementioned results, it is obvious that the prepared hydrogel is applicable for the removal of crude oil in any oily wastewater.

## 4. Conclusions

As a conclusion, a chitosan-based PAAm was synthesized using grafting method by gamma ray to prepare an efficient flocculants hydrogel. The FTIR analysis confirmed the occurrence of grafting. Destabilization of oil in water was successfully performed by application of this hydrogel, which showed a synergistic enhancement for the effective adsorption of crude oil. The prepared hydrogel at 40% AM concentration and 5 kGy showed maximum adsorption of crude oil compared with the other hydrogels prepared at different AM concentrations (20, 30 and 50%) and at different radiation doses (10, 15 and 20 kGy). The adsorption of crude oil on hydrogel is higher at pH=3 compared with pH=7 and 9. All isotherm data fitted with the Freundlich and Langmuir models. This concludes that the prepared hydrogel has a favorable adsorption characteristic. Adsorption kinetic of crude oil onto hydrogel follows the pseudo-second order kinetic model. The adsorption capacity of the prepared hydrogel for crude oil from sea water is 1.8 g/g. Therefore the prepared hydrogel could be useful as a crude oil adsorbent in the oily wastewater. The significant uptake of crude oil on the prepared hydrogel was further proved by SEM micrographs.

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