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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.

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 purcliased 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}Co-γ-ray at different irradiation doses 5, 10 and 15 kGy. The grafted copolymer was then dried at 50 °C and then grinded to mesch size 300 μm.

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:

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

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:

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

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).

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

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.