Separation of Kerosene from water by using a locally Produced Biopolymer from Agricultural Waste

Asst.Prof. Dr. Hayder M. Abdul-Hameed
Seemaa B. Abdulmaged
Department of Environmental
Engineering-University of Baghdad
Email: hayderabdul_hameed@yahoo.com

seemabasim92@yahoo.com

ABSTRACT:-

In this research a biopolymer were locally produced using an agricultural waste (potato peels). The present study is to evaluate bio-sorption process using locally produced biodegradable sorbent from agricultural waste (potato peels) to remove kerosene from water at both batch and continuous process were used. The physical property of the produced biopolymer were measured and it found to have melting point of (188 ^{o}C), density of (1.65 gm/cm^3), porosity range (67.9-89.2 %), Tensile modules of (41.2 GPa) and a Tensile strength of (6.1 MPa). According to the above specification the produced biopolymer can be categorized as a (PGA) type. The influence of different operational conditions such as flow rate, pH, initial concentration, particle size on the dynamic behavior of the adsorption process has been investigated. To achieve these goals, analytical instrumental techniques, experimental procedures and equipments that is employed throughout the present study. Experiments were carried out at various flow rate Q L/min., initial concentrations C_o mg/L, pH, particle size, and bed height with keeping the other variables constant for a given run. The optimum condition for the batch experiments were found to be as follows (Mass of biopolymer=57.62 gm, ($v_{kerosene}/v_{water}$), volume ratio=10/90, Agitation speeds=250 rpm, pH=4, Experimental temperature=35^{o}C). Different continuous systems were achieved to measure the breakthrough curve for kerosene and distilled water carried out at various conditions.

Keyword :(bio-sorption, uptake, biopolymer, potato peels, agricultural waste).

1. Introduction

The presence of toxic materials in water sources is an important issue in water and wastewater treatment, as their consequences on human health have been well established [11].The contamination of the environment has become a main problem in the last few decades. Continuously discharging of wastewater to the ecosystem and the environment resulting for massive industrialization,causing contamination and toxicity for all living and non-living species [10]. The aquatic ecosystem, particularly the marines are the most vulnerable media that affected negatively by the pollutants, especially oil contamination [6]. Oil in water causes reduction of dissolved oxygen due to transformation of the organic component into inorganic compounds, loss of biodiversity through a decrease in amphipod population that is important in food chain, and eutrophication. Short-term toxicity in fishes includes lymphocytosis,epidermal hyperplasia, hemorrhagic septicemia [5]. The photo - enhanced toxicity in fish and aquatic invertebrates appears to occur through activation of chemical residues that bio accumulate in these organisms [7]. Oil spill cleaning operations may cause more damage to a brittle coastal marshland environment than the oil itself. One of the main fates of spilled petroleum oil in the coastal environment is its incorporation into the sediments [2]. Petroleum hydrocarbon contamination of the environment may arise from oil well drilling production operations, transportation and storage in the upstream industry, and refining, transportation, and marketing in the downstream industry. Petroleum hydrocarbon pollution could also be from anthropogenic sources [15]. A biopolymer it is a polymer that is developed from living beings. It is a biodegradable chemical compound that is regarded as the most organic compound in the ecosphere. The name “Biopolymer” indicates that it is a bio-degradable polymer, a huge number of biodegradable polymers (e.g. cellulose, chitin, starch, polylactide, polycaprolactone, collagen and other polypeptides…) have been synthesized or are formed in natural environment during the growth cycles of organisms. Some microorganisms and enzymes able of degrading such polymers have been recognized [12]. In spite of crude oil source or processing history, kerosene's main components are branched and straight chain alkanes and naphthenic (cycloalkanes), which usually account for at least 70% by volume. Aromatic hydrocarbons in this boiling range, such as alkyl benzenes (single ring) and alkyl naphthalene (double ring), not typically greater than 25% by volume of kerosene streams [3]. The major natural factor that affects oil products polluted beach areas is biodegradation. Oil that covers rocks and stones, and that permeates into sandy beaches, is quickly colonized by hydrocarbon degraders, even in cold water environments [13]. Beach areas will be much more affected by air temperature, which means that in summer months, increased degradation activity can be expected. In addition, physical reworking of the oil due to wave action in the winter months and input of alternative carbon sources (algal biomass, plant litter, etc.) will often completely affect the oil degradation activities [20]. The acute health risks involved in handling and using minimal kerosene that provided the product(s) are used in agreement with present safety practices [9]. The most important hazard associated with kerosene is chemical toxicity, following intake or breathing of kerosene liquid or polluted water. An unusual difficulty of kerosene intoxication may be cardiac arrhythmia and ventricular fibrillation, attributed to increased myocardial sensitivity to endogenous catecholamine. At the same time as kerosene vapors may be gently irritating to the respiratory system [4], exposure is not likely to be fatal as the low volatility of kerosene [19] limits air concentrations to below (100 mg/m^3) [17] ,which is the estimated no clear adverse effect level in several animal species [16] .

2. Materials

2.1 Preparation of bio-adsorbent

Potato peels are one of the refuses matters that a produced in large quantities by the food industries. Its availability and the presence of starch, pectin, and cellulose make it a potential, sustainable and renewable raw material for polymer products. The potato peels were collected and washed with tap water to remove external dirts, to produce potato starch. The shredded potato was grinded into grinder stone with grated by using shredder, as shown in **Fig. (1a)** (100 ml) of water was added to help to draw out the potato juice. Then, the juice was poured into beaker through a fine strainer, as shown in **Fig. (1b),** and kept for (10) minutes, the starch was left to settle out, as shown in **Fig. (1c).** After that, (100 mL) water was added to rinse the starch. This process was repeated where the water was decanted off again to get the potato starch, as shown in **Fig. (1d)** [22]:

a) Potato peels after grinding.

b) Potato peels were soaking.

c)Settled out mixture. **d) Starch after settling and draw out water**

. Fig. (1): (a), (b), (c), (d) natural potato peels after grinding and soaking to prepare starch

The dried biopolymer were grinded and sieved to a size of (500 µm, 710 µm, 600 µm) to study the effect of various particle sizes on the adsorption process, as shown in **Fig. 2.** The samples were stored in air tight container.

Particle size (500µm)

Particle size (600µm)

Particle size (710µm)

Fig. 2 Different particle sizes of produced biopolymer.

3. Experimental Procedure

Two types of experiments were carried out:

3.1 Batch Experiment

Five different batch experiments were conducted in order to obtain the best condition for maximum removal of kerosene from water, and as follows:

a) Different weights of the biopolymer:

Different volumes of locally produced biopolymers were used as follows (5, 10, 15, 20, and 25 mL), after that the real density was measured in the (ministry of oil / petroleum R&D center) and found to be (2.305 gm/cm^3) and the masses of produced biopolymers that were used in the batch adsorption experiment as bio-adsorbent are (11.52, 23.05, 34.57, 46.10, 57.62 gm) to determine the best mass of biopolymer for bio-sorption was prepared containing the desired ($v_{kerosene}/v_{water}$) solute ratio (50 mL) of kerosene and (50 mL) of distilled water measuring it experimentally. Samples of (100mL) of the solution were taken. The pH was measured equal to (7) and temperature was (25 °C). Then 5 flasks placed in shaker and agitated at (100 rpm) continuously for (24) hours. The solution then filtered through filter paper [18] the percentage of the uptake for both kerosene and water was measured.

b) Different ($v_{kerosene}/v_{water}$) volume ratio:

From the step (a), it found that the best mass of bio-adsorbent (biopolymer) is (57.62 gm). Then, this mass is used in the second step to obtain the best ($v_{kerosene}/v_{water}$) ratio. The pH was measured equal to 7 and temperature was (25 °C). Then 5 flasks placed in shaker and agitated at (100 rpm) continuously for (24) hours. The solution then filtered through filter paper.

A Solution was prepared containing the desired solute ($v_{kerosene}/v_{water}$) ratio and as follows according to **Table. 1**:

Table 1. Different ($v_{kerosene}/v_{water}$) ratio experiments.

Kerosene, mL	Water, mL
10	90
20	80
30	70
40	60
50	50

3.2 Continuous System

A. Equipment

A glass cylinder was used of length (80 cm) and diameter (3.5 cm) (inner diameter).A mesh was used to prevent any losses of produced biopolymer from the bed, and then the solution (kerosene and distilled water) pass through it. A cylindrical plastic container was used with the volume of (120 L) to contain the solution. One flow meter was used to measure the flow rate ranged (1.8- 18 L/min). The solution (kerosene and water) was pumped by means of two pumps from the feed container to the bed. The complete set up of the system shown in **Fig. 3:**

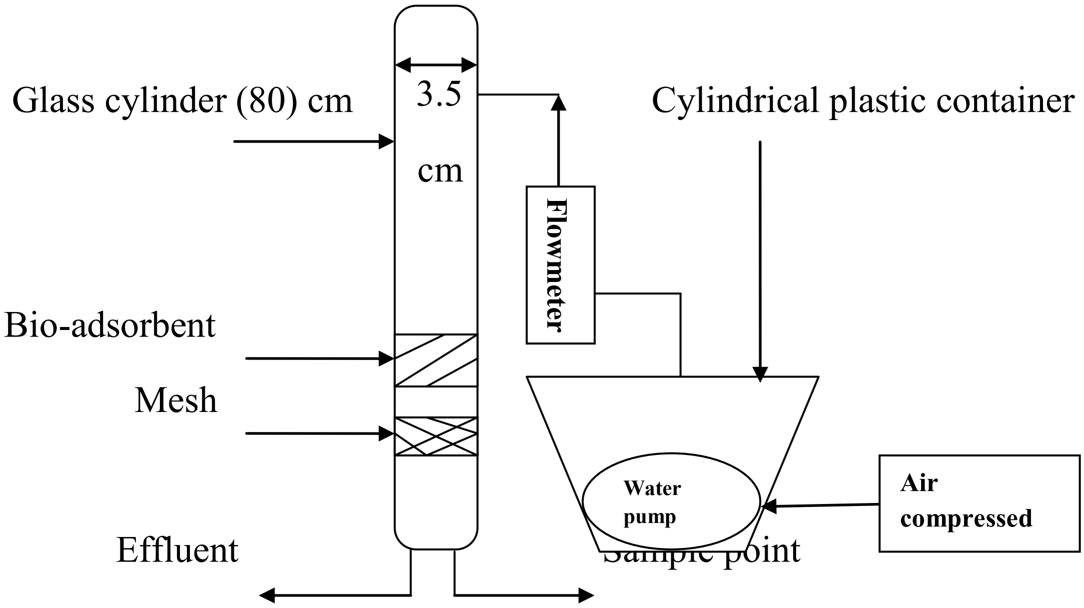

Fig. 3 Schematic diagram of the continuous system.

4. Results and Discussion

4.1 Adsorption Equilibrium Isotherm (Batch Process)

In order to identify the adsorption isotherm, batch process for kerosene was carried out to investigate the type of produced adsorbent equilibrium isotherm relation. The adsorption isotherm system was conducted by using produced bio-adsorbent from potato peel.

The adsorption isotherm was obtained by plotting the weight of the solute adsorbed per unit weight of bio-adsorbent (q_e) against the equilibrium concentration of the solute in the solution (C_e) [8]. The type of model is linear and the data is listed as show in **Fig. 4:**

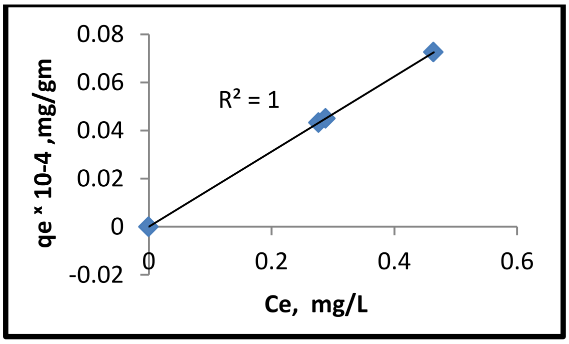

Fig. 4 Adsorption isotherm for (water/kerosene) onto produced biopolymer.

The linearity shape of the isotherm is refers to:

1. There is semi-equality behaviors of the bio-sorption for both the solute and the solution that leads to an equally division of the adsorption isotherm, i.e. both favorable and non-favorable behavior will expect simultaneously.

2. The reason for the above is due to the double nature behavior of the produced bio-adsorbent as (hydrophilic/hydrophobic) properties, that in turns balancing the uptake (rather than to be favorable and/or non-favorable).

3. A certain amount of kerosene will suffer an absorption process (in addition to the adsorption) that will deviate the adsorption isotherm either from favorable or non-favorable to the linear form.

Recall to the article (3.1a) the optimum result for the mass of bio-adsorbent is found to be (57.62 gm). The water and kerosene percentage contents (uptake) for different bio-adsorbent were measured, as shown in **Fig. 5**

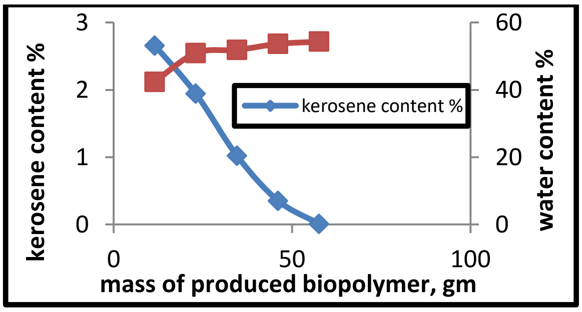

Fig. 5 water and kerosene percentage content for different masses of bio-adsorbent.

Fig. 5 shows that the uptake of water increases with increasing mass of bio- adsorbent. The uptake of kerosene decreases quickly with increasing masses of bio-adsorbent. The fact of that, with an increase in the mass of bio-adsorbent, more bio-adsorbent surface area is available for the solute to be adsorbed; furthermore, more hydrophilic matter will be available for more water attraction (bio-sorption) leads to a noticeable increase in the water content, in turn reduction (hydrophobic) of the kerosene content in the biopolymer [14].

Recall to the article (3.1b) and the optimum result for the ($v_{kerosene}/v_{water}$) is found to be (10) mL of kerosene with (90) mL of water. The water and kerosene contents (uptake) for different bio-adsorbent were measured, as shown in **Fig. 6.**

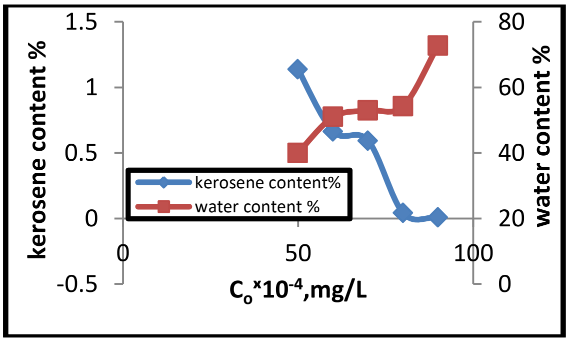

Fig. 6 water and kerosene percentage content for different ($v_{kerosene}$ / v_{water}) volume ratio.

Fig. 6 show that the uptake of water increases with increasing of water volume in the solution. The uptake of kerosene decreases rapidly with decreasing of kerosene volume in the solution, this is due to, as increasing the water volume in comparing with the kerosene volume, that will increase the domination of the matter that have an attracted phenomena to the biopolymer, hence increasing it content in the biopolymer in addition to the increase in the mass of bio-adsorbent [21].

5. Adsorption models:

Two major models (Langmuir, Temkin) were conducted and used to measure how the data were matched with the proper model, the results of each models were shown in **Fig.s 7,8 respectively.**

a) Langmuir model:

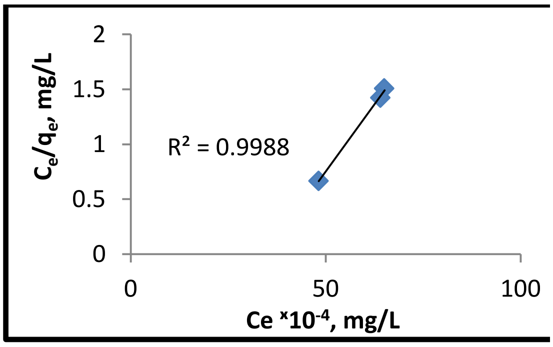

Fig. 7 Langmuir model.

b) Temkin model:

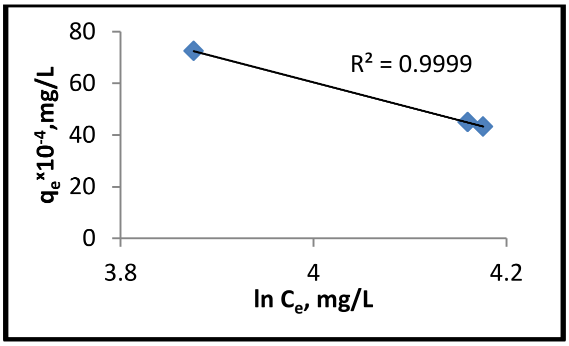

Fig. 8 Temkin model.

6. Fixed Bed Experiments (continuous process)

The fixed bed adsorber was used for determination the breakthrough curves based on different conditions of operation. Where temperature set to 25°C.

1. Effect of the bed height:

The effect of using various bed height (0.5 cm, 1cm, 1.5cm, 2cm) of the produced bio-adsorbent on the breakthrough curve were studied by keeping the other parameters constant flow rate (0.1 L/min), initial volume ratio ($v_{kerosene}/v_{water}$) of kerosene (50 ml) to water (50 ml), particle size (500µm) and pH (7) and temperature (25°C) , the samples were taken every (10) minute .The Breakthrough curve is presented in **Fig. 9:**

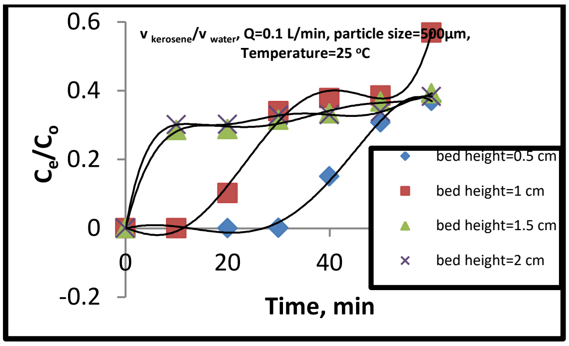

Fig. 9 Breakthrough curves for bio-sorption of kerosene onto the bio-adsorbent at different bed heights.

From **Fig. 9** it can be observed that as the bed height increases, the breakpoint increases. This shows that at smaller bed height the effluent adsorbate concentration ratio increases more rapidly than for a higher bed height. Furthermore, the bed is saturated in less time for smaller bed heights. Smaller bed heights corresponds to lesser amount of bio-adsorbent, consequently, a smaller capacity for the bed to adsorb adsorbate from solution. As the flow rate kept constant, then increasing the bed height will increase the contact time of the solute with the bed.

2. Effect of the particle

The effect of using various particle size (500µm, 600µm, 710µm) of the produced bio-adsorbent on the breakthrough curve were studied by keeping the other parameters constant flow rate (0.1 L/min), bed height (2 cm) initial ratio (v $_{\text{kerosene}}$ /v $_{\text{water}}$) of kerosene (10 ml) to water (90 ml), pH (7) and Temperature (25°C), take sample every (10) minute. The breakthrough curves are presented in **Fig. 10**

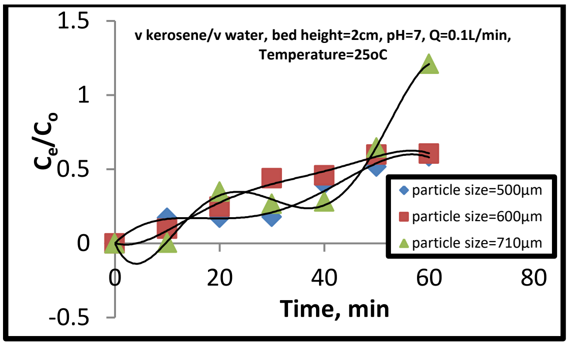

Fig. 10 breakthrough curves for bio-sorption of kerosene onto the bio-adsorbent at different particle size.

From **Fig. 10**, the breakthrough curves show that the time required for reaching the breakpoint increases as the particle size decreases. This is because when the particle size decreases surface area available for adsorption will increase (i.e. more sites available for adsorbate) and the capacity of adsorption increase. Therefore it will increase the time for saturation as the particle size decrease, and increasing in the thickness of stagnant film around the particles, also inside the pore the total length path increases. Under these conditions, the overall kinetics of the process is low; due to the time for molecule of adsorbate is more to reach the adsorption site, as the diffusion path along the pores is large [1].

6. Conclusions

1. Potato peels offering attractive raw materials to produced a biopolymer having a physical specification approaching to PLA.
2. The produced biopolymer holding both hydrophilic/hydrophobic natures, Hence, then can be conducted in a wide spectrum usage for wastewater treatment technologies.
3. The batch experiments revels that the adsorption isotherm is of a linear type that reflecting the balancing nature (hydrophobic, hydrophilic) behavior of the produced biopolymer.
4. The kerosene/water system that it follows (freundilch isotherm).
5. The optimum conditions for the batch experiments show that (Mass of biopolymer=57.62 gm, ($v_{kerosene}/v_{water}$), volume ratio=10/90, Agitation speeds=250 rpm, pH=4, Experimental temperature=$35^{o}C$).
6. In the continuous experiments it found that the adsorption capacity, Hence, with increasing the adsorbent mass, pH and temperature decrease with decreasing flow rate, $V_{kerosene}/V_{water}$).
7. The produced biopolymer have a good degradation nature as is degrade totally in soil with (70-92) days for different soil nature.

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فصل الكيروسين من المياه عن طريق استخدام البوليمر الحيوي المنتجه محليا من المخلفات الزراعية

م.أ.د. حيدر محمد عبدالحميد

سيماء باسم عبدالمجيد

قسم الهندسة البيئية

كلية الهندسة- جامعة بغداد/ العراق

الخلاصة

في هذا البحث تم إنتاج البوليمر الحيوي محليا باستخدام المخلفات الزراعية (قشور البطاطا). تم قياس الخواص الفيزياوية للبوليمر الحيوي المنتج ووجد ان درجة الانصهار (188 درجة مئوية)، الكثافة (1.65 غم/سم^3)، والمجموعة المسامية بمعدل (67.9-89.2٪)، ومعامل الشد (GPa41.2) وقوة الشد (MPa6.1). وفقا للمواصفات المذكورة أعلاه البوليمر الحيوي المنتجة يمكن تصنيفها على أنها من النوع (PGA). أجريت مجموعتين من التجارب لدراسة تأثير البوليمر الحيوي المنتجة لإزالة النفط من المياه، في تجاربBatch وجدت لتكون ذات شكل خطي وهذا دليل على حقيقة ان البوليمر الحيوي ممكن ان تكون hyderophilic , hyderophobic في نفس الوقت، ويمكن استخدامها للبقاء النفط في المياه والعكس بالعكس. وقد طبقت ثلاثة نماذج للبيانات وأنها وجدت أن (نموذج) مطابقة تماما مع $R^2 = 1$. تمت دراسة خاصية قابلة للتحلل من خلال زراعة البوليمر الحيوي المنتجة في نوعين مختلفين من التربة (الغريني، الرملي) وجدت أنه تتحلل تماما ضمن المدة (70-92) يوما على التوالي. تم العثور على افضل الظروف للتجارب Batch لتكون على النحو التالي (كتلة البوليمر الحيوي = 57.62 غم، النسبة الحجمية للنفط و المياه = 90/10، الانفعال بسرعة = 250 دورة في الدقيقة، ودرجة الحموضة = 4، ودرجة الحرارة التجريبية = 35 درجة سيليزية). في حين لتجارب Continuous عوامل مختلفة اجريت وهي كالتالي (الكمية الممتزة، النسبة الحجمية للكيروسين والمياه، معدل التدفق، ودرجة الحموضة، وكانت أجرت درجة الحرارة) و معدل الامتزاز له علاقة مباشرة مع الكمية المممتززة ، ودرجة الحرارة، وبصورة عكسية مع حجم الدقائق ، ودرجة الحموضة، ومعدل التدفق لمعدل امتصاص الماء وبالطريقة المعاكسة عند النظر في معدل امتصاص النفط.