Oil by-Product Removal from Aqueous Solution using Sugarcane Bagasse as Absorbent

Hamid Sarkheil, Javad Tavakoli, Reza Behnood

Abstract— ***Recently many researchers have proved the capability of agricultural solid wastes as adsorbents to remove many types of pollutants including petroleum hydrocarbons. This study was examined oil adsorption capacity of modified sugarcane bagasse to explore their practical application in treating oil spills within water. All type of oil by-products are toxic and cause severe problems to aquatic environment. Sugarcane bagasse can remove some oil by-product, although need modification. The oil by-product capacities of sugarcane bagasse vary, depending on the pH of solution, initial oil concentration, adsorbent dosage and its size, process temperature and salinity of aqueous. Maximum adsorption capacity of modified micro size bagasse was seen about 20g oil by-product per 1g sorbent.***

Index Terms—Oil by-Product, sugarcane bagasse, pollutants, modification.

I. INTRODUCTION

Oily wastewater is one of the environmental concerns nowadays. The seriousness of oil pollution problem comes in sync with the expansion of oil exploration and production activities, as well as industrial growth around the world [1]. Oils in wastewater can be found in various forms such as fats, lubricants, cutting oils, heavy hydrocarbons, and light hydrocarbons [2]. Oil and its derivatives are some of the products with high polluting potentials, because besides being stable to light and to heat, they are also very difficult to undergo biodegradation [3]. These oils can be further divided into two categories, namely free and emulsified oils. The free oil fraction of the wastewater is easier to treat by physical techniques [4] in contrast, emulsions or the oil droplets dispersed in water phase, are more difficult to treat due to their high stability in aqueous phase [5] .Adsorption is one of the most effective processes of advanced wastewater treatment, which reduces trace hazardous organic and inorganic wastes left in effluents after the conventional treatment. It is also used to remove toxic inorganic and organic compounds from contaminated groundwater [6]. The relative advantages of adsorption over other conventional advanced treatment methods are: 1) it can remove both organic as well as inorganic constituents even at very low concentrations, 2) it is relatively easy and safe to operate, 3) both batch and continuous equipment can be used, 4- no. sludge formation, and 5- the adsorbent can be regenerated and used again. Moreover, the process is economical because it requires low capital cost and there are abundant low-cost materials available, which can be used as adsorbents [7].

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Vegetal tissues, with large surface area and big pores, tend to adsorb organic contaminants through physical and chemical mechanisms, in a similar way to charcoal [8] - [10]. Several researchers, while studying adsorption of oil by-products using different types of biomass, have observed the promising character of these materials as adsorbents [11]. bagasse can be used as a support for new adsorbents as well as being used "in-nature", representing thus a great reduction in costs [12]. Table 1 presents a brief literature review of sugarcane bagasse uses as adsorbent. It is interesting to notice that most of references used modified sugarcane bagasse. Although it can be seen that modified bagasse is very efficient to adsorb a variety of compounds, the pre-treatment can add important costs to the process [13].

Table 1 A Brief Literature Review of Sugarcane Bagasse uses as Adsorbent

Absorbent	Adsorbate	PH	Adsorption capacity (mg/g)	Ref.
Treated sugarcane bagasse	Pb	5.0	227.7	[14]
Mercerized sugarcane bagasse	Cu(II) Cd(II) Pb(II)	5.4 7.0 6.0	153.9,250, 500	[8]
Mercerized sugarcane bagasse	Ca(II) Mg(II)	10.0 9.0	54.1,42.6	[15]
Modified sugarcane bagasse	Sulphate ions	10.0	38,400	[16]
Chemically modified sugarcane bagasse	Cu(II) Cd(II) Pb(II)	5.5 6.6 7.5	139,313,313	[17]
Modified sugarcane bagasse	Cr(VI)	3.0	103	[18]

II. EXPERIMENTAL

A. Preparation of the Sorbent Material

At first sorbent is made in micrometer size, raw bagasse was crashed for 2hr in vegetable crasher. Then it was passed through different sieve for particles with micro size, substance were selected under sieve with mesh number 100 (149µm) and mesh number 200 (74µm). Before the use in the adsorption experiments, micro size sugarcane bagasse was washed in tap water and then in distilled water to remove the water-soluble particle and surface adhered particles and then dried in oven for 16hr at 80°C. then Chemical activation of the adsorbent was carried out. 15g of micro size sugarcane bagasse was well mixed with 300 ml acetic anhydride and 3g NBS (N-bromomsuccinimide),

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and were put in a 500ml Pyrex batch reactor that was equipped with a reflux condenser. This setup was put in oil bath at 100°C for 2.5hr. after treatment the biomass was separated and thoroughly washed with ethanol and acetone until removed the un-react acetic anhydride and acid by-product. Then biomass was dried in a hot air oven at 60°C for 16hr.

B. *Sorbent Water-Soluble*

In this study solubility in water for sorbent were measured according to ASTM(American standard test) D5029-98. A known quantity of the adsorbent (10g) was placed into a aqueous solution of oil by-product with a predetermined concentration (100ml) reflux apparatus. The mixture was reflux for 15min under specified condition. At the end of the adsorption process, the sorbent was separated by filtration and an aliquot of the filtrate (20ml) was evaporated to dryness at 150±5°C for 1hr and the oil by-product concentration was then analyzed. Water soluble are determined by weighting the dry residue and expressing the result as a percentage of dry carbon weight [19]. The following equation is used for a general calculation of water-soluble (equation (1)):

$$\text{Water-soluble \%} = \frac{(B-A)(D)(100)}{(C)(E)} \qquad (1)$$

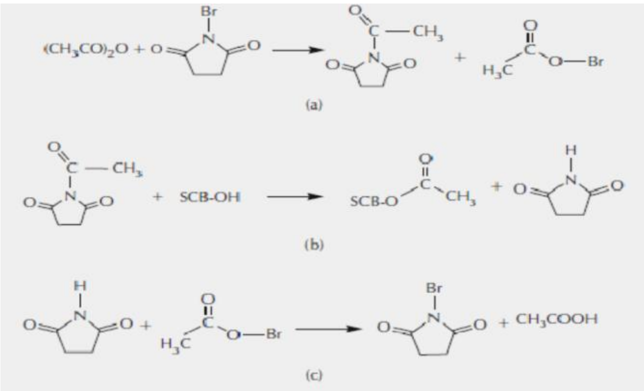
Where A (g) mass of evaporated dish, B (g) mass of evaporated dish plus residue, C (g) mass of carbon, D (ml) volume of water used in extraction and E (ml) volume of aliquot used.

C. *Oil by-Product Adsorption Procedure*

To determine the sorption capacity in this study, the experiments are done in batch system according to: ASTM F726-99 for sorption experiment. To simulate the wastewater contaminated by oil by-products and creation a stable oil emulsion mixture, commercial oil by-product was dispersed in water and the surfactant between 80 in proportion of 0.5% volume present was used. This sample was mixed for 24hr and stirring speed 1000 rpm. To perform the adsorption, 100 ml of contaminated water were placed in the flask. The flask was put in the incubator with a determined temperature and et the speed of 150 rpm for 3hr. In the end of experiment, the samples were filtered under vacuum using paper in Buchner funnel, sealed. The COD test was used in the experiment to determine the concentration of oil in water in the initial and final sample. adsorbate/adsorbent ratios were used to obtain the kinetic curves of oil by-product adsorption on sugarcane bagasse.

III. Results and Discussion

Raw bagasse is a combination of cellulose, lignin, and other minor components. A material absorbs hydrophilic and hydrophobic materials. The mechanism is partly because there are hydrophilic and hydrophobic sites of bagasse that can attract these materials, respectively [20]. Bagasse is typically treated by modified reactions to improve sorption capacity. Cellulose molecules are more attracted to hydrophilic than to hydrophobic materials [20]. To improve this properties of bagasse, micro size bagasse was modified by acetylation reaction with acetic anhydride, using NBS(N-bromomsuccinimide) as a catalyst. While the role of NBS is not clear but it attributed to Br+ [21]. Figure 3.1 shows the mechanism of this reaction based on the study of



acetylation of alcohols.

Figure 1 Mechanism of Acetylation of Raw Bagasse using NBS as a Catalyst (a, b & c) [2]

A. *Analysis of FTIR Test*

Figure 2.a and 2.b shows FTIR spectra for raw sugarcane bagasse and sugarcane bagasse modified with acetic anhydride and NBS (N-bromomsuccinimide). FTIR study was performed to characterized the chemical structure of sorbent. The O-H stretching vibration in a hydrogen-bonded dimmer is observed in the 3500-2500 cm-1 range rather than in the usual 3700-3600 cm-1 range. In Figure 2.a the strong signal at about 3400 cm-1 is typical from cellulose and a medium signal, between 1500-1700 cm-1, is due to the carboxylic groups, present in lignin and hemi-cellulose.

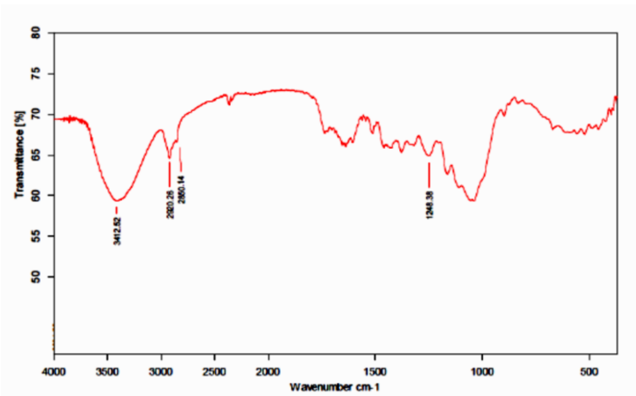


Figure 2.a Infrared Spectrum of Modified Bagasse

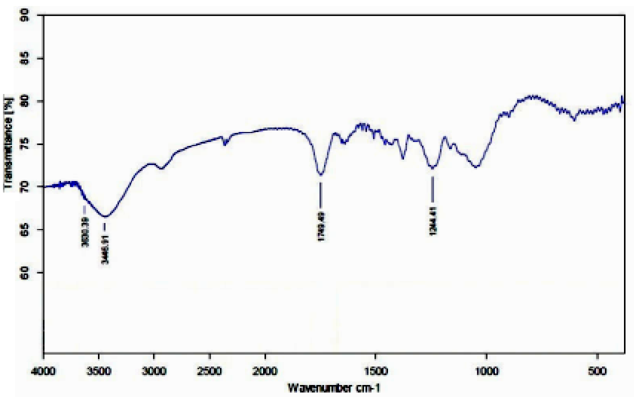


Figure 2.b Infrared Spectrum of Modified Bagasse

Major change before and after treatment are reduced peak in region, 3700-3400 cm-1 for O-H, at 3446 cm-1 that indicated after reaction. The other changes are occurrence of two important ester band at 1749, and 1244 cm-1, which are attributed to adsorption by carbonyl bonds (C=O ester), and -C-O- stretching in ester (-C-O- in acetyl group), respectively.

B. Effect of Different Variables on Efficiency of Adsorption

The results for the characterization of the prepared sugarcane bagasse are discussed in this study. The tests for characterization include initial oil by-product concentration and sorbent dosage.

C. Effect of Initial Oil-by Product Concentration

Oil initial concentration affects oil removal from wastewater as the oil initial concentration influences the oil adsorption kinetics [23]. It seems that, at high oil concentration, oil occupies the sorbent surface thus saturation is reached much faster and high amount of unattached oil is left [24]. But What we've seen Is inconsistent with what would be expected. To study the effect of the initial concentration of oil by-product in the solutions, the experiment were carried out at a fixed modified micro size bagasse dose (6 g) and at different initial oil by-product concentrations (200, 600, 1000 ppm) other parameter such as retention time and temperatures and PH are fixed at 3 hr and 25 °C and 7 respectively. Figure 3 shows this result.

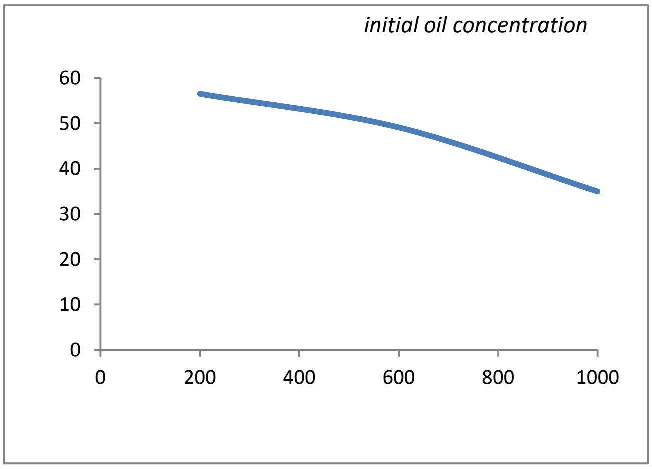


Figure 3 Initial Oil Concentration (ppm) vs. Removal Efficiency

D. Effect of Sorbent Dosage on Oil by-Product Adsorption

With increase the sorbent dosage, oil removal efficiency will increased. The phenomenon is associated with an increase in available binding sites for adsorption in higher sorbent dosage [27]. However, sorption capacity decreases with an increase in sorbent dosage, mainly due to the increase of unsaturated oil binding sites [28]. In addition, saturation effect also causes a decrease in oil removal efficiency when maximum sorption capacity has been reached [29]. The experiments are done for oil by-product concentration (600 ppm) and different sorbent dosage (2, 6, 10 g). Figure 4 shows the effect of sorbent dosage in removal efficiency.

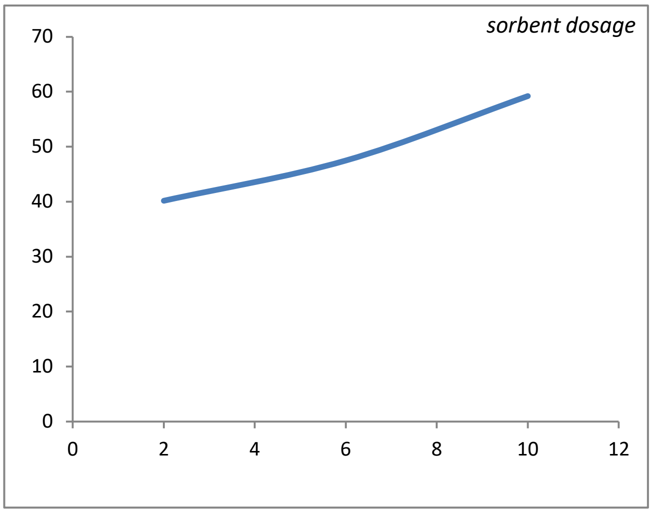


Figure 4 Sorbent Dosage (g) vs. Removal Efficiency

E. Equilibrium Isotherms

Adsorption isotherms describe how adsorbates interact with adsorbents and are important in optimizing the use of the latter. The Langmuir and Freundlich models are the most frequently employed models. In the present work Langmuir model was used. Langmuir isotherm [30] has found successful application in many real adsorption processes and is expressed in linear form as an equation no. 2:

$$\frac{C}{q} = \frac{1}{Qmax.b} + \frac{C}{Qmax} \qquad (2)$$

Where q (ml/g) is the equilibrium adsorption capacity, Qmax (ml/g) is the maximum amount of oil by-product per unit weight of the cell to form complete monolayer coverage on the surface bound at high equilibrium oil by-product concentration C (ml/mL) and b (ml/ml) is Langmuir constant related to the binding sites affinity. Qmax represents the practical limiting adsorption capacity when the surface is fully covered with metal ions, assisting the comparison of adsorption performance, and b indicates the adsorption reaction bond energy between metal and material [31]. With linearized plot of Ce/qe versus Ce, b. Qmax and b are computed from the slopes and interceptions of straight lines.

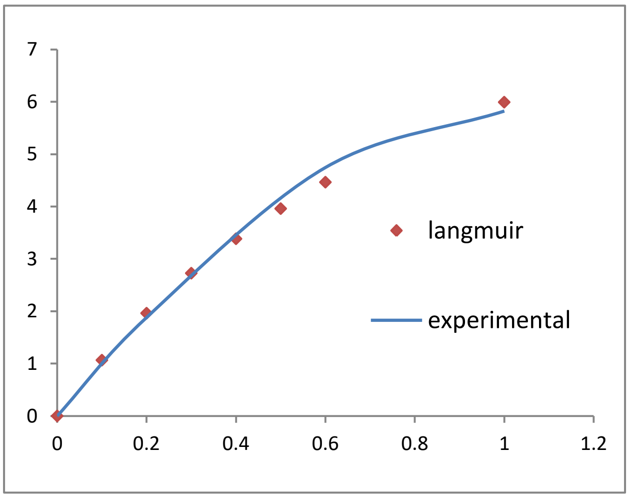


Figure 5 Adsorption of Oil by-product at room temperature (adsorbed amount (ml/g) vs. Ce (ml/mL)

Table 2. Langmuir isotherm constants.

Material	Q_{MAX}	b	R^2
Oil by-product	12.30	0.949	0.9355

Figure 5 presents the adsorption isotherms of oil by-product on sugarcane bagasse at room temperature. Data are presented with the results that obtained through the isotherms of Langmuir. The shape of plot is relatively common behavior in physic adsorption with strong interaction force between adsorbate and adsorbent. When the concentrations of oil by-product in water are low, until adsorption surface of sugarcane bagasse is covered by monolayer of oil by-product, the entire isotherm fitted the experimental data. But probably for high concentrations, the experimental data didn't confirm the Langmuir model and errors between them are increased. This behavior was expected for the Langmuir model because it limits the adsorbed amount to the formation of the monolayer [32]. The class of this shape of isotherm which shown in Fig 3.3.1 is named class L [32]. For this class of isotherm, large amounts can be adsorbed at low concentrations of solute. This was observed by the high percentage of adsorbed oil by-product in this region According to Giles et al [32]. This class of isotherm have some sub-group that this shape is classified in sub-group 1. Table 2 also presents the parameters obtained by the fit of experimental data with the corresponded correlation coefficient for Langmuir isotherm.

IV. CONCLUSION

Based on the results of this study, it can be concluded that sugarcane bagasse have good performance to adsorb of oil by-product from polluted water especially for high concentration of pollutant. The cost is a important variable to select the adsorbent that is a advantage of bagasse which makes it a popular for used to recovered and adsorbed oil by product from industrial waste water. Kinetics of adsorption of oil by-product in aqueous solution using micro-sized sugarcane bagasse at room temperature is relatively fast. The shape of the isotherm for the oil by-product adsorption in aqueous solution is characteristic of favorable type in multilayer adsorption according the classification of liquid isotherms proposed by Giles et al in 1960 [32]. Although the Langmuir isotherm model do not present a good performance as regards to experimental data but can be used for low concentration. The result also indicate that micro-sized sugarcane bagasse is a favorable sorbent for non-polar substance such oily product.

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