Oil Spill Adsorption Capacity of Activated Carbon Tablets from Corncobs in Simulated Oil-Water Mixture

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Abstract*–Oil spill in bodies of water is one of severe environmental problems that is facing all over the country and in the world. Since oil is an integral part of the economy, increasing trend for its demand and transport of has led to a great treat in the surface water. One of the promising techniques in the removal of the oil spills in water bodies is adsorption using activated carbon form waste material such as corn cobs. The purpose of this study is to determine the adsorption capacity of activated carbon tablets derived from corncobs in the removal of oil. The properties of activated carbon produced have a pH of 7.0, bulk density of 0.26 g//cm^3, average pore size of 45nm, particle size of 18% at 60 mesh and 39% at 80 mesh, iodine number of 1370 mg/g and surface area of 1205 g/m2. The amount of bentonite clay as binder (15%,20%,30%), number of ACT (1,2,3) and time of contact(30,60,90 mins) has been varied to determine the optimum condition where the activated carbon will have the best adsorption capacity in the removal of oil. Results showed that at 15% binder, 60 mins contact time and 3 tablets of activated carbon is the optimum condition which give a percentage adsorption of 22.82% of oil. Experimental data also showed that a Langmuir isotherm was the best fit isotherm for adsorption of ACT.*

Keywords*: activated carbon, adsorption, corncobs, Langmuir isotherm, oil spill*

INTRODUCTION

One of the severe environmental problems which persist in marine waters across the world, especially in the Asia-Pacific region which includes the Philippines, is oil spill[1]. This recurring problem has grown to an alarming magnitude with an increased level of the production and transport of oil. Oil spill pollution is petroleum hydrocarbon discharged into the environment, either marine or land, accidentally or operationally whenever oil is produced or transported. The first step in removing oil is separating it from the water. Considering Stokes' Law, given time and enough surface area, oil and water will eventually separate, forming two distinctive layers. Oil has a lower density compared to water causing it to float and forming a thin layer known as slick. Due to this, its contact with a high adsorbent material can be a way to collect the oil that is present in water. One commonly used technique for remediation of petroleum-contaminated water is adsorption. Adsorption is a physical process wherein polluting chemicals adhere to the surface of a solid[2]. Typically, most adsorbents are in a form of small pellets, beads or granules which has porous structure with many fine pores and occurs in monolayer[3]. A wide range of materials for water remediation have actually been employed in recent years and these include activated carbon. Due to its high surface area, high bulk density and particle size distribution, activated carbon has been used for the removal of organic compounds such as oil from water [4]. Carbon is chemically activated to produce more sites for adsorption thus increasing its adsorption capacity.

Nowadays, utilization of adsorbents with large surface area and affinity to organic compounds derived from cost-effective and readily available agricultural by-products are considered. Lignocellulosic materials from agricultural by-products which are locally available and proven to be effective in addressing this problem—one that could satisfy this requirement is corncobs which are abundant in the Philippines. The characterized physical properties of corncobs which are deemed useful in the production of activated carbon is its carbon content having 46.3% of its mass. This proves that it is an excellent precursor as activated carbon for oil spill adsorption [5].Binder is required to improve the mechanical property of the activated carbon in forming it to tablets. Calcium bentonite can be a candidate for ion adsorption of fats and oils [6].It can therefore be possible to use as binder for activated carbon from corncobs.

Conversion of waste material into a usable form specifically in solving environmental issues like oil spill is necessary. This study is significant to the environment especially marine or inland water, corn-producing industries as it suggest a way of utilizing agricultural waste and converting it into a usable product instead of disposal and to the future researchers.

OBJECTIVES OF THE STUDY

The study aimed to focus on the determination of oil spill adsorption capacity of activated carbon tablet (ACT) from corncobs in simulated oil-water mixture. Specifically, it sought to answer the following questions:

1. What are the physicochemical properties of activated carbon from corncobs in terms of ph, bulk density, pore size, particle size distribution, iodine number, surface area and surface morphology.
2. What is the effect of varying the amount of bentonite clay (15%, 20%, 30%), time of contact (30, 60, 90 mins) and number of ACT(1,2,3) in the adsorptive capacity of ACT on simulated oil-water mixture?
3. Is there a significant difference on the percentage oil concentration before and after treatment using the best condition?
4. What type of adsorption isotherm can be generated from the above data?

MATERIALS AND METHODS

The experimental method of research was utilized in this study. It was composed of a total of twenty - seven (27) set-ups. The parameters varied were amount of binder (15%, 20% and 30%), contact time (30, 60, 90 mins) and amount of activated carbon tablets (1,3,5) in a 1.5L simulated waste water.

Corncobs, regardless of corn variety were collected from Batangas City and Bauan Public Market. These were manually chopped to reduce its sizes and washed with distilled water. It was then sun-dried for 2 days and dried again in the oven for 6 hours. Calcium bentonite, which served as the binder, was purchased from Industrial Specialties Co., Inc., Pasig City, Metro Manila. Potassium hydroxide pellets used for impregnation were acquired from the Lipa Quality Control Center. Diesel oil mixed with distilled water was utilized for the simulated oil-water mixture at a concentration of 1% diesel oil by volume. Diesel oil was procured from Petron Corporation.

A Thermolyne Small Benchtop Muffle Furnaces Model FB1410M-26 manufactured by Barnstead International was utilized in the carbonization of prepared corncobs. This has a total capacity of 2.1 L and allows for temperature of up to 1100°C.Drying was performed using the Memmert UM100 oven. This has a capacity of 13.1 L and temperature range of 30 to 220ºC.For the determination of pore size and surface morphology, a Hitachi S-510 Scanning Electron Microscope was used.

For the preparation of activated carbon corncobs, crushed corncobs were impregnated by mixing with KOH pellets and adequate amount of distilled water at impregnation ratio of 4:1 (KOH pellet: corncobs) with continuous stirring for 6 hours at 80°C using magnetic stirrer hot plate.The mixture formed was filtered using a vacuum filter then oven-dried at 120°C for 12 hours. The dried sample was carbonized and activated in the furnace at 600°C for 1 hour. Afterwards, the activated carbon produced was cooled down to room temperature. This was washed using a 3 N hot HCl solution to attain a pH of 6.5 – 7. After vacuum filtration of the neutral activated carbon, repeated washing with 80°C distilled water was carried out next for the removal of residues. The prepared activated carbon was dried in the oven at 120°C for 12 hours. Final steps include cooling and storing of the activated carbon in a desiccator for further analyses.[5],[7],[8]

Activated carbon tablets were prepared into a 6grams tablet. Bentonite and activated carbon were mixed in three different set-ups based on parametric proportions which are 15%, 20%, and 30% by weight bentonite. Enough water was mixed with the adsorbent-binder mixtures which will allow homogenous mixing. A specific amount of these mixtures were placed in a 5-cm molder and manually pressed. After the adsorbents are pushed out of the molder, they were dried at 120°C for 12 hours.

The simulated oil-water mixture was prepared by mixing 15 mL of diesel oil with 1.5L water in a 25 cm x 20 cm x 15 cm container. The pH of the mixture was

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measured afterwards. The oil adsorption experiment was performed with three amount of binder (15%,20% and 30%), with varying contact times (30, 60, 90 minutes) and with varying amount of tablets (1, 3, and 5).

To evaluate the effect of varying parameters in the adsorption capacity of activated, Two-Way Analysis of Variance was used (*Sigmaplot® v12.0)*.

RESULTS AND DISCUSSION

Physicochemical Properties of Activated Carbon from Corncobs

Table 1 summarizes the analysis of the physicochemical properties of the activated carbon used in the study.

Table 1. Properties of Activated Carbon from Corncobs

Properties	Results
pH	7.0
Bulk density	0.26 g/cm^3
Average pore size	45 nm
Particle size distribution	18% 60 mesh 39% 80 mesh 53% 100 mesh
Iodine number	1370 mg/g
Surface area	1205 g/m^2

A high pH indicates too much contaminants and a low pH means that the acid has not been properly rinsed away. A neutral pH stands as an indication that the base activator, which functions solely as perforator of the carbon surface, had been completely washed off the carbon making the pores available for oil adsorption. The activated carbon produced has minimal contaminants and no traces of acid or base as indicated by its neutral pH.

The bulk density is a property of activated carbon that is used to find out how many kilograms of activated carbon must be used to fill up a certain volume of container. This is affected by the raw material used and the degree of activation. This property does not affect the effectiveness of the activated carbon measured in adsorption per unit weight, but will affect adsorption per unit volume. The bulk density of the activated carbon produced (0.26 g/cm^3) is quite low and is suitable for use in the production of large tablets that are efficient for adsorption.

The average pore size defines the available pore volume of a carbon which is categorized into three pore size regions: micropore region, which are less than 2 nm in diameter; mesopore region, which are about 2 nm to 50 nm in diameter; and macropore region, which are more than 50 nm in diameter. The average pore size obtained falls on the mesopore region (2-50 nm) which indicates that most of its pores are suited for adsorption of macromolecules. The high average pore size enables macromolecules, specifically oil, to be adsorbed on the surface of the carbon.

A large percentage (approximately 53%) of the carbon was at 100 mesh size. Smaller particle sizes expose more surface area than large particles. This increases internal diffusion and the rate of mass transfer through the pores of the particles. Thus, equilibrium can be easily achieved and nearly full adsorption capability may be attained.

In theory, molecules of different sizes will be adsorbed at sites of their corresponding size. In that sense, chemists use different molecules to gauge and model adsorption analogically. Since iodine has relatively large molecules, it can be a good indicator of the capacity of the activated carbon in adsorbing other macromolecules such as oil.

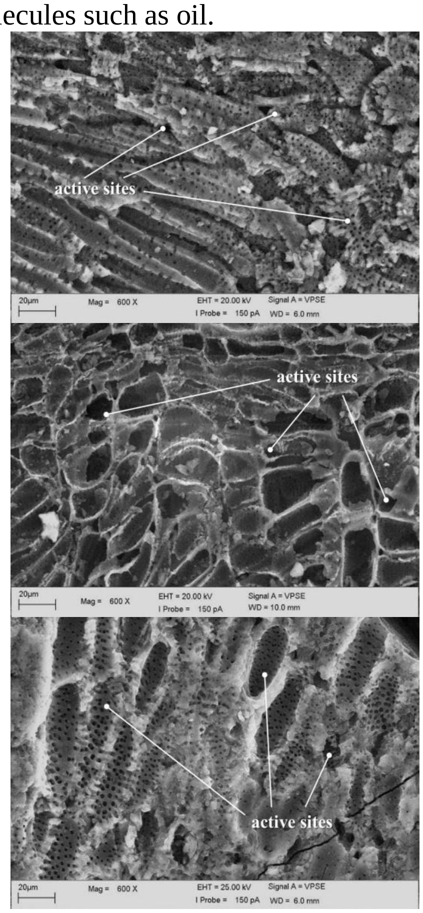

Figure 1. SEM Image Showing the Active Sites of the Activated Carbon

Iodine number is a measure of the equilibrium mass of iodine adsorbed on a surface from excess. A typical value of iodine number for activated carbon is 900 mg/g and values greater than 1000 represents a good grade of carbon. The iodine number of the activated carbon produced (1370 mg/g) signifies a high grade of carbon for adsorption [9].

Under an electron microscope, the high surface area structures of the activated carbon are revealed. Shown in Figure 1 are the images of activated carbon samples at 600x magnification. It can be clearly observed that the individual particles are complexly arranged and have different kinds of porosity. These pores provide excellent conditions for adsorption to occur since the adsorbate can interact with many surfaces simultaneously.

Effect of Varying Parameters on the Adsorptive Capacity of the Activated Carbon Tablets

It can be noticed in Figure 2 that the adsorption capacity decreases as the amount of binder is increased. But this trend does not show on samples where only a single tablet was used. The amount of binder in these single-tablet samples was not enough to exhibit a significant effect.

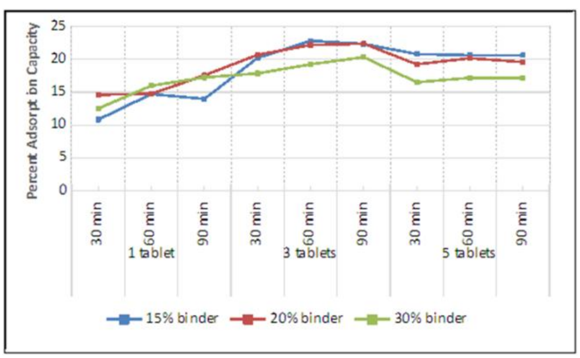

Figure 2. Percent Adsorption Capacity at Varying Amount of binder

When the amount of binder is increased, the surface area exposed to the adsorbate is reduced. Bentonite occupies the space that could have been active sites for adsorption. Although the binder has adsorptive characteristics by itself, it is not comparable to that of the activated carbon. There are spaces where the adsorbate is in direct contact with the binder instead of the more adsorptive carbon.

Figure 3 shows the effect of varying the number of tablets on the adsorption capacity. On almost all of the samples, the highest adsorption capacity was obtained on three-tablet samples and the lowest on single-tablet samples. Using a single tablet covers a small surface area since only few active sites are available for adsorption.

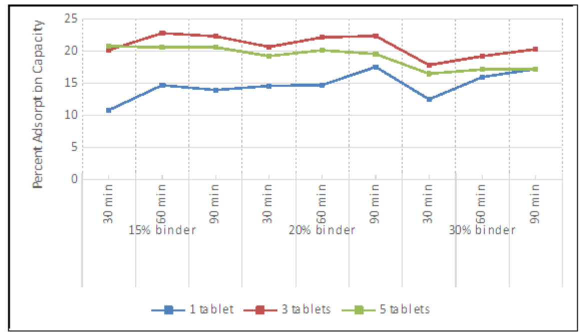

Figure 3. Percent Adsorption Capacity at Varying Number of Tablets

Theoretically, the oil reduction should be greater by using multiple tablets. But then, it is observed that the percent adsorption capacity is reduced when five tablets are used. One factor that caused this is the limited area of the experimental setup. The concentration of the activated carbon in the media is too high that the equilibrium shifted and favored desorption rather than adsorption.

Figure 4 shows the effect on absorption capacity at varying contact time. The adsorption capacity increases as the contact time is lengthened. The longer the time of contact between the adsorbent and the adsorbate, the more complete the adsorption will be.

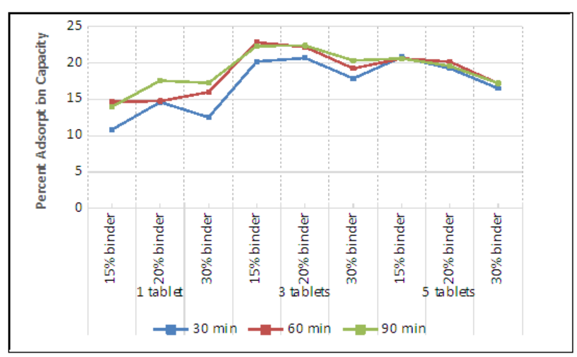

Figure 4. Percent Adsorption Capacity at Varying Contact Time

It can also be observed from the graph that the adsorption capacities are greatly varied at single-tablet samples but are almost identical on five-tablet samples. This indicates that the rate of adsorption on five-tablet samples is greater compared to the other samples. The adsorption capacity varies discreetly even at different contact times because equilibrium was reached before 30 min. Whereas, on the three-tablet samples, there is a noticeable increase in the adsorption capacity from 30 minutes to 60 minutes but almost similar values are obtained at 60 minutes and 90 minutes. From these data, we can conclude that equilibrium was reached at a time between 30 to 60 minutes. Lastly, on single-tablet samples, the adsorption capacity is greatly varied which means that equilibrium has not been reached even at 90 minutes.

Table 2 shows that contact time has no significant effect in the adsorption capacity of ACT. As the contact time increases, there will be a negligible effect in adsorption capacity. It is also presented on the table below that amount of binder has no significant effect in the adsorption capacity of ACT. As the amount of binder increases, there will be a negligible effect in adsorption capacity. The only parameter that has a significant effect on the adsorption capacity of ACT is the number of tablets. As the amount of tablet increases, there will be a significant change in adsorption capacity.

Table 2. Summary of ANOVA

Source	F_c and F value		Decision	Interpretation
Amount of bentonite	0.8484 3.305	<	Accept H_o	Not Significant
Number of ACT	26.9163 3.305	>	Do Not Accept H_o	Significant
Contact time	0.9874 3.305	<	Accept H_o	Not Significant

**Analyzed by SigmaPlot V12.0*
***Fcritical obtained from Microsoft Excel 2007*

Percentage Oil Concentration at the Best Condition Before and After Treatment

Shown in Table 3 is the percentage oil concentration before and after treatment. After statistical treatment of the results, it was proven that there is a significant change in oil concentration after adsorption with ACT.

Table 3. Oil Concentration Before and After Treatment

	Oil Concentration (w/v) Before Treatment	After Treatment
Trial 1	0.00832	0.00507
Trial 2	0.00832	0.00514

Generated Adsorption Isotherm on the Best Condition

The adsorption isotherm data were fitted to linear, Langmuir and Freundlich isotherms. The r-squared values obtained are 0.4739, 0.9596 and 0.7931 for linear, Languir and Freundlich isotherms, respectively.

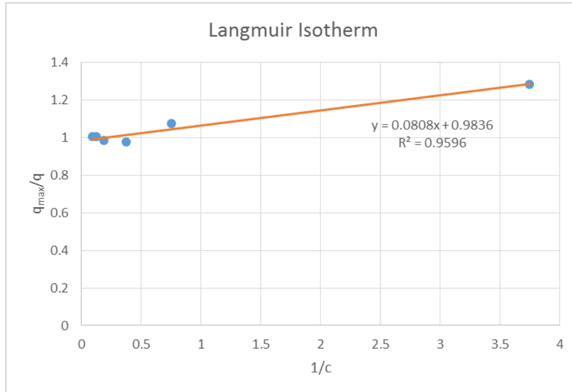

Figure 5. Linearized Langmuir Isotherm

Having the highest r-squared value of 0.9596, the Langmuir isotherm as shown in figure 5 is the isotherm generated which fits the experimental data This fit of the experimental data to the Langmuir model suggests that the adsorbate covers only a single layer on the surface of the activated carbon. The model equation for the adsorption of activated carbon from corn cobs is $q = 3.3544c / (1+12.3762c)$.

CONCLUSION AND RECOMMENDATION

Overall, the results obtained proved that the produced activated carbon has good properties for the adsorption of oil spill. Varying the amount of binder and contact time produced no significant effect in the adsorption capacity but the number of tablets proved to have a significant effect on the adsorption capacity of the activated carbon tablets. Optimum number of tablets was three. After treatment, a significant difference on the oil concentration was observed at the best condition. The activated carbon tablets from corncobs are efficient for the adsorption of oil spill. Langmuir isotherm model fits the experimentation data and suggests that only a single layer of adsorbate was formed on the surface of the activated carbon.

As the study sought to find the physicochemical properties of activated carbon only, it is suggested that mechanical properties of ACT be tested for more improvements of the said product.

Since the study has the limit of small scale (1.5 L of oil-water mixture), it is suggested that experiment will be performed in larger scale with oil-contaminated seawater to simulate actual conditions.

It is recommended to study other methods of activation to determine the probability of producing a more efficient carbon using other activation methods.

Aside from cylindrical tablets, use tablets of different shape in forming activated carbon that could increase its adsorption capacity.

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