Organic Sorbent from Eichhornia crassipes Stems

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Abstract— **Water Hyacinth (*Eichhornia crassipes*) is one of the world's worst invasive aquatic plants which often found covered rivers and ponds surface. Recent studies show the feasibility of water hyacinth as a sorbent for oil spill clean-up. Compare to the leaf and the root, the stem of water hyacinth has the highest oil sorption capacity and buoyancy, even though with the smallest surface area. Increasing its surface area may result in higher sorption capacity. The active surface area can be potentially increased either by physically, chemically treatment or both which resulted in higher sorption capacity. The objective of this work is to increase the surface area of water hyacinth's stem in 3% of HCl and investigate the treated stem's characteristics and sorption capacity towards diesel, gasoline, toluene, and hexane. The dried powdered stems were sieved to a particle size of 63 μm. The surface area of powdered water hyacinth's stem become larger up to 56% compare to the raw sorbent. This is due to the presence of micro pores resulted from the removal of exchangeable ions. Surface morphology image shows hollow stem structure that provides more active binding site maximize the oil entrapment. The change in sorbent characteristics affected to the increases in sorption capacity towards diesel, gasoline, toluene, and hexane of 10.23, 8.98, 10.30 and 6.67 g/g in dry system. Consistent absorption capacity was found in the wet system with 3.5% salinity.**

Index Terms—**Organic sorbent, water hyacinth, HCl-treated.**

I. INTRODUCTION

Energy quest has leads to massive exploration, production, transportation, and storage around the globe raise the risk of oil spill [1]. The spill into the seas, water bodies, and land surfaces occur due to the failure of operations, tankers and pipelines leaks, accident or natural disaster [2]. Due to its severe environmental impact, oil spills have become a major concern for many countries [3]. Conventional methods used to clean up the oil spill are in-situ combustion, chemical degradation, and mechanical extraction [4]. The use of sorbent as mechanical extraction is considered to be one of most desirable choices and an effective method to collect, transfer, and recover the oil [4, 5]. The sorbent materials are grouped into three classes; polymers, natural material (minerals and organic materials), and treated cellulosic materials. The use of organic natural fiber is an attractive alternative sorbent due to its low cost and biodegradability, have high sorption capacity, for instance, kapok, cotton, and milkweed [6].

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The feasibility studies of *E. crassipes* sorbent had been investigated for organic compound cleanup [7, 8]. Water hyacinth has been classified as the world's worst invasive aquatic plant [9] which was responsible for drainage and irrigation canals problem in the paddy field [10]. *E. crassipes* stems have highest oil sorption capacity and buoyancy were tested on organic compounds like diesel, mineral oil, fresh and used motor oil, lubricant and castor [7, 8]. The stem's hydrophobicity and surface morphology are predicted as the contributor to the capillary action which results in high sorption capacity [8]. Grinding can cause finer particle size of the sorbent, resulting in the larger surface area. Chemical treatment such as HCl increased sorbent sorption capacity by enhancing its surface roughness [11], with the formation of new microporous and mesoporous, and decomposition of impurities that resulted in the opening of blocked active site [12]. This work investigates the effect of HCl treatment on the oil sorbent's characteristics of water hyacinth' stems. Sorbent properties of surface area and porosity, surface morphology and element content, bulk and particle density, and functional groups were investigated. The sorption capacity towards diesel, gasoline, toluene, and hexane in different contact time and salinity were also evaluated and compared. Recoverability and reusability performance of the sorbent was evaluated as well.

II. MATERIAL AND METHODS

A. E. crassipes Stem

E. crassipes was collected from wild grown plant invading the lake located in 5 km northern part of Seri Iskandar area. The individual stem was separated and washed with tap water and rinse in distilled water to remove impurities. The stems were oven dried for 24 hrs at 65°C and ground into powdered before sieved to get particles size of 63 μ. A weight of 3 g stem powdered were placed into 3% HCl solution for 24 hrs. The wet powdered stems were retrieved by vacuum filtration, washed several times with distilled water and dried at 45°C until the stable weight is achieved.

B. Sorbent Characterization

Sorbent's BET surface area and pore size were evaluated by Surface Area and Pore Size analyzer (Micromeritics ASAP 2020). Sorbent's surface morphology and element content were determined using Scanning Electron Microscope (SEM). Sorbent's functional group was examined by using Fourier Transform Infrared Spectrometer (FTIR) while sorbent bulk and particle density were evaluated by graduated cylinder method and gas pycnometer respectively.

C. Sorbate Characterization

The density of the diesel, gasoline, toluene, and hexane was measured using portable density meter at ambient temperature Sorbate viscosities were measured by using Brookfield 2000+ Viscometer at 700 rpm, spindle 1 at ambient temperature.

D. Sorption Capacity in Dry System

0.15 gram of raw and HCl-treated sorbents were enclosed in a small fabric mesh respectively, each sorbent was placed on top of 10 ml of different sorbates in 100 ml glass beaker in different contact times (5, 30, and 60 minutes). The sorbent was retrieved using forceps and drained for one minute. The sorption capacity, q in mg/mg was determined by Equation 1 [7].

$$q = \frac{m_f - (m_o + m_w)}{m_o} \qquad (1)$$

Where m_f is the weight of the sorbent after drainage (g), m_o is the initial weight of the sorbent (g), and m_w is the weight of water (g). For a dry system, m_w is zero.

E. Sorption Capacity in Wet System

Brine solutions containing 1% and 3.5% of dissolved NaCl were prepared. The control solution with 0% salinity was prepared by deionized water. 2 ml of sorbate was added (oil thickness approximately 1 mm) to 10 ml of water medium and let to stabilize, where 0.15 gram of raw and HCl-treated sorbents were spread onto the surface of the mixture of oil and water. After finish contact time (absorption period), sorbents were retrieved by forceps and drained.

The sorbent was then squeezed by a syringe and adsorbed mixture of oil and water was centrifuged at 4000 rpm, for 15 minutes at ambient temperature. The oil sorption capacity (q) was determined by Equation 1. Replicate experiment was conducted for conformity purposes

F. Recoverability, Regeneration, and Reusability

Sorbent recoverability (%) was calculated by Equation 2.

$$Recoverability = \left[1 - \left(\frac{m_{after\,squeezed} - m_o}{m_o} \right) \right] x100 \qquad (2)$$

Each sorbent was regenerated by exposed to air-dried for 5 minutes after being squeezed before reused for 2 times for a complete 3 cycles absorption process. Similarly, the oil sorption capacity was estimated using Equation 1.

III. RESULT AND DISCUSSION

A. Sorbent Characterization

1. FTIR Spectra

The broad peak at 3400 cm^{-1} indicates bound O-H band presence in both samples (Fig.1) with a lower intensity found in acid treatment. Free O-H stretching was also observed at 3620 and 3695 cm^{-1}, but disappear after acid treatment and a new peak of 3743 cm^{-1} appear indicating the presence of Si-OH (silanol) stretching.
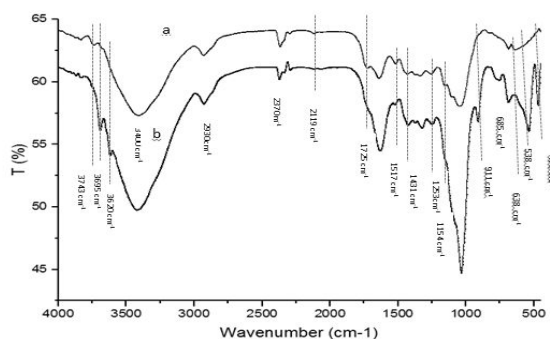

Fig. 1: FTIR Spectra of (a) HCl-treated and (b) raw sorbents

Major intense bands at 2930 cm^{-1} and 2370 cm^{-1} which indicate C-H symmetric stretching of CH$_2$ (alkane) and O=C=O (carbon dioxide) respectively, appeared in both spectra. A new peak of 2119 cm^{-1} and 1725 cm^{-1} present in small intensity after acid treatment, indicate the appearance of C≡C stretching (alkyne) and C=O stretch (aldehydes) respectively. A functional group which remains the same after treatment was COH at 1640 cm^{-1}, this is in agreement with Ibrahim et al. [13].

In fingerprint region, low-intensity peak of 1517 cm^{-1}, 1431 cm^{-1}, 1253 cm^{-1} and 1154 cm^{-1} are observed indicate asymmetric stretching vibration of COO$^-$, C-C stretch (in a ring) aromatics, C-N stretching (aromatics amine), and antisymmetric bridge stretching of C-H wag (-CH$_2$X) alkyl halides groups accordingly. These peaks also observed in untreated spectra but its higher intensity is shown by acid treatment. Backbone C-O stretching vibration at 1040 cm^{-1} appear in both spectra. Out of plane =CH bending (alkene) at 911 cm^{-1} disappear in HCl-treated spectrum while C-H deformation at 685 cm^{-1} remains in the sample. In fact, the more C-H group appears after treatment which is at 638 cm^{-1}. Moreover, peak at 538 cm^{-1} which represent C-Br stretch (alkyl halides) and O-Si-O at 470.52 cm^{-1} disappear after the acid treatment, possibly bonding with free –OH compound. The functional group is associated with sorbent polarity; for oil sorbent, the non-polar group is favorable because it attracts oil and repelled water since water belongs to the polar group. In summary, both spectra have the polar groups such as OH$^-$, COH, and CO but also contains non-polar group such as CH$_2$ and CO$_2$. The presence of polar group indicates that the samples may also attract water in their contact. Moreover, it should be marked that acid treated sample contain additional polar and non-polar group even tough in small intensity such as C≡C, CH$_2$ group for non-polar and CO and COO for the polar group.

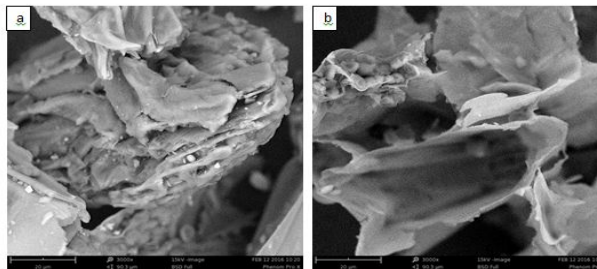#### 2. Surface Morphology and Elemental Analysis

Fig.2: Photomicrograph of (a) raw and (b) HCl-treated sorbents

Fig. 2, shows surface morphology of water hyacinth's stems before and after HCl treatment. Raw water hyacinth stem has granules-like structure while acid treatment indicates appearance of hollow structures. The collapse of the granules-like structure reveals that even small concentration of acid treatment can cause the change to the *E. crassipes'* stem. The surface area of the treated sorbent was expanded, suggesting more binding sites are available for absorption. The presence of hollow structure helps in maximize oil entrapment between its empty lumen. However, untreated *E. crassipes* with rough surface structure provide higher fluid adhesion at their surface.

Most of the element content of *E. crassipes'* stems are carbon (C), oxygen (O) and nitrogen (N) for both raw and HCl-treated sample. Potassium (K) and chlorine (Cl) were also detected in raw material but disappear after the treatment, suggesting that K and Cl have interacted with HCl solution and washout during samples filtering and washing as shown in Table 1.

TABLE 1: Elemental analysis

Element Symbol	Raw material (weight %)			HCl-treated sorbent (weight %)		
	Spot 1	Spot 2	Spot 3	Spot 1	Spot 2	Spot 3
K	9.7	2.1	6.6	-	-	-
Cl	4.2	1.6	4.5	-	-	-
C	21.0	19.8	22.8	23.1	21.1	21.9
O	32.4	43.4	28.2	31.5	42.8	39.5
N	32.7	33.1	37.9	45.5	36.2	38.6

3. BET Surface Area and Pore Size

TABLE 2: surface area and pore size of the sorbents

Parameter	Raw material	HCl-treated sorbent
BET Surface Area (m^2/g)	1.5923	2.4855
Pore Size (Å)	94.0366	77. 4499

The pore size of HCl-treated *E. crassipes'* stems are finer than the raw material (Table 2). This resulted in a larger surface area up to 56% due to the presence of micro pores indicate by the BET report which directly improves sorption capacity. Micro pores appeared due to the elimination of exchangeable ions through dissolution. Thus, explains the removal of K and Cl in element analysis.

4. Sorbent Density

HCl treated sorbent is lighter than the raw sorbent (Table 3). However, both samples float on the surface of oil and water in the bulk state. This condition is favorable to oil sorbent for retrieval and recovery purposes. In term of particle density, both samples have a higher density than water's and hence most common oil. Therefore, the sorbent must be pack in bulk quantity for absorption to take place.

TABLE 3: Bulk and particle density of the sorbents

Sample	Raw material	HCl-treated sorbent
Bulk Density (g/cm^3)	0.2126	0.078
Particle Density (g/cm^3)	1.5529	1.5636

B. Sorbate Characterizations

Based on oil density, toluene has the highest density followed by diesel, gasoline, and hexane (Table 4). Diesel has the highest viscosity followed by gasoline, toluene, and hexane. Based on this result, it was predicted that diesel more likely to have lower absorption capacity but good retention time and recoverability. In addition, hexane which was most volatile compared to toluene, gasoline, and diesel relate to the low percentage of recoverability.

TABLE 4: Density and viscosity of the sorbates

Sorbate	Density (g/cm^3)	Viscosity (Cp)
Toluene	0.862	0.49
Hexane	0.662	0.2
Gasoline	0.759	0.56
Diesel	0.84	4.137

C. Sorption Capacity in Dry System

Optimum contact time was achieved in the first 5 minutes by the sorbent with indicating fast response on the tested sorbates. The sorbates occupied most of the active site, before reach equilibrium and remain consistent with insignificant changes in absorption capacity (Fig. 3 and Fig. 4). Sorption of diesel slightly reduces after 5 minutes reasonably due to it volatility in the raw sample may be because of the oil absorbed to the active site surface but in contrast to HCl-treated sorbent where it been trapped inside the hollow structure.
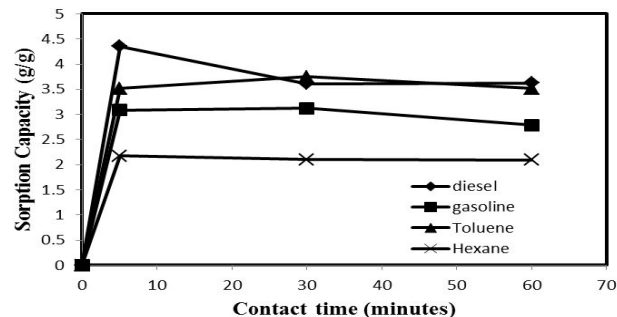

Fig. 3: Sorption capacity of raw sorbent at different contact time in dry system
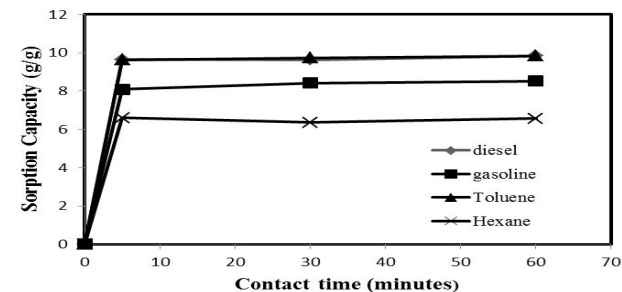

Fig. 4: Sorption capacity of HCl-treated sorbent at different contact time in dry system

Toluene shows highest sorption capacity among all the sorbates in the HCl-treated sample. On the other hand, diesel exceeds other sorbates for raw sorbent. HCl treatment intensified aromatics ring as a functional group present in toluene which characterized toluene for a better absorption.

Previous finding [7], shows that the higher the viscosity of oils, the lower is its sorption capacity which in agreement, with toluene as the third lowest viscosity among the oils experienced the highest sorption capacity. In general oil sorption capacity of HCl-treated sorbent always higher, more than double in sorption capacity compared to its raw sorbents. This is due to the appearance of micro pores, causing in increase in active surface area by hollow surface morphology.

Based on the range of sorption capacity as in Table 5, diesel sorption capacity is double in HCl-treated sorbent, 10.23 g/g compared to the raw sorbent of 4.66 g/g. Previous work using raw stems of 9.01 g/g [7] and stalk sorbents, 10.6 g/g [8] which work on 75 μ sorbent. However, no experiment on particle size effect has been conducted in this study [11].

TABLE 5: Sorption capacity of the sorbents in dry system

Sorbate	Range of sorption capacity (g/g)	
	Raw material	HCl-treated sorbent
Diesel	3.298 - 4.660	9.044- 10.235
Gasoline	2.527 - 3.723	7.549 - 8.981
Toluene	3.259 - 4.202	9.371-10.302
Hexane	1.816 - 2.365	6.036- 6.672
Hexane	1.816 - 2.365	6.036- 6.672

D. Sorption Capacity in Wet System

Based on the result obtained from the dry system, the work was extended to the wet system in alkaline mediums in 5 minutes of contact time for both sorbents.
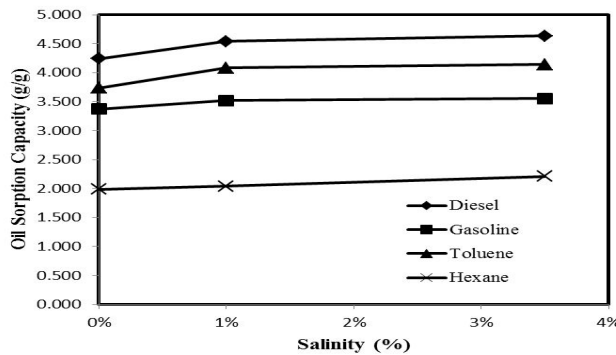

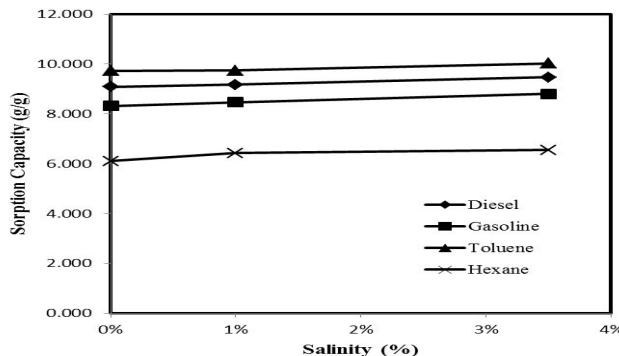Fig. 5: Sorption capacity of raw sorbent in saline water

Fig. 6: Sorption capacity of HCl-treated sorbent in saline water

There is no significance effect on different salinity towards sorption capacity on both sorbents (Fig. 5 and 6). Nevertheless, there is slightly increase when the percent of salinity increase. The optimum oil sorption capacity was achieved at 3.5% salinity for all sorbates. This similar trend

also can be seen in raw material sorbent. However, the increase from 0% to 1% can be seen more significantly in raw material sorbent compare to the HCl-treated material.

These phenomena might be caused by the decrease in electrostatic repulsion and salting out effect. Salt addition can lower functional group electrostatic repulsion in the adsorbed layer [14]. Electrostatic repulsion is the force between two particles which has the same charge to repel each other. With increasing salinity, this force is becoming lower, leading to an increase in the absorption.

Beside lower electrostatic repulsion, salting out effect may also contribute to higher oil sorption capacity [15]. Salting out effect related to the solubility of organic material which will reduce when the salt content of water increases, thus enhance hydrophobic interaction between the sorbent and oil. However, the insignificant different on the salinity effect of the wet system towards oil sorption capacity of the sorbent means it can be applied to the broad environmental medium.

As shown in Table 6, there is no significance difference between the minimum and maximum sorption capacity obtained from both raw and HCl-treated sorbents compared to the dry system. The comparison on sorption capacity between dry and wet condition can be clearly seen in Fig. 7. HCl-treated sorbent in the wet condition shows a slight decrease in oil sorption capacity, due to some amount of water are in contact.

In contrast, raw sorbent exhibits very small difference of sorption capacity in the dry and wet systems except for hexane, due to its high volatility. In overall, HCl-treated sorbent still performance better than raw sorbent.
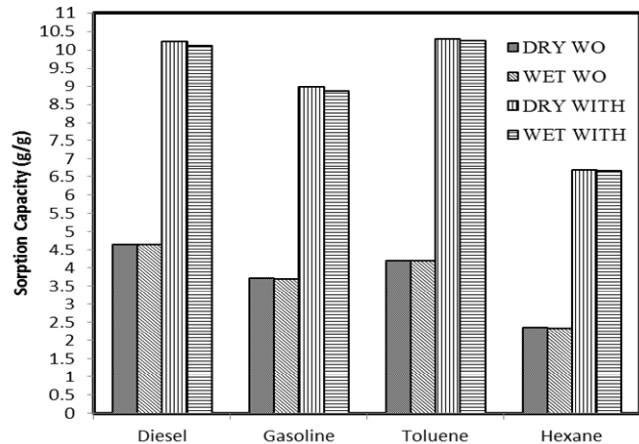

Fig. 7: Comparison of maximum sorption capacity of raw and HCl-treated sorbents in wet and dry systems

TABLE 6: Sorption capacity of the sorbents in wet system

Sorbate	Range of sorption capacity (g/g)	
	Raw material	HCl-treated sorbent
Diesel	4.241- 4.658	8.115-10.121
Gasoline	3.323- 3.695	8.122- 8.858
Toluene	3.309-4.194	8.324-10.258
Hexane	1.882-2.341	5.672-6.646

E. Recoverability and Reusability

TABLE 7: Recoverability of the sorbents in wet system

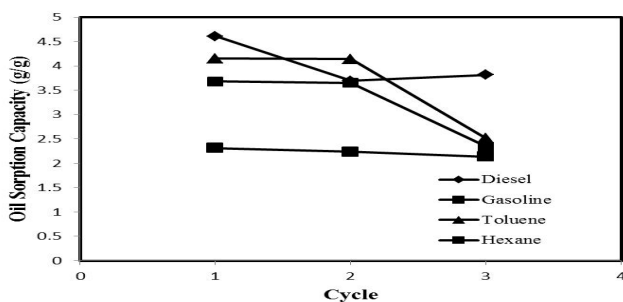| Sorbate	Salinity (%)	Raw material (%)	HCl-treated (%)
Diesel	0 %	71.26	77.75
	1 %	71.94	79.19
	3.5 %	74.86	76.39
Gasoline	0 %	72.83	75.10
	1 %	75.40	73.29
	3.5 %	71.00	78.22
Toluene	0 %	76.00	74.44
	1 %	83.98	76.20
	3.5 %	76.00	71.61
Hexane	0 %	64.15	68.12
	1 %	69.24	77.09
	3.5 %	74.61	73.28

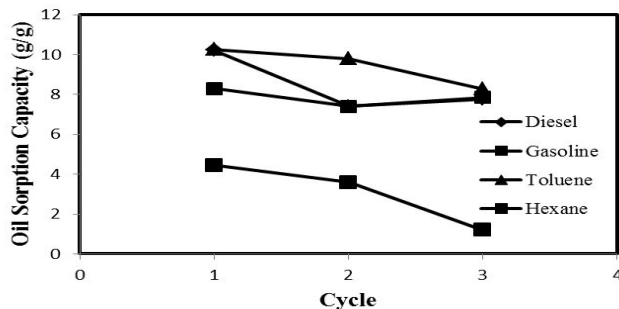Fig. 8: Sorption capacity of raw sorbent after regeneration and reused

Fig. 9: Sorption capacity of HCl-treated sorbent after regeneration and reused

Percent of recoverability for both sorbents are shown in Table 7. More than 70% percent of oil can be recovered from the sorbent by mechanical pressure. Only hexane exhibit lower recoverability, this is due to its high volatility that may cause it to evaporate in sorbent drainage process. Diesel sorption capacity significantly reduces on the second cycle, while gasoline, toluene, and hexane can maintain its sorption capacity until the second cycle in HCl-treated sorbent (Fig 9). This may due to high diesel entrapment in the sorbent, causing only small space available for another cycle. A similar trend is observed for raw sorbent generation and reusability cycle (Fig 8). Toluene, gasoline, and hexane evaporate easily upon drying, unlike diesel resulted in more active binding site for resorption to occur.

CONCLUSIONS

In conclusion, HCl treatment does alter the characteristics of raw sorbent. Shown by smaller pore size because of the more micro pores due to the dissolution of exchangeable ions, this was shown by element content analysis which confirms the removal of K and Cl after the treatment. Smaller pore size leads to a higher surface area of HCl-treated sorbent. Surface morphology of raw sorbent changes from granule-like structure to the hollow structure that provides more active binding site and maximize oil entrapment. Furthermore, acid treatment intensifies the functional groups which responsible for oil sorption such as $C{\equiv}C$, CH_2, and aromatic rings, even though it also intensifies the polar groups such as CO and COO^- which causing HCl-treated sorbent to take up more water during the absorption process. Both sorbents adsorbed sorbates within five minutes of contact time and at 3.5% of the salinity. Sorption capacity is more than double in the HCl-treated sample in both dry and wet systems confirming the characteristics change in the sorbent. Sorbents recoverability of up to 70% are achieved which can be regenerated and reused until two cycles but with lower oil sorption capacity. It is suggested that the effect of particle size and sorbent dosage towards oil sorption capacity is conducted to find sorbent optimum dosage and particle size.

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