EFFECT OF GO/CHITOSAN COATED SAND IN ENHANCING WATER FILTRATION

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Abstract—**This paper portrays a technique to upgrade filtration in water treatment because of water contamination contributed by Petroleum and chemical industry either in processing, production and utilities plant itself. In order to increase the water treatment performance, a natural quartz sand was improvised as the sand act as a filter bed in filtration. Sand sample from a local beach, Pantai Rusila is selected as it match the size criterion for sand water filtration. Enhancing the medium of sand by surface alteration helps water treatment execution. The adsorbent was grafted to the surface of the sand through the chemical reaction between functional group such as -COOH, -C=O, and -OH, on the surfaces of GO. These functional groups are essential for the high sorption of heavy metal ions. The sand will be coated with a two different adsorbent which is Graphene Oxide (GO) and chitosan. GO and chitosan were chosen to be coated with sand due to strong adsorption performance for organic matter and heavy metals ions compared to sand itself. The morphologies and rheology of the GO/chitosan coated sand were affirmed by utilizing Fourier-Transform Infrared Spectroscopy (FTIR), digital microscope, Field emission scanning electron microscopy (FESEM) and X-ray powder diffraction (XRD).**

Keywords— Go, chitosan, water treatment

I. INTRODUCTION

Petroleum and chemical industry is a field that unavoidably generates a large volume of oily wastewater [1]. This condition causes the field as one of the field that contribute to the environmental problems. The water is the most often discharged to the environment which is to the sea, local river course or near coastal waters from oil terminals and offshore production platforms. This condition can bring to severe health problems in humanity and animal beings [2]. Nevertheless, the water may have contained some hydrocarbons which could be recovered and returned to the main production system. Improving the medium of sand by surface modification can boost water treatment performance [3]. Cost-effectiveness, high activity, nontoxicity and stability over continuous use are the major requirements in engineering nanomaterials for water treatment. However, each approaches must have pros and cons in every aspect such as cost, complexity and efficiency. The application of this study may be applied in utilities plant where the waste water treatment plant will handle waste water from customers such as chemical industries plant. Demin water plant is an example of utility plant that provide a system for water treatment. The system major component which is multimedia filter consists of sand bed filter. A multi media filter is used to reduce the level of suspended solids in incoming feed water. A lot of proof from a followed journal that functionalization of nanomaterials by graphene could highly enhance the photocatalytic and adsorption properties as this substance has high carrier mobility, high transmittance, large surface and good adsorption. Graphene also is a good optical transparency and mechanical flexibility [4] . On the other hand, biopolymers are listed as a potential adsorbents due to their biodegradability, non-toxicity, and efficiency [5]. Adsorbent characteristic of chitosan, a biopolymer can help in enhancing the sand filtration of water treatment. By implying practical and cost-saving methods to prior, the sand is used as a support material for the immobilization of chitosan. Further enhance on its metal binding capacity helps to improve to a better water treatment as aim of the research conducted is to find out the elimination of heavy metals. The sand that is coated with the adsorbent will be utilized as the sorbent for the removal of turbidity, organic matter, heavy metal ions such as Cd (II) and Zn (II) ions from the wastewater sample. Natural quartz sand (NS) is known extensively for its use in water treatment as a water filtration method. There are two major characteristics of granular media treatment systems which are effective particle size and uniformity coefficient (Uc) [6]. Therefore, a study on the on the viability of GO/Chitosan in enhancing water filtration is conducted to verify how effective this method is in order to provide valuable insight for oil and gas industrial application in clean, usable water production field. Also, a comparison of the removal efficiency was investigated to choose the better option for wastewater water filtration treatment.

II. METHODOLOGY

GO was prepared by following a Modified Hummers' method. For details and characterization of GO/Chitosan, UV-Vis, XRD, FESEM and ICP-MS equipment were used in next procedure. The performance of the GO/chitosan coated sand were determined by analyzing the water collected in beaker at the end of the adsorbance process.

A. Preparation of Graphene Oxide

A procedure of extracting Graphene Oxide (GO) was done by using Hummer's method [7]. For the synthesize of GO, firstly a 10g of graphite powder, 5g of Sodium Nitrate ($NaNO_3$), 60g of Potassium Permanganate (KM_nO_4) and 400 ml of H_2SO_4 were measured and prepared. 10g of Graphite powder along with 5g of $NaNO_3$ was diluted with 400 ml of H_2SO_4 inside a 2 L beaker. The mixture was stirred by using magnetic stirrer at speed of 350 rpm for 1 hour. Next, the mixture was cooled down to below 15℃ inside an ice bath. The mixture was left stirred for 1 hour. Under continuous stirring, a small portion of KM_nO_4 slowly added into the reaction within 2 hours duration. Meanwhile, the temperature need to be maintain below 15℃. After the mixture was stirred for 2 hours, the ice bath was withdrawn. The stirring of the mixture was continued at room temperature for another 22 hours. This condition is kept on for 22 hours until the dark brown colour was formed. Next, the mixture was heated up to 70℃ and was kept

constant for 3 hours respectively. 100 ml of distilled water was slowly added to the mixture in order to increase the temperature to 90°C. The mixture was kept stirred for another 1 hour. In the next step, 60 ml of hydrogen peroxide was added into the mixture.

After resulting mixture was cooled down, the mixture would undergo washing repeatedly with diluted HCl for 3 times. 160 ml of HCl was mixed with 1840 ml distilled water to produced diluted HCl. Each washing was about 24 hours or more, depending on how long the sediment of the mixture will form. The mixture was washed continuously by using distilled water and acetone for 3 times for an estimated and controlled time. After completing the washing steps, the mixture undergoes centrifuged at a temperature of 25°C with 10000 rpm speed for 25 minutes. The mixture need to be heated in the oven in order to get a GO in a powder form. The mixture was dried in oven for 24 hours with temperature around 65°C-70°C. Lastly, the mixture was scattered until it forms a powder, which is a GO powder.

B. Characterization of adsorbent

The purpose of characterization was to study further details about morphologies and structures of GO/chitosan. X-Ray Diffraction (XRD) using equipment PERKIN ELMER FT-IR spectrometer is used to determine the crystallinity of a compound. In other words, the structure, composition and physical properties of materials can be identified. From XRD analysis, intensity is found as the function of the diffraction angles. Accordance between the diffraction angles of a reference materials using XRD analysis produce positive ID.

C. Characterization of synthetic waste water solution

In order to determine the present of a chemical in the synthetic waste water, the solutions were analyzed by using an equipment which is Inductively Coupled Plasma Mass Spectrometry (ICP-MS). ICP-MS is capable to detect metals and several non-metals at a concentrations as low as one part in 10^{15} ppq on non-interfered low-background isotopes. The sample were ionized with inductively coupled plasma and a mass spectrometer were used to separate and quantify those ions.

D. Sand coating with adsorbent GO/Chitosan

Natural sand from Pantai Rusila, Terengganu with a selected particles size is collected and undergo pre-treatment method to make sure the impurities were removed [7]

i. Natural quartz sand was coated with adsorbent (1) which is GO. 50 g of washed sand was put in a 250 ml beaker with 3 ml of 20 mg/ml GO by using a soaking method for 24 hours. The mixture was heated up to 15°C in a vacuum oven for 3 hours until nanocomposite was hardly attached on the surface of the sand. [7]

ii. Natural quartz sand was coated sand with an adsorbent (2) which is chitosan. Stirred about 5 g of chitosan and 100 g of sand in 300 ml of 5% (v/v) HCl for 5 hours approximately. 1 N of NaOH was added drop by drop until neutralization occurred. The adsorbent was allowed to settle and washed with deionized water. After that, dried-oven the chitosan coated sand for 24 hours at 65°C.

E. Field Emission Scanning Electron Microscope (FESEM)

To confirm the interface bonding between the quartz natural sand and the coated element before and after surface modification, FESEM and digital microscope were used in this determination of:

i) Bonding between GO and quartz natural sand
ii) Bonding between chitosan and quartz natural sand

F. Wastewater Preparation of Synthetic Oily

The synthetic oily wastewater was prepared using the following ratio as suggested [8][9]. Synthetic wastewater samples were formulated by using analytical grade Copper Sulphate, Zinc Chloride and Cadmium Nitrite. The stock solution contain 100 ppm Cu(II), Zn and Cd(II) each.

G. Heavy Metal Ion Determination

The experiment was conducted by using a single solutions of the adsorbates maintained at pH of 4.5 [5].

i. A 2.5 g GO coated sand (GOS) was combined in a synthetic waste water solution in Erlenmeyer flasks. The equilibrium time of mixing was for 24 hours at a static speed of 150 rpm. After achieving equilibrium condition, filtered the solution by using Whatman #40 filter paper. The filtrate was then analyzed using an ICP-OES analysis.

ii. The same amount of 2.5 g chitosan coated sand (CCS) was then combined in a synthetic waste water solution in Erlenmeyer flasks. The equilibrium time of mixing was for 24 hours at a static speed of 150 rpm. After achieving equilibrium condition, filtered the solution by using Whatman #40 filter paper. The filtrate was then analyzed using an ICP-OES analysis. The amount of Cu (II) ions and Pb (II) ions adsorbed per unit mass of CCS were calculated by using equation 1 below:

$Q_e = [(C_o - C_e)\, v] / m$ ..... Equation 1

c_e = initial equilibrium of metal ion solution

ce = equilibrium concentration of metal ion solution

v = volume of the solution in a liter (L)

m = mass of CCS in grams (g)

H. Turbidity Determination

The turbidity was measured with a turbidimeter equipment. UV was measured with spectrometer. The concentrations of metal ions were determined by ICP-MS. 5g of each GOS/CCS sample was placed in the sample cell. Filled the cell with 15ml of distilled water. The cell was capped and shaken vigorously to suspend the particles present for 30 s ± 5 s. The sample cell was then placed in the turbidimeter for measurement. The reading was taken in NTU unit. 21.03 NTU is an indication of turbidity of raw water [10]. In this study, since only a simulation on adsorption were done, distilled water were used as a prime solution in preparation of synthetic oily wastewater. The distilled water may register up to 1 or 2 NTU. Turbidity removal efficiency was then obtained by a comparison between GOS and CCS performance.

III. RESULTS AND DISCUSSION

A. Structural and morphologies studies of adsorbent

XRD analysis technique were used in order to characterize the crystalline material of GO. The results of XRD graph for graphite and GO were shown in a figure below. The graphite powder shows a diffraction peak at $2\Theta = 26.6°$ while GO showed a diffraction peak at $2\Theta = 10.0°$ with the intensity higher than 1000. The intensity that were higher than 1000 indicated a good quality of sample were performed. The range value of diffraction peak indicated that GO synthesized were successful as the value followed the journal[4]. The increased interlayer spacing of the GO sample was due to the oxidation of graphite and this indicates that the oxygen bond was found between the interlayer. The peak

changed from 26.6° to 10.0° and increased in d-spacing has proved that GO was successfully synthesized in the experiment.

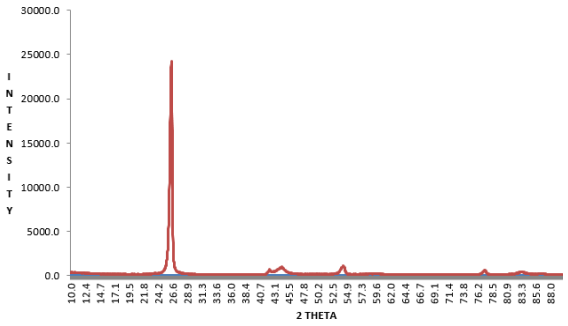


Figure 1(a): (XRD) of graphite

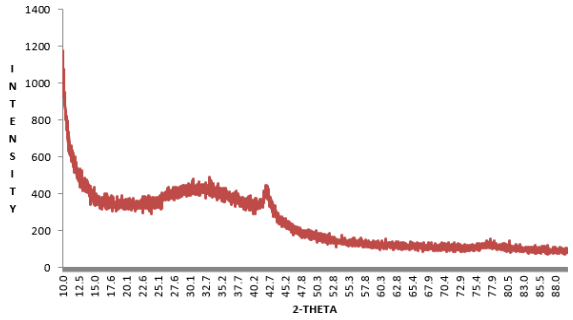


Figure 1(b): (XRD) of GO

FTIR result of graphite labelled as graphite (1), GO (2), and GO coated sand (3) are shown in figure 2(a) below**.** From figure 2(a) 1, the spectrum of GO showed an adsorption band at 3200-3600 cm^{-1}, corresponding to O-H stretching. The absorption band at 1624.11 cm^{-1} correspond to C=C stretch, outlining the skeletal structure of grapheme [4]. In the spectra of Figure 2(a) (3), the characteristic absorptions of amide II at 1542.8 cm^{-1} were clearly observed, it can be concluded that the GO has been incorporated into the surface of sand [10]. Chitosan was prepared for a surface coatings with natural sand to produce a formation of a shallow film that serve as a better adsorbent. Figure 2(b) show FTIR result of chitosan and sand coated with chitosan. After the coating, the spectrum show the presence of C–F stretch at 1027.81 cm^{-1} based on figure 2(b). This condition had proven that chitosan was successfully coated around the sand particle.

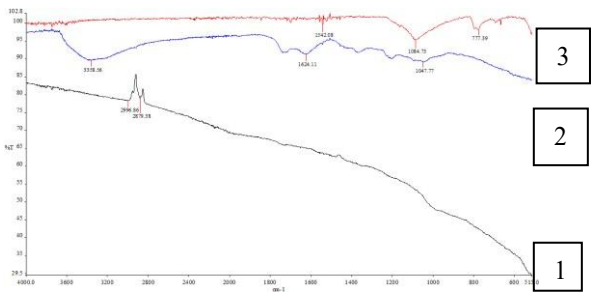


Figure 2(a): FTIR Spectra of graphite powder, synthesis GO and GO coated sand

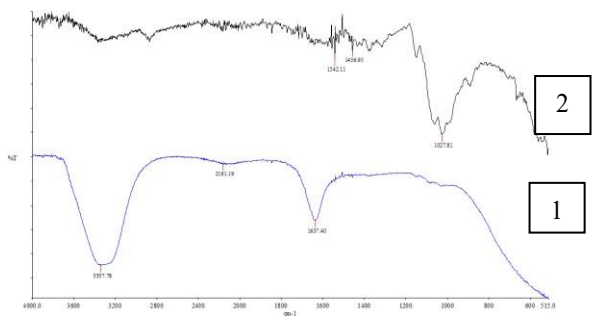


Figure 2(b): FTIR Spectra of chitosan and after the chitosan is coated with sand.

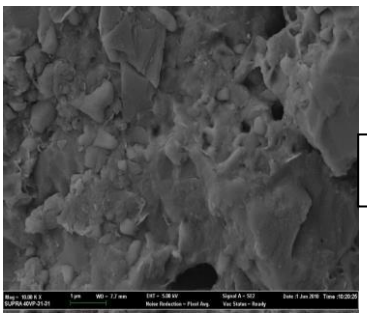
B. Optical microscopy study

Sample of the coated sand were examined under the digital microscope with a magnification of 40x (4x times 10x). By referring figure 3 below, the results showed a presence of the adsorbent around the sand structure. Physically, after the sand were coated, the color of the natural quartz sand changed into black color, showing presence of GO. Meanwhile, the chitosan coated sand can be seen by naked eyes showing a successful coating. These images become opaque, as observed through the optical, thus further assessment were directed by utilizing FESEM.

Figure 3: Optical microscopy images of natural quartz sand after coated with chitosan (above, left) and GO (below, left).

C. Field Emission Scanning Electron Microscopy (FESEM)

Field Emission Scanning Electron Microscopy (FESEM) was used to describe the morphology of the coating sand with the adsorbent. Natural quartz sand sample had a splendid clear morphology before being coated by GO/chitosan. After the coating procedure had been done with a magnificent of 10,000, the morphology structure changed to a dull, lustrous look because of sticky covering over the surface. For a better understanding on the elemental composition of the material, the composite was analyzed by using EDAX [5]. From EDAX, the natural quartz sand displayed major elements such as oxygen, silica and carbon. The presence of carbon, hydrogen and oxygen in GO coated sand affirm the successful coating of the natural quartz sand.



a) Image of natural sand

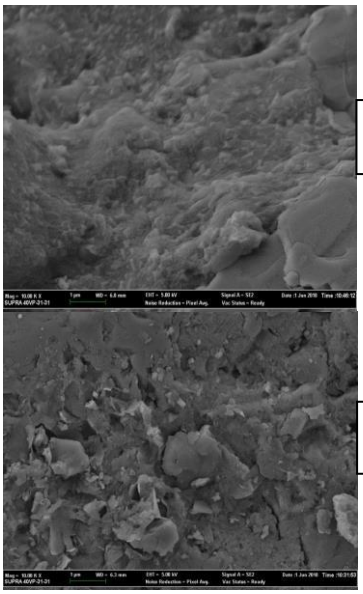


Figure 4: FESEM images of before sand coating and after sand coating with adsorbent.

D. Sand coated with adsorbance

From figure 5, it can be concluded that the coating were highly successful due to physical change of sand surface. Over heated in the sand coated process may causes the GO coating to be fall off easily. Therefore, the procedure need to be followed thoroughly. Further confirmation on the coated bonding had been conducted by digital microscope and FESEM equipment.

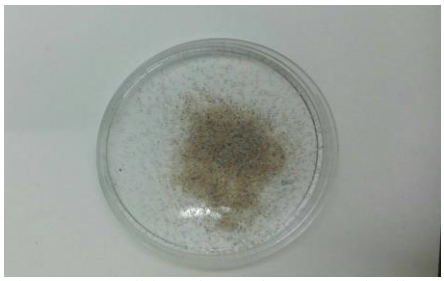


Figure 5a: condition of natural quartz sand collected from

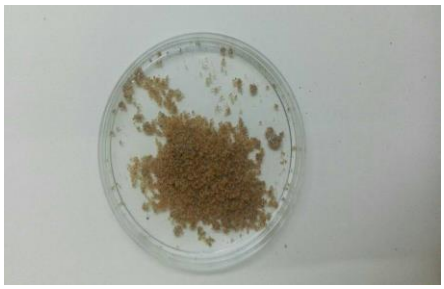


Figure 5b: condition of sand after being coated with chitosan

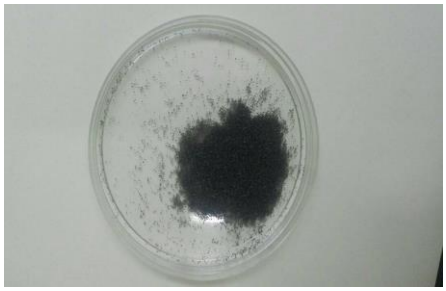


Figure 5c: condition of sand after being coated with chitosan

E. Adsorption of Cd^{2+}, Zn^{2+}, and Cu^{2+} by GO and chitosan

In order to find out whether GO coated sand or chitosan coated sand would provide higher adsorbance of heavy metal ions, adsorption studies were conducted. Aqueous solution (100 ppm) of Cd2+, Cu2+, and Zn2+ metal ions were prepared by dissolving Cd(NO3)2, CuSO4 and ZnCl2 in distilled water at room temperature 25°C, further diluted to the required concentration just before usage [10] Comparative study of adsorbent GO and chitosan is conducted. From the result tabulated in the table above, it shows that chitosan works better as adsorbance because the adsorbance capacity of chitosan coated sand was higher than GO coated sand.

Table 1: heavy metal ion determination

Heavy metal ions determination in GO coated sand		
sample	Concentration before (ppm)	Concentration after (ppm)
$Cd(NO_3)_2$	32.77	32.98
$ZnCl_2$	25.85	42.02
$CuSO_4$	32.60	13.46

Table 2: heavy metal ion determination

Heavy metal ions determination in chitosan coated sand		
sample	Concentration before (ppm)	Concentration after (ppm)
$Cd(NO_3)_2$	32.77	29.25
$ZnCl_2$	25.85	23.45
$CuSO_4$	32.60	0.04

F. Turbidity removal

With a specific end goal to explore the execution of the new material in the field of water treatment, the removal of turbidity was studied. The amount of suspended particles were tabulated in table 4.1. From the table, the result showed that turbidity efficiency of GO is better than chitosan. However, this happened because the potency of chitosan to embedded onto the sand in 24 hours during were lacking compared to GO. After reaching 12 hours of continuous stirring, the chitosan fall off the sand, causing secondary pollution which contribute to higher turbidity reading compared to GO. After the experiment, GO was seen onto the sand surface, showing that it did not peel off from the sand. GO has a hydrophilic surface with plenty of oxygen-containing groups, and good dispersion in water. Both hydrogen bonding and π-π interaction were expected to be responsible for the adsorption of contaminant [10].

Table 2: Turbidity removal by GO and chitosan

sample	Turbidity (FTU) of GO coated sand	Turbidity (FTU) Chitosan coated sand
Cd^{2+}	2.5	37
Cu^{2+}	1.3	18
Zn^{2+}	8.5	3

IV. Conclusion

In this studies, by using graphite powder, GO were produced and been grafted on the sand particles. FESEM shows successful thin coating layer between the adsorbance and sand particles. The significance if this study is to have a better solution for a waste water treatment by any mean of economical ways. The first and second objective were achieved as the synthesization of GO is successful. Meanwhile, the adsorption of heavy metals ions showed that chitosan have higher adsorbance capability compared GO. Chitosan coated sand had demonstrated high efficiency in removing the metal ions from water. Adsorptive removal of

organic matter and heavy metal ions is widely applied compared to others approaches because this practice is easy to handle, economical in term of cost spending and effective at low concentration. This study has proved the conceivable adsorption conduct of chitosan coated sand to remove contaminations. In conclusion, possibility of using chitosan to establish inexpensive large scale filters as permeable reactive barrier for metal removal is higher compared to GO. In this studies, new finding were sorted where the local sand beach may be potentially developed and being used as a bed filter in water filtration. In this case, the sample of natural sand is from Pantai Rusila, Terengganu.

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