Carbon Spheres for the Removal of Hevay Metal Ions From Refinery Effluents

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Abstract: An environmentally-friendly hydrothermal procedure was employed to synthesize carbon spheres (CS) from glucose solution at 170^{0}C. To study the effect of reaction time, four CS samples were synthesized at 12h, 14h, 16h and 19h, respectively. A portion of the samples were surface activated by the treatment with 0.5M NaOH, the other portion treated with 0.5M CH_3COOH, and the remaining samples were left untreated (native). All samples were characterized using various methods including SEM, XRD, Raman spectroscopy, N_2 adsorption and FT-IR. Batch adsorption experiments were carried out at room temperature to remove heavy metal ions (Ag^+ and Cu^{2+}) from aqueous solution. It was found that increasing reaction time resulted in CS with a lower amorphous content and lowered adsorption capacity, NaOH-treated CS had the highest adsorption capacity of 454 mg Ag^+/g and 172 mg Cu^{2+}/g, while CH_3COOH-treated CS had a lower Ag^+ and Cu^{2+} uptake than untreated CS. The adsorption isotherms were well fit by the Langmuir isotherm equation (for base-treated CS) and the Freundlich isotherm equation (for acid-treated CS). The CS showed a high potential for the removal of heavy-metals from aqueous solutions.

Keywords: Adsorption, Carbon, Nanosphere, water treatment, metal ions.

INTRODUCTION

A wide variety of techniques are implemented for the removal of contaminants from waste streams. Some of the most commonly used ones are ion exchange, membrane filtration, chemical precipitation and adsorption [1]. In practice each one of these techniques has pros and cons and the specific technique to be used depends on factors such as equipment cost, removal efficiency and type of contaminant being treated. Adsorption allows the selective removal of specific substances from mixtures even in minute quantities. This fact, along with its simplicity in process design and operation, have made adsorption a widely used separation technology in wastewater treatment. [2].

Currently, the most widely used adsorbents are activated carbons [3]. Activated carbons can be produced from different carbon-containing raw materials and by different activation processes. The most common raw materials are wood, wood charcoal, peat lignite and lignite coke, hard coal and coke, bituminous coal, petrol coke as well as residual materials, such as coconut shells, sawdust, or plastic residuals [4]. The effectiveness of activated carbons as adsorbents is mainly due to their high adsorption capacity, highly developed porosity, large surface area, variable characteristics of surface chemistry and high degree of surface reactivity [5, 6].

However, there continue to be major shortcomings to using activated carbons, including relatively high production costs, high synthesis temperature and difficulty of regeneration [7, 8].

Recently, there has been a significant amount of research effort put into producing colloidal micro- and nano-sized spheres with specific intrinsic properties. By varying factors like chemical composition, crystallinity, diameter and bulk structure, the physical and chemical properties of the spheres can be manipulated. Carbon spheres (CS) contain C-OH and C=O groups on their surfaces and the density of these functional groups can further be increased by treatment with a suitable reagent. Song *et al.* [9] have shown that NaOH-treated CS is an efficient adsorbent of organic dyes from aqueous solutions.

Any waste generated by installations involved in the processing of crude oil (including petrochemicals) is classified as petroleum refinery effluent [10].The estimated volume of effluent generated is 0.4-1.6 times the volume of petroleum processed [11]. Using the worldwide total crude oil production of 4011 million tons for 2011 [12], it can be said that approximately 1604 million tons of refinery wastewater is generated annually. The wastewater stream of a refinery is a combination of streams from numerous sources within the refinery. As an example, the major wastewater sources and their percent contribution to the overall effluent stream of Al Ruwais refinery are listed in Table **1**. Part of this water is reused in the refinery while the remaining is treated to make sure it complies with environmental regulations in its metal and pollutant concentrations before being discharged to water

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Table 1: Source and *Percentage Contribution* to Al Ruwais Wastewater Stream [13]

Source	Volume % of total effluent
Hydro-cracker wastewater	15
Hydro-skimmer wastewater	15
Crude Tank	2
Hydro-skimmer flare	2
Hydro-cracker flare	2
Sour water	20
Condensate wastewater	15
Condensate flare	4
De-salter wastewater	18
Sanitary wastewater	5
Laboratory water	5

bodies. The composition of the effluent is largely dependent on the type and complexity of the refinery.

Heavy metals are elements having atomic weights between 63.5 and 200.6, and a specific gravity greater than 5.0 [14]. In addition to petroleum refineries, heavy metal wastewaters are directly or indirectly discharged into the environment by rapidly developing industries such as fertilizer industries, metal processing facilities, tanneries, pharmaceutical industries, paper industries, organic chemical production facilities, mining operations, lumber and wood production, etc. [15-20]. Once heavy metals enter the environment, they are transported by runoff water or streams and can cause serious damage to living things - including microorganisms, plants and animals. Since heavy metals are non-biodegradable they tend to accumulate within living organisms and can also be chemically changed by the reactions that take place within microorganisms to digest food. Toxic heavy metals such as mercury, chromium, zinc, nickel, lead and copper are paid particular attention to in the treatment of industrial wastewater owing to their higher potential for harm.

Copper is a key component of enzymes that are involved in the catalysis of reduction-oxidation reactions. Adequate daily requirements are 2-3 mg/day for humans. Despite being an essential trace element, it is much more toxic to cells than such nonessential elements as nickel and cadmium [21]. The Maximum Contaminant Level Goal (MCLG) for copper is 1.3 ppm. According to the USEPA, short term exposure to levels higher than the MCLG causes gastrointestinal distress and long term exposure may cause liver and kidney damage or even death.

Silver is an important heavy metal that is usually found in a combined state in the environment [22]. Its rareness and harmfulness make it a particularly interesting heavy metal. In addition to its use in making jewelry and silverware, it has numerous other uses in industry, one of which is for the manufacture of photographic film [23]. Monovalent ionic silver (Ag^+) with its highly undesirable anti-microbial properties, has been shown to cause discoloration in human skin (argyria) at high ingestion concentrations [24]. The United States Environmental Protection Agency (USEPA) regards silver as a contaminant and sets its maximum concentration in drinking water at 0.1 parts per million (ppm).

The deleterious effect of heavy metals on not only the environment but also biological species, has led to the introduction of more stringent environmental regulations on their concentration in wastewater. Petroleum refineries are major contributors to the discharge of wastewater containing significant amounts of heavy metals. Consequently, it is of great importance to develop an efficient, cost- effective and environmentally benign adsorbent for removal of heavy metals from refinery effluents.

2. MATERIALS AND METHODS

2.1. CS Synthesis

Native CS was synthesized using the method reported in the literature [25, 26]. In brief, 6g of glucose (D-Glucose, Fisher Scientific, 99+%, anhydrous) was dissolved in 40ml of distilled water to form a clear solution, which was then placed in a Teflon-lined autoclave (Parr Instruments, Series 4750, maximum

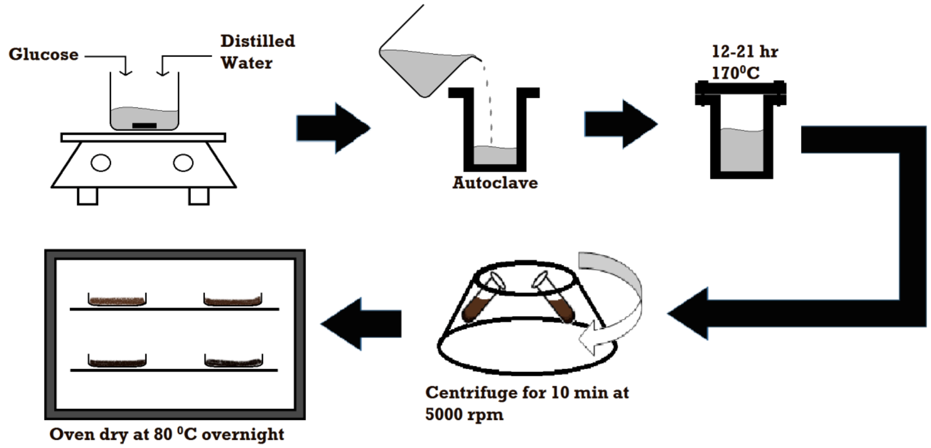

Figure 1: Schematic diagram for cs synthesis.

capacity: 300ml) and maintained at 160-170^{o}C for 12-21hrs. The resulting black products (CS) were isolated by centrifugation, cleaned by three cycles of centrifugation-washing-dispersion in deionized water and ethanol and finally oven-dried overnight at 80^{0}C. The schematic diagram of the synthesis process is shown in Figure **1**.

Four different CS samples were synthesized under the conditions listed in Table **2**.

Table 2: Reaction Parameters for CS Synthesis

	CS-1	CS-2	CS-3	CS-4
Concentration [M]	0.8	0.8	0.8	0.8
Temperature [^{0}C]	170	170	170	170
Time [h]	12	14	16	19

2.2. CS Surface Activation

For the efficient adsorption of metal ions from aqueous solution, the as-prepared native CS were surface activate with different functional groups (acidic or basic). To activate (graft) with basic (hydroxyl-) groups, the CS were treated with aqueous solutions of sodium hydroxide. Briefly, 0.12 g of dry powder was dispersed in 100 mL of NaOH aqueous solution of 0.5M concentration. The mixture was stirred at 300 rpm for 1 h at room temperature. The product was collected by centrifugation and washed with a copious amount of deionized water (about 1 L) to remove the residual NaOH until the pH of the filtrate reaches near neutral. The activated CS samples were air-dried in an oven at 80 ℃ for 18 h. In order to compare the effect of activating with an acidic group as opposed to the hydroxyl groups, the activation process described above was repeated by using 0.5M CH_3COOH instead of NaOH. The Samples activated with NaOH were labeled as CS/OH and those activated with 0.5M CH_3COOH were labeled CS/COOH. The native CS samples were labeled as CS.

2.3. CS Characterization

The surface and structural properties of the CS samples were characterized with a number of technologies, as described below:

Fourier transform infrared spectroscopy (FTIR): FTIR spectra of all samples were obtained using a Bruker VERTEX 70 FTIR spectrometer. After obtaining background spectra of pure KBr, the samples were finely ground together with KBr for recording CS sample spectra. For all samples the number of scans was set at 64 with a resolution of 4 cm^{-1}.

Raman spectroscopy: crystallographic disorder was studied using the spectra obtained from a Raman microscope (Horiba Scientific labRAM HR) in back scattering configuration at 633nm laser wavelength [27].

Scanning Electron Microscope (SEM): An SEM was used to characterize the morphology of the samples. Approximately 20 μg of the samples were set on standard aluminium SEM sample holders (stabs) using conductive super glue and an FEI Quanta 250 FEG SEM was used for analysis. Imaging studies were performed at 20kV.

X-ray diffraction (XRD): The crystallographic structure of the carbonaceous materials was studied using an X-ray Diffractometer (PANalytical, X'pert Pro MPD), with a Cu-Kα radiation.

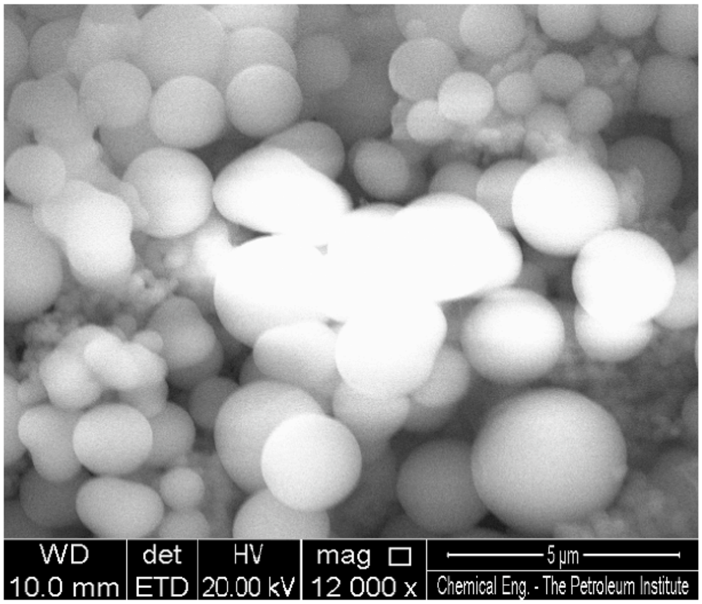

Figure 2: SEM image of as-synthesized carbon spheres.

N_2 adsorption: The surface area of the samples was determined by means of a nitrogen isotherm at 77K using a surface area and pore size analyzer (Quantachrome, Autosorb 6iSA). Degassing of samples was carried out for 8 hours at 423K prior to N_2 adsorption, in order to remove any residual water and/or organic vapors. The Barrett-Joyner-Halenda method (BJH) was used to determine the pore size distribution (PSD).

2.4. Adsorption Studies

The adsorption capacity of native and activated CS was studied in a series of batch adsorption experiments. Mother solutions of 320 ppm Ag^+ (from silver nitrate) and Cu^{2+} (from copper (II) nitrate trihydrate) were prepared and 25 ml of stock solutions at various concentrations (10-270ppm) were prepared by dilution. The freshly prepared metal ion solution was than mixed in a conical flask along with 25mg of CS. The mixture is then stirred at 250rpm for 12 h at room temperature before being filtered by a syringe filter of 0.2µm pore size. The clear filtrate is then diluted in 2% HNO_3 for determination of metal ion concentration by means of an inductively coupled plasma mass spectrometry (ICP-MS).

To calculate the amount of adsorbate that got adsorbed onto the adsorbent, the following equation was used:

$$q_e = \left(c_0 - c_{eq}\right)\frac{V}{m} \tag{1}$$

Where c_o (mg/l) is the initial concentration of adsorbate in solution, V (l) is the volume of the aqueous solution and m (g) is the dosage of the adsorbent in the solution.

The adsorption data were fit to two isotherm models, namely Langmuir and Freundlich model. The linearized Langmuir model is given as:

$$\frac{c_{eq}}{q} = \frac{1}{q_m b} + \frac{1}{q} C_{eq} \tag{2}$$

A dimensionless constant, $R_L = 1/(1+b*c_o)$, was used to determine whether the adsorption isotherm was favorable ($0 < R_L < 1$), unfavorable ($R_L > 1$) or irreversible ($R_L = 0$).

The linearized Freundlich isotherm is given as:

$$\log q = \log K + n \log c \tag{3}$$

Where K and n are the isotherm constants.

3. RESULTS AND DISCUSSION

3.1. Properties of CS

It was observed that immediately after discharge from the autoclave the product solution was orange or brown in color and had an increased viscosity. This may be the result of the formation of some oligosaccharides and aromatic compounds in the polymerization step of the synthesis [28]

Table 3: Peak Position and Interlayer Spacing Values of Carbon Spheres

	Θ (^{0})	D (Å)
CS 1	9.24	4.80
CS 2	9.53	4.65
CS 3	9.56	4.64
CS 4	10.24	4.33

Figure **2** shows an SEM image of the as-synthesized CS sample. A majority of the fully-formed spheres had diameters ranging from 1-3µm. The smaller spheres, with diameters of a few hundred nanometers, formed in groups rather than in a uniformly dispersed manner; possibly due to the agglomeration and inadequate stirring.

Using a λ value of 1.54056 Å and obtaining θ from the diffraction patterns, the interlayer spacing for CS 1, CS 2, CS 3 and CS 4 was calculated (Table **3**).

Plotting patterns of the Figure allows us to compare the relative sharpness of the peaks (Figure **3**). The general trend is that of increasing peak sharpness with increasing reaction time, which further confirms that CS 4 is the most crystalline sample. One possible reason is that a longer reaction time allows for the deposition of more graphitic flakes on the surface of spheres.

The average interlayer spacing of the four samples is 4.6 Å, which when compared to the 3.34 Å spacing of bulk graphite, indicates the possibility that the carbon spheres have a turbostratic carbon structure [29].

Based on the XRD pattern and texture of the four samples, CS 2 (most amorphous) and CS 4 (most crystalline) were selected for further treatment and characterization.

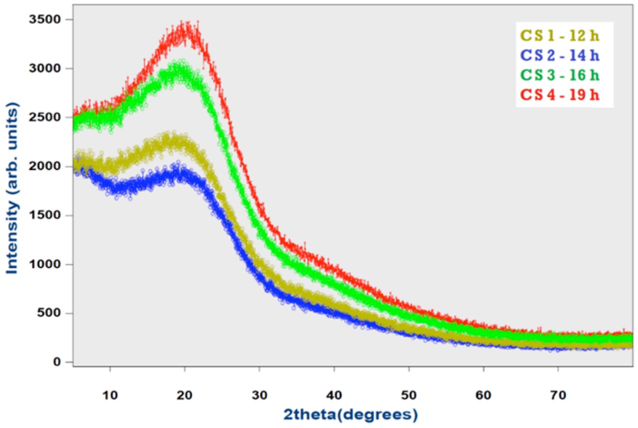

Figure 3: XRD patterns of the carbon spheres.

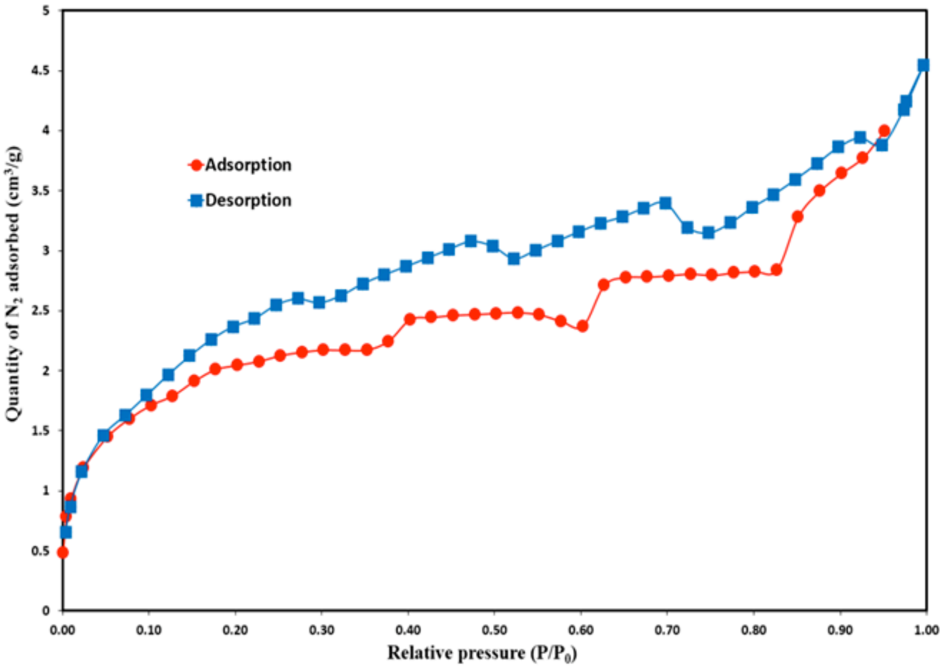

Figure 4: Nitrogen adsorption-desorption isotherm of CS sample.

N_2 adsorption on CS resulted in a Type II isotherm, as the one shown in Figure **4** for CS 2. This type of isotherm is frequently encountered when adsorption takes place on nonporous structures or powders with diameters exceeding micro-pores [30]. The surface area of CS was obtained using the multipoint BET method, which was used to calculate the area of CS 2 and CS 4 as 8.5 m^2/g and 17.9 m^2/g, respectively. In addition, pore volume was found to be 0.007 cc/g for CS 2 and 0.02 cc/g for CS 4. These results suggest that the CS are basically non-porous in structure. The small fluctuations (experimental errors) in adsorption/desorption isotherms also pointed to this structural characteristics.

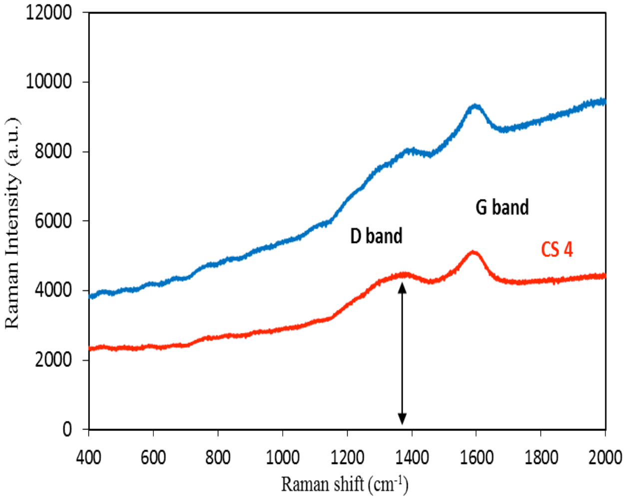

Figure 5: Raman spectra of CS2 and CS 4.

Raman spectra of native carbon spheres showed two distinct bands at 1360 cm^{-1} and 1580 cm^{-1}

The 1580 cm^{-1} band is attributed to the in-plane vibrations of crystalline graphite and is commonly known as the 'G', or graphite, band. The peak at 1360 cm^{-1} is due to a vibrational mode associated with graphite edges [31] and is known as the 'D', or disorder, band. The difference in intensity between these two peaks is a good indication of the amorphous nature of the material. If the difference of G band intensity (I_G) to D band intensity (I_D) is small it implies that the material has a high quantity of amorphous content. Hence, CS 4 ($I_G - I_D = 622$) can be said to have a higher degree of disorder than CS 2 ($I_G - I_D = 1066$).

The FTIR spectra of native CS 2, native CS 4 and glucose are shown in Figure **6**.

The broad band in the range 3100 – 3400 cm^{-1} is attributed to hydroxyl (-OH) stretching of carboxylic bonds [32]. The peak at 2925 cm^{-1} found in CS 4 and glucose spectra is the result of asymmetric stretching of C-H in aliphatic hydrocarbon groups. The band at 1700cm^{-1} is due to the stretching vibration of undissociated carbonyl (C=O) groups and the neighboring band at 1615cm^{-1} is attributed to C=C stretching [33-36]. Joule and Mills [37] suggest that the three peaks found at 1604,1510 and 1395 cm^{-1} may be the result of bond vibrations of five-member

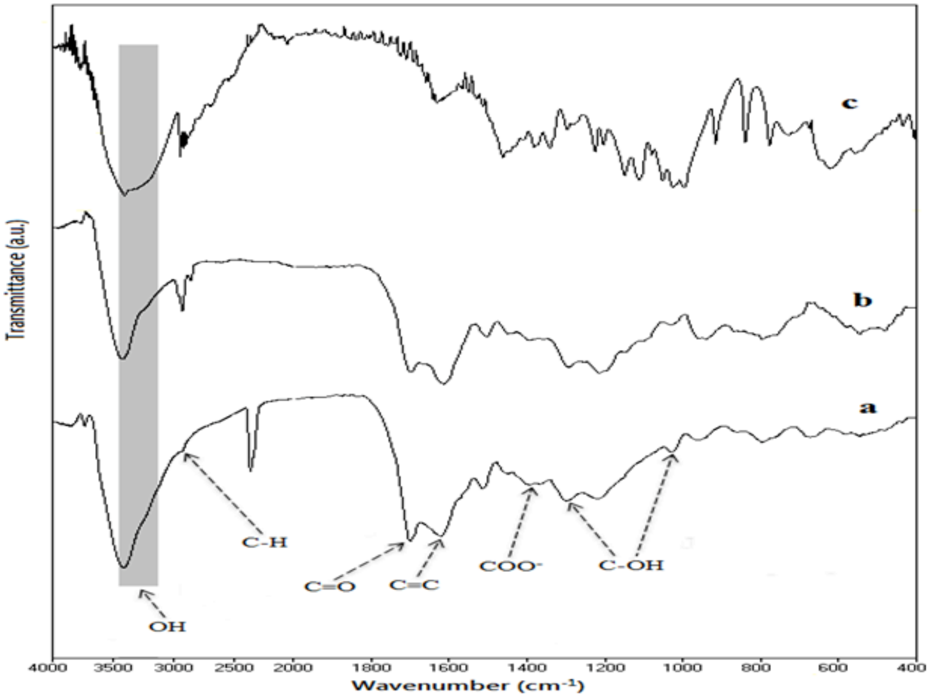

Figure 6: FTIR spectra of (a) CS 2, (b) CS 4, and (c) glucose.

heteroaromatic rings with double bonds (Furan) [29, 38].

The symmetric stretching vibration of deprotonated carboxylate group (-COO$^-$) centered at 1385 cm^{-1} is barely noticeable for CS 2 and CS 4 but is clearly visible for glucose [39, 40]. The bands at 1302 cm^{-1} and 1023 cm^{-1} correspond to C-OH stretching and OH bending vibrations in C-OH, respectively [25, 41].

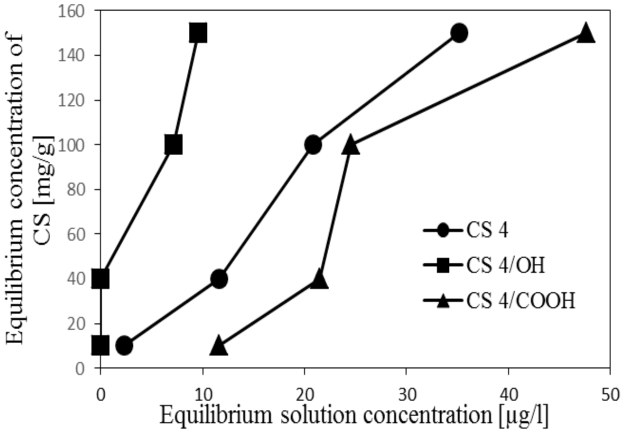

Figure 7: Effect of NaOH and CH_3COOH treatment of CS 4 on silver ion adsorption capacity.

3.2. Adsorption Studies

3.2.1. Effect of Acid and Base Treatment on Silver Ion Adsorption Capacity

The effect of NaOH and CH_3COOH activation on adsorption capacity of CS 4 is shown in Figure **7**. CS 4/OH exhibited superior adsorption performance over both CS 4 and CS 4/COOH. At the similar silver concentration of 10 µg/l, the capacity of CS 4/OH is about 5 times that of CS 4 and 15 times that of CS 4/COOH. This dramatic increase in silver adsorption capacity can be attributed to the large quantity of deprotonated carboxylate groups and hydroxyl groups found in CS 4/OH. Also, it can be observed that in a similar manner to CS 2 (data not shown), the adsorption capacity of CS 4/COOH was lower than that of CS 4. Hence, adsorption capacity was in the following order: CS 4/OH > CS4 > CS 4/COOH.

3.2.2. Silver ion adsorption isotherms

Figure **8** shows the Ag$^+$ adsorption isotherm of CS 2/OH, CS 2/COOH, CS 4/OH and CS 4/COOH. It can be seen from the low equilibrium solution concentration values that CS 2 has an extremely high removal efficiency for silver ions. The maximum adsorption capacity was not reached for initial Ag$^+$ concentration of 320ppm (the highest concentration tested for in this study). The CS 2/COOH isotherm revealed that acid-treatment slightly lowered the Ag$^+$ removal efficiency. At a given equilibrium solution concentration, CS 2/OH had about a 10 times higher adsorption capacity than CS 2/COOH.

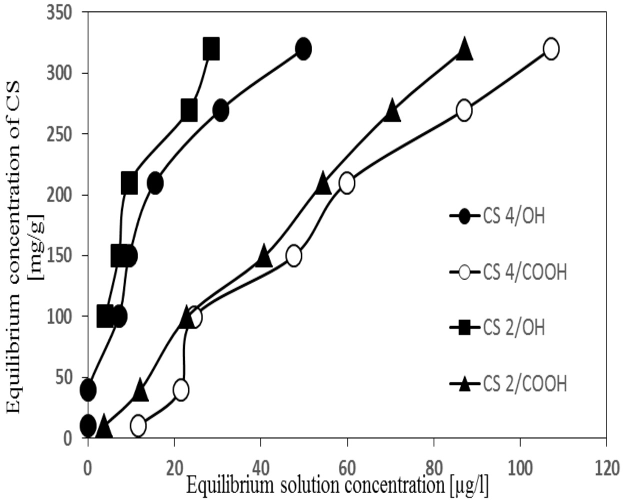

Figure 8: Silver adsorption isotherms of NaOH-treated and CH_3COOH-treated CS.

Complete removal was obtained for low initial Ag$^+$ concentrations of 10 ppm and 40 ppm. Based on the adsorption capacity, CS 4/OH is a slightly poorer adsorbent than CS 2/OH but better than CS 2/COOH. The CS 4/COOH isotherm also indicates that acid-treatment is not as effective in increasing adsorption capacity as treatment with a base.

Table 4: Langmuir And Freundlich Parameters for Adsorption Of Ag$^+$ On Cs

	Langmuir				Freundlich		
	q_m [mg/g]	b [L/mg]	R^2	R_L	K [(mg/g)(L/mg)$^{1/n}$]	n	R^2
CS 2/OH	454	0.0728	0.97	0.04	50.3	0.556	0.95
CS 2/COOH	-1250	-0.0025	0.27	5	2.55	1.101	0.99
CS 4/OH	454	0.0467	0.98	0.0627	39.2	0.558	0.93
CS 4/COOH	-204	-0.0069	0.29	-0.83	0.47	1.456	0.90

The Langmuir and Freundlich adsorption models were used to further analyze the adsorption behavior (Table **4**).

As in the case of previous literature [26], the Langmuir isotherm equation produced a better fit than the Freundlich isotherm for CS 2/OH and CS4/OH while the Freundlich equation produced a better fit for CS 2/COOH and CS4/COOH [41]. Langmuir isotherm is derived based on the assumption of a homogeneous surface and single layer of adsorbate. In most cases, this type of isotherm is used to describe chemisorption processes [42]. Hence, adsorption of Ag^+ of NaOH-treated CS may be a mainly chemisorption process rather than physisorption.

Freundlich isotherm is based on energetic heterogeneity of the adsorbent's surface and multilayer adsorption. The value of n obtained for CS 2/COOH and CS 4/COOH lie between 1 and 10 and therefore represents beneficial adsorption [43, 44].

The theoretical maximum adsorption capacity, q_m, for CS 2/OH and CS 4/OH is found to be 454 mg/g and the dimensionless constant R_L lies between 0 and 1, indicating favorable adsorption. CS 4/COOH had a higher n value than CS 2/COOH, i.e. a higher level of energetic heterogeneity, and a lower adsorption capacity. This fact, coupled with the lower adsorption capacity of acid-treated CS, indicates that changes other than the modification of functional groups are taking place. Demir-Cakan *et al*. [41] have suggested that treatment of carbonaceous materials with acids results in a decrease in pore volume in addition to increasing the density of acidic surface functional groups.

Compared to the maximum Ag^+ adsorption capacity of 2000 mg/g obtained using copolymer adsorbents [45], the maximum value obtained by this study may appear to be low. However, CS 2/OH has a higher adsorption capacity than other heavy metal adsorbents such as activated carbon (25 mg Ag^+/g) [46], peat (1 mg Ag^+/g) [47], biomass from brewery waste (43 mg Ag^+/g)([48], coke (0.9 mg Ag^+/g) [47], Spruce wood (0.06 mg Ag^+/g) [47] etc. The negative values of q_m and b are only to show the mathematical fitting of the data. The reasons for these negative values are that the isotherm is basically linear and there is a lack of constraint at high concentration region. The Ag^+ adsorption capacity of all samples was generally in the order of CS 2/OH > CS 4/OH > CS 2 > CS 4 > CS 2/COOH > CS 4/COOH.

3.2.3. Effect of Acid and Base Treatment on Copper Ion Adsorption Capacity

Figure **9** shows the effect that acid and base treatment had on the Cu^{2+} adsorption capacity of CS 4. The difference in adsorption capacity of native CS 4 and CS 4/OH was not as much as that for CS 2 (data not shown) but in both cases CS treated with NaOH had the highest adsorption capacity for Cu^{2+}. Also, acid treatment of CS 4 resulted in a slightly improved Cu^{2+} adsorption capacity. The order of Cu^{2+} adsorption capacity on CS 4 is CS 4/OH > CS 4/COOH > CS 4.

3.2.4. Copper Ion Adsorption Isotherms

The adsorption isotherm of CS 2/OH and CS4/OH shown in Figure **10** reveals that at low initial Cu^{2+} concentrations >99% removal was obtained. There was a gradual decrease in the percent removed with increasing C_e. The maximum adsorption capacity

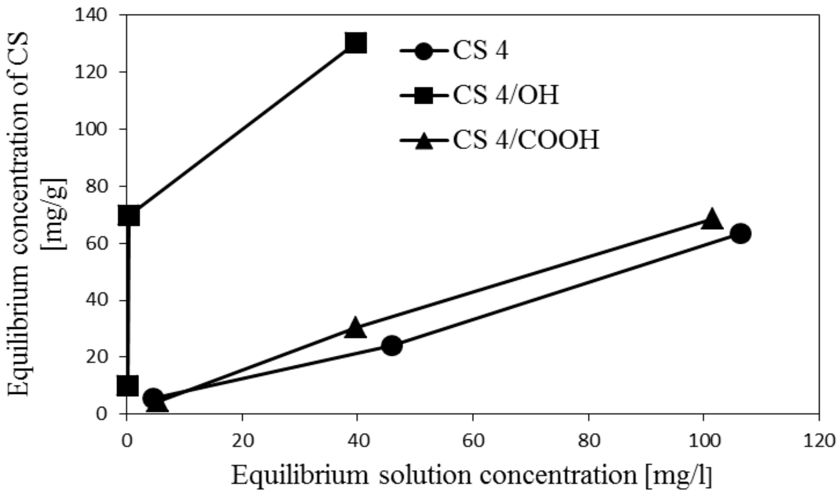

Figure 9: Effect of CH_3COOH and NaOH-treatment of CS 4 on copper ion adsorption capacity.

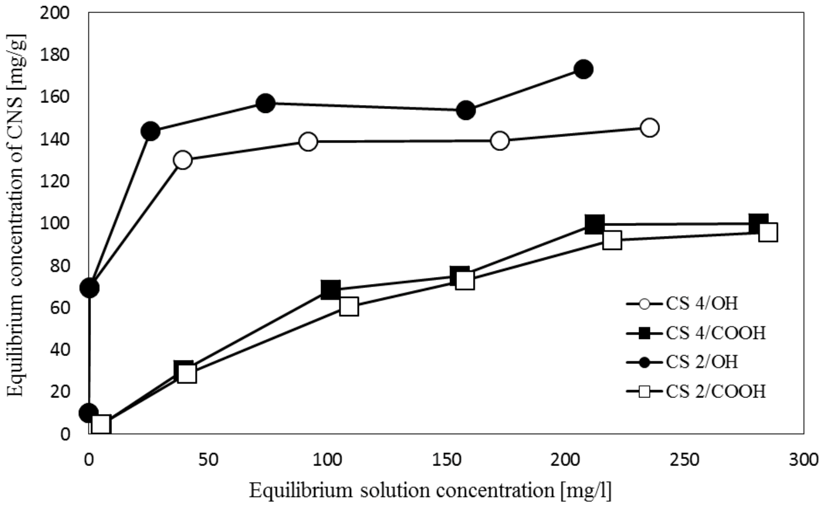

Figure 10: Copper adsorption isotherms of NaOH-treated and CH_3COOH-treated CS.

obtained was 172 mg Cu^{2+}/g, which is higher than some commonly used adsorbents such as cellulose pulp (4.98 mg Cu^{2+}/g) [49], Compost (12.77 mg Cu^{2+}/g) [49], rolling mill scale (40 mg Cu^{2+}/g) [50], coal (1.62 mg Cu^{2+}/g) [51] and blast furnace sludge (18 mg Cu^{2+}/g) [52].

CS 2/COOH and CS4/COOH had a much lower Cu^{2+} removal efficiency of only 49% and 46% being removed at the lowest concentration tested and a maximum adsorption capacity of 95.8 mg/g and 100.1 mg/g, respectively.

Langmuir and Freundlich fit of the data showed that CS 2/OH and CS 4/OH were better fit by the Langmuir equation and CS 2/COOH and CS4/COOH were better fit by the Freundlich equation, as shown in Table **5**.

The R_L value for Cu^{2+} adsorption on CS 2/OH CS4/OH lie in the acceptable range of 0 to 1 and the value of n for CS 2/COOH and CS 4/COOH are between 1 and 10, which indicates beneficial adsorption of Cu^{2+}.

Comparing overall CS 2 and CS 4 results reveals that CS 2 is a better Cu^{2+} adsorbent than CS 4. Hence, a shorter reaction time and a lower amorphous content results in a higher Cu^{2+} adsorption capacity.

4. CONCLUSIONS

In this work, colloidal carbon spheres were developed for removal of heavy metals from aqueous solutions which resemble the refinery affluents. Increasing the reaction time resulted in CS with a more amorphous nature, as revealed by XRD patterns and Raman spectra. N_2 adsorption-desorption isotherm confirmed that CS have low surface area (< 20 m^2/g), are nonporous in nature and that adsorption on CS is a mainly chemisorption process. It was also found that base-treatment caused an increase in the density of deprotonated carboxylate groups and hydroxyl groups on the surface. On the other hand, acid-treatment had a relatively small effect on the organic surface functional groups.

The adsorption studies for CS 2 and CS 4 revealed similar trends. In both cases, acid-treatment lowered

Table 5: Langmuir and Freundlich Parameters for Adsorption of Cu^{2+} On Cs

	Langmuir				Freundlich		
	q_m [mg/g]	b [L/mg]	R^2	R_L	K [(mg/g)(L/mg)$^{1/n}$]	n	R^2
CS 2/OH	454.5	0.073	0.97	0.035	50.27	0.556	0.95
CS 2/COOH	-1250	0.003	0.27	0.467	2.55	1.102	0.99
CS 4/OH	144.9	0.379	1.0	0.007	39.1	0.38	0.86
CS 4/COOH	-204	0.0069	0.29	-0.61	1	0.844	0.96

the adsorption capacity for Ag^+ and Cu^{2+} below that of untreated CS, while base-treatment greatly enhanced the amount adsorbed. In modeling the individual isotherms, it was found that base-treated CS is better fit by the Langmuir isotherm model and acid-treated CS is better fit by the Freundlich isotherm model. The more amorphous CS 2 generally had a higher adsorption capacity than CS 4. CS 2/OH had the biggest adsorption capacity from all the samples tested with maximum adsorption capacity of 454 mg Ag^+/g and 172 mg Cu^{2+}/g. All the results indicate that CS is a promising adsorbent for the removal of heavy metals from refinery effluents.

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