Sorption of cadmium from aqueous solution by surfactant-modified carbon adsorbents

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ARTICLE INFO

ABSTRACT

Sorption capacities for cadmium, Cd(II) on indigenously prepared, steam activated, untreated, surfactant-modified carbon powder, from husk and pods of *Moringa oleifera* were investigated. The optimized conditions for all the experimental runs were pH 8.0 ± 0.2, temperature $30 \pm 0.5\,^{\circ}$C, contact time 120 min, agitation speed 160 rpm, initial metal concentration $30\,mg\,L^{-1}$ and adsorbent dosage $1.0\,g\,L^{-1}$, respectively. Maximum Cd(II) removal, 98.0% was observed when cetyltrimethyl ammonium bromide (CTAB), cationic surfactant-treated carbon was used as an adsorbent. The Cd(II) removal percentages for sodium dodecyl sulphate (SDS), anionic surfactant, Triton X-100 (non-ionic surfactant) treated and untreated powder activated carbons were found to be 95.60, 81.50 and 73.36%, respectively. SEM images and BET surface area, porosity and pore volume measurements have revealed that surfactant-treated carbons have superior porosity and enhanced surface area than untreated carbons. The sorption data were correlated better with the Langmuir adsorption isotherm than Freundlich isotherm with R^2 values ranging from 0.91 to 0.98.

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1. Introduction

The contamination of the environment and specifically water by toxic heavy metals, has persistently posed a global challenge due to increasing environmental pollution [1]. Unlike organic pollutants, the majority of which are susceptible to bio-degradation, heavy and noble metals are not bio-degradable [2,3]. They are toxic to aquatic flora and fauna even if they are present in relatively low concentrations. Some of these are capable of being assimilated, stored and concentrated by organisms. Cadmium, Cd(II), for example can be accumulated in human body, causing erothrocyte destruction, nausea, salivation, diarrhea and muscular cramps, renal degradation, chronic pulmonary problems and skeletal deformity [4]. Today, cadmium emissions have increased dramatically, as cadmium-containing products are rarely re-cycled, but often dumped together with household waste. Cigarette smoking is also a major source of cadmium exposure. Many states of health are linked to elemental imbalance leading to the generation of multifarious diseases [5,6]. Therefore, measures should be taken to reduce the pollution caused by heavy metal contamination in general and cadmium exposure in particular, to minimize the risk of adverse effects on health and the environment.

Numerous efforts including the development of chemical processes such as electrofloatation, chemical precipitation, ion exchange, biosorption, co-precipitation/adsorption, flocculation and membrane filtration have been developed to reduce the hazardous effects of toxic metals [7]. Adsorption is considered as the most practical and economical way to remove heavy metals. The ability of activated carbon to scavenge the pollutant's molecules is mainly attributed to higher specific surface area. Activated carbon from cheaper and readily available resources like, coke, peat, wood, saw dust, coconut shell [8], rice husk [9], papaya wood [10], etc. have been successfully employed. Various kinds of agricultural, domestic and industrial wastes such as sugarcane bagasse, *Moringa oleifera* (*M. oleifera*) husk and pods [11], cotton stalk, wastes rubber [12] have been utilized in the preparation of activated carbon. In Pakistan, Moringa is represented by only two species: *M. concanensis* and *M. oleifera*. The dried seeds can be crushed to produce high-quality vegetable oil and the resulting press-cake mixed with water and strained to form a coagulant for water treatment [13–15]. The residue-containing seed husk is currently discarded as waste. It has been reported that the simple steam pyrolysis procedure [11,16] can produce high-quality microporous activated carbons from both the waste husks and pods of *M. oleifera*.

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Surface-active substance or surfactants are amphipathic substances with lyophobic and lyophilic groups making them capable of adsorbing at the interfaces between liquids, solids and gases. They form self-associated clusters, which normally lead to organized molecular assemblies, monolayers, micelles, vesicles, liposomes and membranes. Depending upon the nature of hydrophilic group, they can be anionic (negative charge), cationic (positive charge), non-ionic (no apparent charge), and Zwitterionic (both charges are present). The critical micelle concentration (CMC) is the concentration of an amphiphilic component in solution at which the formation of aggregates (micelles, round rods, lamellar structures, etc.) in the solution is initiated [17,18]. For these characteristics, surfactant-modified adsorbents are not only superior in terms of removal efficacy than the conventional adsorbents, but also encourage selective adsorption [11]. As it is nowadays, other than for environmental remediation, surfactants are being utilized in almost every industry including paints, textiles, cosmetics, pharmaceuticals, agrochemicals, fibers, plastics, petroleum, food and mineral processing. Therefore, emerging technologies represent a vibrant and challenging area in understanding the physico-chemical properties of conventional and non-conventional (gemini, non migratory, etc) surfactants and phase behavior of surfactant based processes involved in the preparation of emulsions, dispersions, suspensions and their subsequent characteristics i.e. stabilization, formation, breaking of interfaces, wetting, spreading, solubilization and adhesion. Moreover, surfactants are also very useful in chromatographic separations of the tedious compounds like pesticides. Their use in the chemical modification of adsorbents can lead to the selective separation and recovery of precious and noble metals as well.

Adsorption behavior can be explained in terms of adsorption isotherms. The linearized form of the Langmuir isotherm equation assumes that every adsorption site is equivalent and the ability of a particle to bind is independent of whether or not adjacent sites are occupied. On the other hand, Freundlich isotherm model assumes that the adsorption takes place on a heterogeneous surface [19]. The objectives of this study were to investigate the effect of surfactant modification on the structural morphology and surface area of indigenously produced activated carbon. This will be accomplished by evaluating the Cd(II) removal efficiency by analyzing the sorption data with the help of Langmuir and Freundlich models.

2. Methodology

2.1. Preparation and structural characterization of activated carbon

Mature pods of *M. oleifera*-containing seeds to be used for the preparation of the carbon adsorbents were collected from plants, within the campus of University of Agriculture, Faisalabad, Pakistan. Seeds were separated from the husk and pods. Activated carbon was produced based on the method as described by Warhurst et al. [11,16]. The precursor (30 g husk material and 10 g pods) was heated in a furnace to eliminate volatiles (carbonization) and concurrently activated by steam flowing from the bottom. Five samples of activated carbon were produced independently following the same procedure, dried in an oven overnight at 110 °C, mixed together, homogenized and sieved to 0.250, 0.149 and 0.074 mm particle sizes respectively. The properties of activated and modified carbon like pore diameter, specific pore volume, BET surface area, SEM images of the adsorbents have been determined by the following similar protocols as reported in our earlier study [11]. The method has also been reported by Gergova and Petrov [20] and is economical in producing effective carbons from the materials such

as apricot stones, grape seeds and coconut shells. These samples are categorized as untreated activated carbon adsorbents and further utilized to optimize the conditions for the sorption of Cd(II) from aqueous solutions.

2.2. Modification with surfactants

Surfactants (cationic: CTAB, $C_{16}H_{33}NCH_3Br$) (anionic: SDS, $CH_3(CH_2)_{11}OSO_3Na$) and (non-ionic: Triton X-100, $C_{14}H_{22}O(C_2H_4O)_n$) were obtained from Aldrich Co., and used as received without further purification. Modification was carried out by treating, 5 g of adsorbent with 100 mL solution of each cationic, anionic and non-ionic surfactant respectively at respective CMCs. All the samples were placed in a temperature controlled orbital shaker with 160 rpm, at 80 ± 0.5 °C for 360 min and left to attain the ambient conditions. Each sample was filtered by Whattman-42 without rinsing, and dried in an oven overnight at 110 °C [11].

2.3. Analysis of Cd(II)

The stock solutions of Cd(II) were prepared in deionized water by $Cd(NO_3)_2$ (Merck, USA) and further dilutions were made according to the requirement. pH of all the solutions containing carbon adsorbents were adjusted to 9 ± 0.1 by dilute solutions of analytical grade HCl or NaOH (Merck, USA). The modified and original samples were evaluated for the removal of Cd(II) at different contact times under previously optimized conditions. Residual Cd(II) concentrations were analyzed by AAS (PerkinElmer, A Analys-300). Triplicate runs of each test were conducted and the obtained data vary less than 1% suggesting the accuracy of the results. The metal concentration retained by the adsorbent phase was calculated using the following relation:

$$Q_e = \frac{(C_0 - C_e)V}{W} \tag{1}$$

Where, Q_e is the equilibrium adsorption capacity, C_0 the initial metal concentration, C_e the equilibrium metal concentration, V the volume of solution-containing adsorbate and W is the mass of the adsorbent.

2.4. Isotherm studies

The relationship between the amount of a substance adsorbed per unit mass of adsorbent at constant temperature and its concentration in the equilibrium solution is called the adsorption isotherm. The Langmuir and Freundlich isotherms are the equations most frequently used to represent data on adsorption from solution. Linearized forms of Langmuir and Freundlich isotherm models equation can be presented as follows [11,18]:

$$\frac{C_e}{x/m} = \frac{1}{K_L V_m} + \frac{C_e}{V_m} \tag{2}$$

$$\log Q_e = \log K_F + \frac{1}{n} \log C_e \tag{3}$$

Where, C_e is the equilibrium solution concentration, x/m the amount adsorbed per unit mass of adsorbent, m the mass of the adsorbent, V_m (mg/g) the monolayer capacity, and K_L, K_F are equilibrium constants.

3. Results and discussion

3.1. Structural characterization

SEM images of steam activated, SDS, Triton X-100 and CTAB-modified activated carbon are presented in Fig. 1. It is evident from
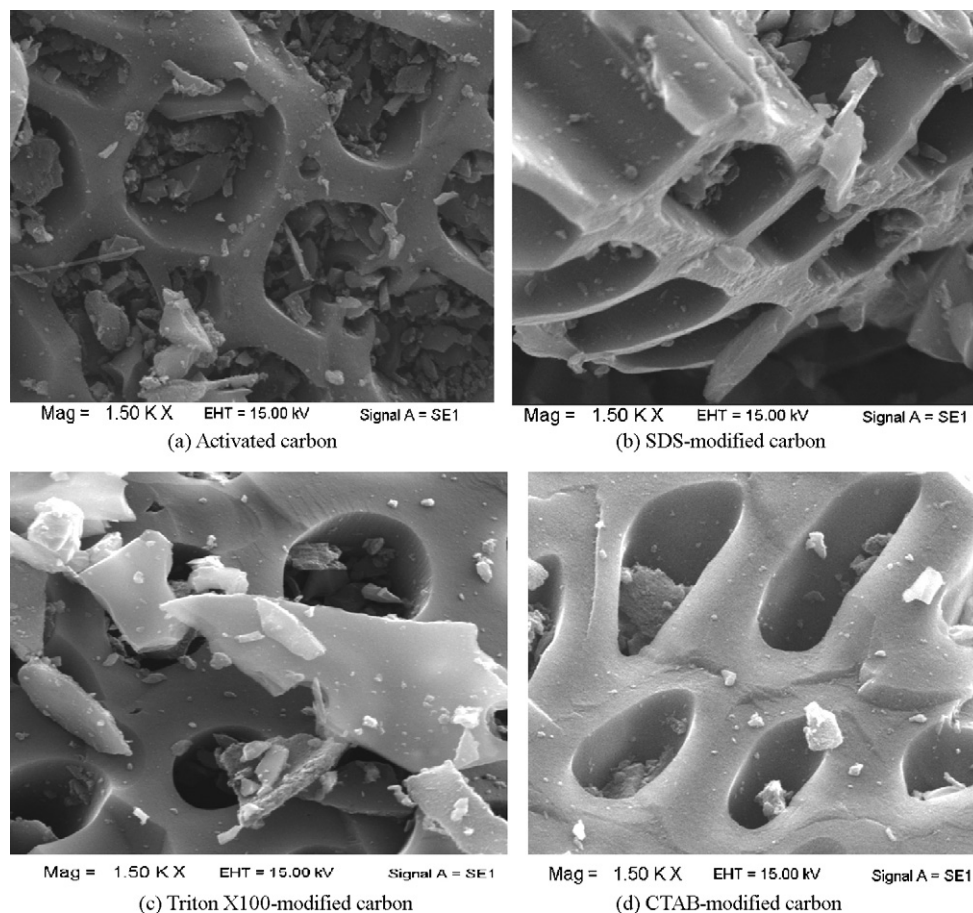
Fig. 1. SEM images of the adsorbents (a) activated carbon, (b) SDS-modified carbon, (c) Triton X-100-modified carbon, and (d) CTAB-modified carbon.

the obtained SEM images that surfactant modification is significantly responsible to alter the physico-chemical properties and porosity of the materials.

BET surface area and porous structure characteristics of the adsorbents are summarized in Table 1. The results not only show that the modified carbon adsorbents have greater BET surface area as compared to the unmodified carbon adsorbent, but also larger pore diameter and specific pore volume. CTAB-treated adsorbents have greater surface area, pore diameter and volume, followed by SDS, Triton X-100 modified and unmodified adsorbents. It further suggests both cationic (CTAB) and anionic (SDS) surfactant enhanced the characteristics of adsorbent better than the non-ionic one (Triton X-100). The enhancement can be attributed to the typical properties of micelle formation, adsorption, wetting and solubilization. Being amphipathic in nature, surfactant-modified surfaces can offer enhanced surface area and wetting (water or oil wet) according to the requirement because surfactant molecules are capable of organizing themselves accordingly. Moreover, the presence of electrostatic interactions facilitate the possibility for

selective adsorption as well [11]. From Fig. 1, the surfactant-modified adsorbents appear to possess more homogenous surfaces and well organized porous structure than the unmodified adsorbent. Significant amount of material debris can be seen occupying the pores of the latter, which may have resulted in its reduced surface area and much lower pore diameter as shown in Table 1. The well-organized porous structure is also prominently observed more in CTAB and SDS-modified adsorbents than in Triton X100. These variations are due to the chemical structures, micellar shapes and the affinities of different surfactants towards the adsorbent.

3.2. Effect of adsorbent dosage

Different amounts of activated carbon varying from 0.05–0.30 g/100 mL of solutions with two initial concentrations of cadmium (30 and 45 mg L^{-1}) have been used to optimize the required amount for maximum removal efficiency of the adsorbent at pH 8 ± 0.2, temperature $30 \pm 0.5\,°C$, contact time 60 min and agitation speed 160 rpm. The pH was maintained at 8 ± 0.2 during the experiments because beyond this pH, removal occurs because of precipitation instead of adsorption. Fig. 2. shows that maximum removal percentages were 26.96 and 25.50 mg g^{-1} respectively for both the solutions with initial metal concentrations 30 and 45 mg L^{-1} respectively at 0.1 g of carbon. This decrease in removal percentage with increase in the dosage of activated carbon and initial metal concentration may be a result of the formation of clusters of carbon particles resulting in decreased surface area. Moreover, when adsorption follows

Table 1
BET surface area and structural characterization of adsorbents.

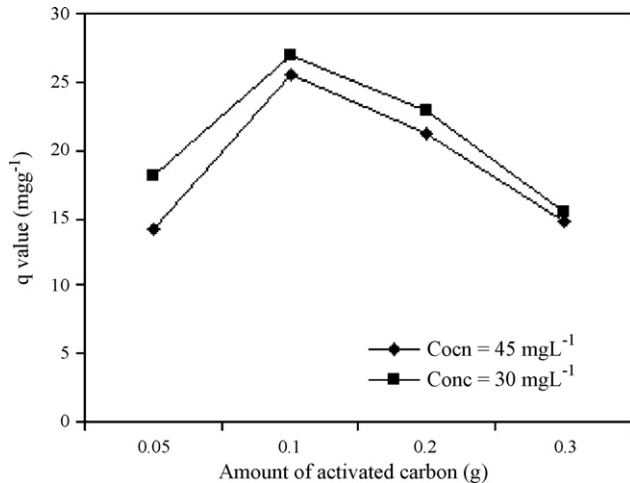| Sample	BET surface area (m^2/g)	Pore diameter (μm)	Specific pore volume (cm^3/g)
Activated carbon	725.0	0.06	0.47
SDS-modified carbon	805.3	1.63	0.72
Triton X-100-modified carbon	792.5	0.98	0.59
CTAB-modified carbon	814.2	2.00	0.84

Fig. 2. Effect of activated carbon dosage on Cd(II) removal.

the model of monolayer formation, increased concentrations of Cd(II) from a particular range, will remain in solution instead of being adsorbed due to the non-availability of the adsorption sites.

3.3. Effect of contact time and initial Cd(II) concentration

Fig. 3 indicates that the sorption increased with increasing contact time, 73.4 and 64.3% for the solutions containing 30 and 45 mg L^{-1} of Cd(II) initially and became almost constant after 120 min. However, with the same adsorbent and contact time, there is a drop in the removal percentage with the increase in the initial metal concentration. At lower initial metal concentrations, sufficient adsorption sites are available for the sorption of metal ions. Conversely, the numbers of metal ions at higher initial concentrations are relatively more as compared to the available adsorption sites. Hence, the percentage of heavy metal removal correlates inversely with the initial metal concentration. As highlighted earlier, the difference in the removal capacity is a result of the difference in their chemical affinities and ion exchange capacity with respect to the chemical functional group on the surface of the adsorbent. In this case, the availability of free adsorption sites dominates [21].
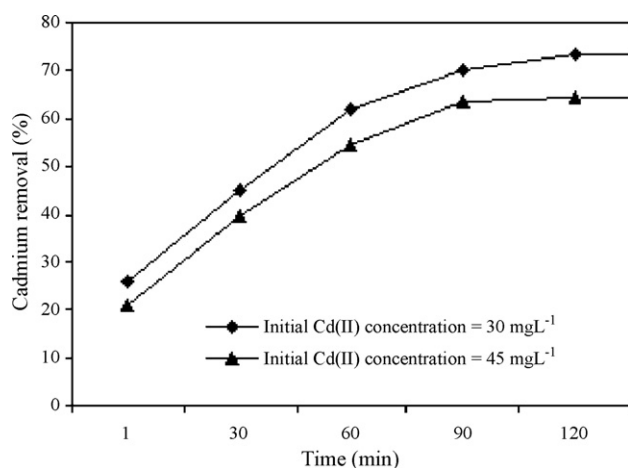

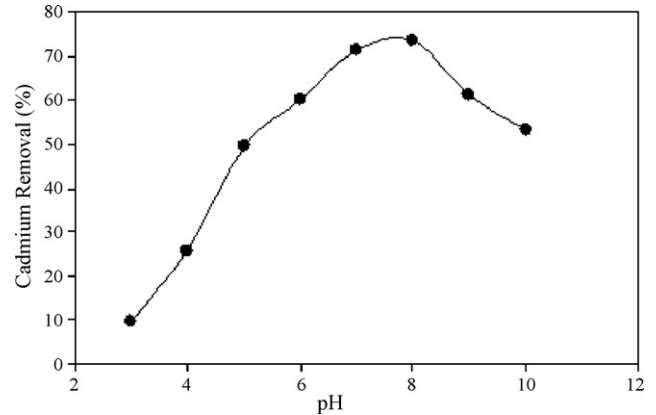**Fig. 3.** Effect of contact time on Cd(II) removal percentage with 0.074 mm particle size.

Fig. 4. Effect of pH on Cd(II) removal percentage with 30 mg L^{-1} initial metal concentration.

3.4. Effect of pH

The effect of pH on adsorption of Cd(II) was studied at $30 \pm 0.5\,^\circ$C by varying the pH of metal solution–activated carbon suspension from 3 to 10. As illustrated in Fig. 4, there is little adsorption in the pH range of 3–4. The percentage of adsorption only started to increase in the pH range of 4–10. The maximum adsorption of 70.3% was achieved at pH $8.0 \pm .0.2$. Beyond this range, precipitation of Cd (II) as Cd(OH)$_2$ could have occurred. It has been reported that precipitation of Cd(II) starts at pH 8.3 with the removal percentage of Cd(II) by precipitation to be less than 10% [22]. At pH 8, it can be safely assumed that the percentage of Cd(II) removal should be caused much greater by adsorption than by precipitation. This was confirmed by analyzing the desorbed amount of Cd(II) using EDTA as an eluting agent (Data not presented). The effect of pH can be explained in terms of electrostatic interactions initiated by the adsorbent. At lower pH, the surface charge of the adsorbent is positive which is similar to the predominant metal species in the solution. Hence, the removal of metals in the pH range of 3–4 is less because of the less inclination of the metal species to migrate to the adsorbent as like-charges repel. As the pH becoming less acidic, there is a greater possibility for the positively charged metal ions to be attracted to increasingly negatively charged adsorbents. In addition, there are also possible sites on the unmodified *M. Oleifera* surface for specific adsorption of H$^+$ ions that can be exchanged with the metal cations in the solution. The reduction in cadmium removal beyond pH 8 and towards more basic pH condition, may suggest the possibility of Cd(OH)$_2$ precipitates occupying

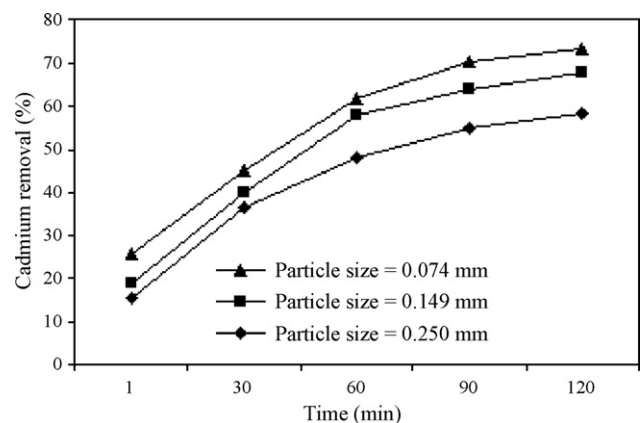**Fig. 5.** Effect of particle size on cadmium removal with 30 mg L^{-1} of initial metal concentration.

Table 2
Adsorption isotherms parameters.

Adsorbents	Langmuir isotherm parameters			Freundlich isotherm parameters		
	K_L	V_m (mg/g)	R^2	K_F	n (mg/g)	R^2
Unmodified carbon	0.005	207.3	0.91	0.463	170.2	0.83
Triton X-100-modified carbon	0.064	232.9	0.93	0.387	183.7	0.87
SDS-modified carbon	1.255	263.2	0.97	1.201	206.1	0.86
CTAB-modified carbon	2.004	279.5	0.98	0.873	209.2	0.91

the adsorption sites, preventing further removal of Cd(II) by adsorption.

3.5. Effect of adsorbent particle size

Three different particle sizes of untreated activated carbon i.e. 0.250, 0.149 and 0.074 mm were utilized under optimized conditions. After 120 min contact time, The sorption capacities were 58.3, 67.71 and 73.36% (initial metal concentration 30 mg L^{-1}, Fig. 5) and 50.18, 55.51 and 64.26% (initial metal concentration 45 mg L^{-1}, data not presented), respectively. Sorption is directly related to available surface area; hence the adsorbent with highest surface area i.e. 0.074 mm has depicted maximum removal percentage.

3.6. Effect of surfactant modification

The result of surfactant-treatment carried out on the adsorbents using 0.074 mm particle size is shown in Fig. 6. Cd(II) removal percentages of 98, 95.6, 81.5 and 73.4% were achieved by CTAB, SDS, Triton X-100-treated and untreated carbon adsorbent, respectively. All the surfactants have shown pronounced effect with regards to their efficiency in terms of percentage of Cd(II) removal. The maximum percentage of removal as exhibited by CTAB-treated activated carbon adsorbent correlates well with the finding discussed in Fig. 1 and Table 1. Monser et al. [23] have reported that by applying tetrabutyl ammonium iodide (TBA), or sodium diethyl dithiocarbamate (SDDC) onto an activated carbon, a substantial improvement in Cu(II), Zn(II) and Cr(VI) removal capacity can be achieved. The ability of surfactant to accelerate the removal efficiency of toxic, noble and rare metals has been attributed to the wetting characteristic and/or micellar solubilization [17]. Moreover, carbon surfaces have both negative (anionic) and positive (cationic) functional groups to attract free ions in solution or suspension. Apart from wetting and solubilization, cationic, zwitterionic and anionic surfactants are also capable of producing electrostatic charges on the surface of activated carbon and in turn creating more available active sites for adsorption. This explains why carbon adsorbents modified by CTAB

and SDS have higher removal percentage of Cd(II) than Triton X-100 modified-adsorbent. It was also observed that the sorption of cadmium was rapid with surfactant-modified carbon adsorbents with maximum removal achieved in 90 minutes as compared to 120 minutes with the unmodified carbon adsorbent. The high speed may be assisted by maximum penetration of adsorbate to mesopores and micropores because of the increased wettability and surface area of the surfactant-modified adsorbents [11].

3.7. Isotherms studies

Isotherm parameters for the Freundlich and Langmuir models for modified and unmodified carbon adsorbents are reported in Table 2. The correlation coefficients (R^2) values for Langmuir and Freundlich models are greater than 0.91 and 0.83, respectively. In general, the correlation coefficients of Langmuir isotherm are closer to 1 as compared to the Freundlich isotherm. Adsorption intensity ($1/n$) for the Freundlich isotherm further indicates that the model is not useful in representing the obtained data. Theoretical calculated values of the remaining concentrations of Cd(II) were found to have a close agreement with the experimentally-measured values (within ±5% difference) for the Langmuir isotherm as compared to the Freundlich (within ±21%). In this study, Langmuir model is therefore more suitable than the Freundlich model in describing the adsorption data. This reinforces the fact that Langmuir isotherm is useful to explain the adsorption from the solution on the current adsorbents when it follows the monolayer mode, rather than the multilayer mode. A basic assumption of the Langmuir theory is that the sorption takes place at specific homogenous sites on the adsorbent. When a site is occupied by an adsorbate, no further sorption can take place at the site. The suitability of Langmuir-type isotherm model in this adsorption studies, using surfactant-modified adsorbents, supports the evidence as shown in Fig. 1 that the treated surface is more homogenous and adsorption is accomplished via monolayer formation. CTAB-treated adsorbent is most suitable for the sorption of Cd(II) from aqueous solutions followed by SDS, Triton X-100 treated and unmodified carbon. The increase in the monolayer capacities of all the adsorbents after treatment with surfactants, indicate the superior homogeneity of the available surface area potentially due to the formation of a uniform microcrystalline layer of the surfactant molecules onto the adsorbent surface which in turn enhance the available surface areas, porosity and pore volumes.

4. Conclusion

This study presents the sorption of Cd(II) from aqueous solution using indigenously prepared and surfactant-modified carbon adsorbents from husk and pods of *M. oleifera*. Adsorption was found to be strongly dependent on pH, adsorbate, adsorbent dosage and contact time. A single step steam pyrolysis performed in this study proven to be an easy and economical method for the conversion of agricultural waste materials like pods and husk of *M. oleifera* into good quality micro-porous activated carbon. BET surface area,
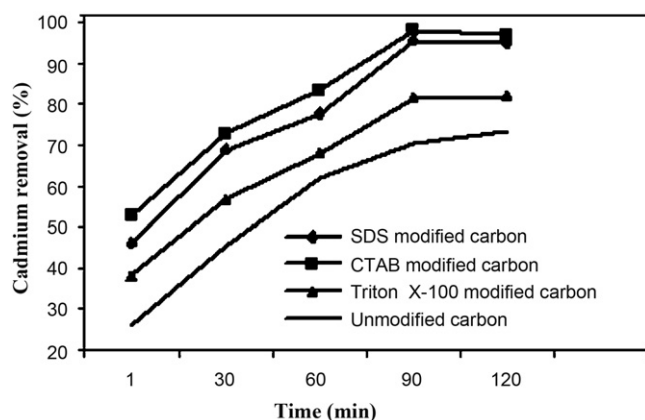

Fig. 6. Effect of surfactant modification on Cd(II) removal.

SEM images, porosity and porous area measurements showed that adsorption capacity can be significantly enhanced by modification with surfactants. This can be utilized as an efficient method for the removal of toxic, hazardous materials from industrial effluents and recovery of precious metals from industrial processes. It was further shown that the obtained experimental data is best described by the Langmuir isotherm, suggesting a monolayer mode of adsorption.

Acknowledgement

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