Evaluation of Efficiency of Thermally Treated and Sulphuric acid Activated *Sesamum Indicum* carbons for Cd(II) removal from Aqueous solution

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ABSTRACT

The efficiencies of activated carbons prepared from oil cake of Sesamum Indicum by thermal and sulphuric acid activation were investigated for the removal of Cd(II) ions from aqueous solutions. Various parameters as a function of contact time, initial pH, initial adsorbent dosage and metal ion concentrations were studied. The optimum time required for the maximum removal of Cd(II) was found to be 1 hr for TAGOC and 2 hrs for STGOC. The equilibrium adsorption data were fitted to Langmuir and Freundlich adsorption isotherm models. The equilibrium adsorption isotherms showed that activated carbon has high affinity and sorption capacity for Cd(II) with monolayer sorption capacities of 44.92 mg/g for TAGOC and 35.97 mg/g for STGOC. The kinetic study indicated that the pseudo-second order rate equation better described the adsorption process. The adsorbent efficiency was also tested for the removal of Cd(II), Cu(II), Ni(II) and Zn(II) from synthetic electroplating wastewater. The results indicated that the prepared both activated carbons are efficient (99.9%), alternative low-cost adsorbent for the removal of Cd(II) and other metal ions from wastewater.

Introduction

In water resources, the presence of heavy metal ions has become important concern due to its detrimental effects on human health and environment. Large volumes of waste generated from various industries are one of the main causes for the pollution of water and other environmental resources with heavy metals. Heavy metals are toxic pollutants and due to their non-biodegradability and persistence, they tend to accumulate in living organisms causing various diseases and disorders [1]. The efforts on reducing cadmium concentration in the industrial wastewaters are focussed by the toxic effects of cadmium on the aquatic world and the risk of contamination of water resources designated for human consumption. Phosphate fertilizers and sewage sludge, cigarette smoking and industrial uses of cadmium have been identified as a major cause of widespread dispersion of the metal at trace levels into the general environment and human food stuffs [2]. Cadmium can be accumulated in human body, causing erythrocyte destruction, nausea, salivation, diarrhoea and muscular cramps, renal degradation, chronic pulmonary problems and skeletal deformity [3]. According to U.S. Environmental Protection Agency (EPA) standards, the permissible limit of cadmium discharge in industrial effluents into water bodies is limited to 0.1 mg/l. Therefore, removal of heavy metal ions from water and wastewater is very important in terms of human health.

Various physical and chemical processes have been used for the removal of heavy metal ions from wastewaters. The most widely used methods which which include ion exchange, chemical precipitation, reverse osmosis, evaporation, and membrane filtration. Most of these methods suffer from some drawbacks such as incomplete removal of metal ions, high capital and operational cost and the further disposal of toxic sludge. Among various techniques, the adsorption processes used exclusively in water treatment and many studies has been carried out to find inexpensive and feasible adsorbent [4-6]. Many studies have been reported on the development of low cost activated carbon from cheaper and readily available materials. Activated carbons are excellent and versatile adsorbents with their high surface area, micro porous character and chemical nature of their surface have made them potential adsorbents for the removal of heavy metal ions from industrial wastewater[7].There are many studies in the literature regarding preparation of activated carbon from various biomaterials such as coconut shells[8] fruit stones[9], pyrolyzed coffee residues[10], pine bark[11], nutshells[12], and olive stones[13], peanut husks[14], sugarcane bagasse pith[15], black gram husk[16], maize cob husk[17], apricot stone[18] and their application for the removal of various heavy metal ions from water and wastewater.

In the present work, the removal of cadmium (II) ion from water and wastewater by using adsorbents produced from *Sesamum Indicum* oil cake by thermal and sulphuric acid activation was investigated. The adsorption capacities of adsorbents were studied using batch experiments. The influence of pH, contact time, metal ions and adsorbent concentrations were investigated. The experimental data obtained were evaluated and fitted using adsorbent equilibrium isotherms, and kinetic models.

Material and Methods

Preparation of thermally activated gingelly oil cake carbon (TAGOC)

20 g of washed and dried *Sesamum Indicum* (gingelly oil cake) was taken in a silica crucible and carbonized slowly in a muffle furnace at the temperature of 600 to 700 [0]C. At this temperature, oil cake catches fire and begins to char with evolution of fumes. As soon as the production of char was

complete (which is indicated by the absence of fumes), the furnace temperature was slowly raised to 800 - 850 ^{0}C for thermal activation under inert atmosphere of nitrogen for a period of 30 minutes. The physico-chemical analysis of the adsorbent was carried out as per standard procedures [19] and the characteristics are given in Table 1.

Preparation of sulphuric acid activated gingelly oil cake carbon (STGOC)

50 g of washed and dried *Sesamum Indicum* oil cake was mixed with 200 g (1:4 ratio, wt. basis) of concentrated sulphuric acid. The mixing was done by adding small quantities of oil cake to acid taken in 1000 mL beaker with vigorous stirring. Charring of the cake occurs immediately accompanied by evolution of fumes. When the reaction subsided, the mixture was left in air oven at 140-160 ^{0}C for a period of 24 h. The product was then washed with approximately 4.0 - 4.5 L of distilled water to remove free sulphuric acid and dried at 110 ^{0}C. The material was sieved (80–120 ASTM size) and used for adsorption experiments. The physico-chemical analysis of the STGOC was carried out as per standard procedures [19] and the characteristics are given in Table 1.

Preparation stock solution

All chemicals and reagents used for experiments and analysis were of analytical grade. Stock solution of 1000 mg/L of Cd(II) was prepared from 3 CdSO$_4$.8H$_2$O (S.D. Fine, Mumbai, India) in double distilled water. The solution was diluted as required to obtain the working solution. The initial pH of the working solution was adjusted using 0.1 N HNO$_3$ or 0.1 N NaOH solutions. Fresh dilutions were used for each study.

Adsorption studies

Batch adsorption experiments were performed by mixing known weight of adsorbent and 100 mL of Cd(II) ion solution of known concentration adjusted to a known pH. The mixture was taken in a polythene bottle of 300 mL capacity and shaken in a mechanical shaker (200 rpm) for a predetermined period at 30 ± 1 ^{0}C. Then the equilibrated solutions were centrifuged and the concentration of Cd(II) ions in the supernatant solution was measured by Atomic Absorption Spectrophotometer. Adsorption isotherm and kinetic studies were carried out with different initial concentrations of Cd(II) ions by maintaining the adsorbent dosage at constant level. Adsorption capacities were calculated from the difference in the metal ion concentration in the aqueous phase before and after the experiment according to the following equation:

$$q_e = \frac{v(C_0 - C_e)}{m} \tag{1}$$

where q$_e$, adsorption capacity per unit mass of adsorbent (mg/g); C$_0$, initial concentration of Cd(II) in the aqueous solution (mg/L); C$_e$ is the final equilibrium concentration of test solution (mg/L); m, mass of adsorbent (g); and v, volume of sample (L).

Results and Discussion

Effect of contact time

Contact time is an important parameter for successful use of adsorbents for practical applications [20]. Effect of contact time on the adsorption of Cd(II) by TAGOC and STGOC was studied in the range of 30 to 240 min and the results are shown in Figure 1. It could be seen that the removal of Cd(II) increases with increase in contact time and attains equilibrium at 60 min for TAGOC and 120 min for STGOC. Basically the removal rate of adsorbate is rapid, but it gradually decreases with time until it reaches equilibrium. The rate in percent of metal removal is

higher in the beginning due to the larger surface area of the adsorbent being available for the adsorption of The removal efficiencies of TAGOC and STGOC were found to be 99.9 % for an initial concentration of 10 mg/L of Cd(II). Therefore, optimum contact time was selected as 60 min for TAGOC and 120 min for STGOC further experiments.
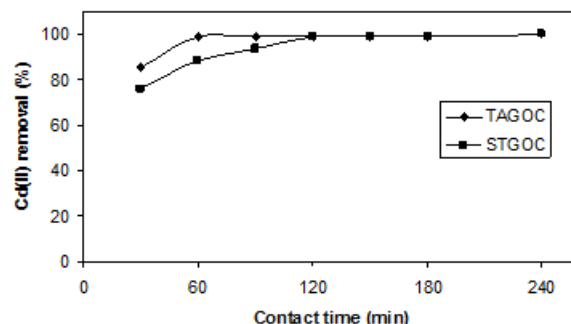

Figure 1. Effect of contact time [Cd(II) concentration .10mg/L, adsorbent dose: 100mg/100mL for TAGOC, 200mg/100mL for STGOC, pH : 5.0 ± 0.1]

Effect of pH

The pH of the aqueous solution is an important controlling parameter in the heavy metal ions adsorption process [21]. Moreover, due to the different functional groups on the adsorbent surface, this became active sites for the metal binding at a specific pH. The effect of pH on percentage removal of Cd(II) for pH ranging between 1 to 10 is shown in Figure 2. It could be seen that 99.9 % removal of Cd(II) was achieved by the adsorbents over the pH range of 5.0 – 8.0 for both TAGOC and STGOC. It is evident from Figure 2, the adsorption of efficiency of Cd(II) increased with increasing the pH of the medium until reaching to the optimum pH range.
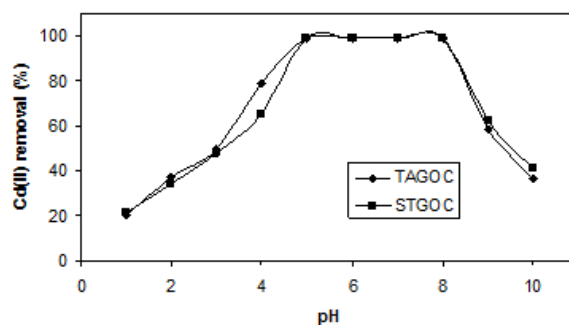

Figure 2. Effect of pH [Cd(II) concentration. 10mg/L, equilibrated time. 1 hr for TAGOC and 2 hrs for STGOC, adsorbent dose. 100mg/100mL for TAGOC, 200mg/100mL for STGOC]

At lower pH values (2-4), H$_3$O$^+$ ions compete with Cd^{2+} ions for exchange sites in the adsorbent. Cd^{2+} uptake was decreased because the surface area of the adsorbent was more protonated. Competitive adsorption occurred between H$^+$ protons and free Cd^{2+} ions and therefore decrease in Cd(II) adsorption. When the pH value increased (5-8), adsorbent surfaces were more negatively charged and functional groups of the adsorbent more deprotonated which results higher attraction of Cd(II) ions. The reduction in Cd(II) removal beyond pH 8.0the8.0 and more basic pH conditions, may suggest the possibility of Cd(OH)$_2$ precipitates occupying the adsorption sites and preventing further removal of Cd(II)[21]. Further experiments were carried out at pH 5.0.

Effect of adsorbent dose

Adsorbent dosage is an important parameter because it determines the capacity of an adsorbent for a given concentration of the adsorbate [22]. The influence of TAGOC and STGOC dosage on the removal of Cd(II) ion is shown in Figure 3. Cd(II) removal increases with increasing the adsorbent dosage. The removal efficiency was found to be 99.9 % at an adsorbent dose of 100 mg of TAGOC and 200 mg of STGOC for the initial concentration of 10 mg/L. The results showed that the adsorption increases with the increase in the dose of adsorbent. This is because of the availability of more binding sites on the surface at higher concentration of the adsorbent for complexation of metal ions.
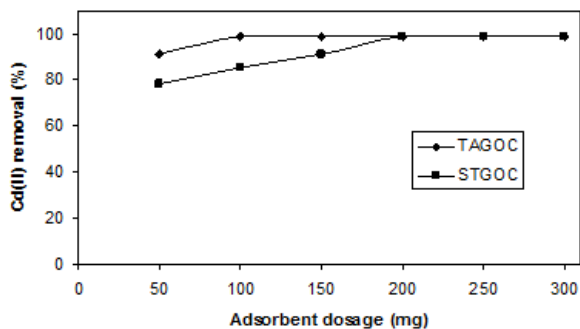

Figure 3. Effect of adsorbent dose [Cd(II) concentration .10mg/L, equilibrated time: 1 hr for TAGOC and 2 hrs for STGOC, pH . 5.0±0.1]

Effect of initial Cd(II) concentration

The removal of Cd(II) ions was carried out at different initial Cd(II) ion concentrations ranging from 10 to 60 mg/L at pH 5.0. The results are presented in Figure 4.
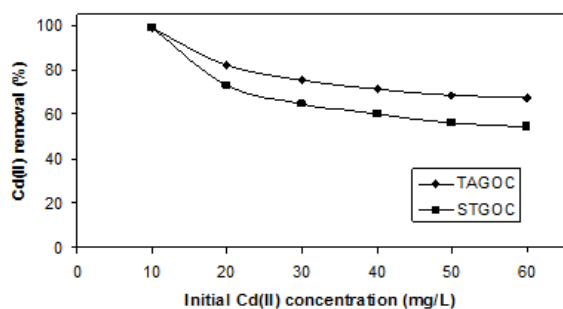

Figure 4. Effect of initial Cd(II) concentration [equilibrated time : 1 hr for TAGOC and 2 hrs for STGOC, pH : 5, adsorbent dose: 100mg/100mL for TAGOC, 200mg/100mL for STGOC,]

Cd(II) removal percentage increases when the initial Cd(II) ion concentration decreases for both adsorbents. At low Cd(II) concentration the surface active sites to the total metal ions in the solution is high and hence all the Cd(II) ions may interact with the binding sites of the adsorbent and may be removed from the solution. However, the amount of Cd(II) adsorbed per unit weight of adsorbent (q_e) is higher at high concentration.

Adsorption isotherms

An adsorption isotherm is characterized by certain constant values, which express the surface properties and affinity of the adsorbent. It can also be used to compare the adsorptive capacities of the adsorbent for different pollutants [23]. The Langmuir and Freundlich models are the most frequently employed models. In this work, both models were used to describe the relationship between the amount of Cd(II) ions adsorbed and its equilibrium concentration in solution at room temperature for 24 h.

Langmuir isotherm

The main assumption of the Langmuir method is that adsorption occurs uniformly on the active part of the surface, and when a molecule is adsorbed on an active site, the other molecules could not be interacted with this active [24].

The linear form of Langmuir equation may be written as

$$\frac{C_e}{q_e} = \frac{1}{q_0 b} + \frac{C_e}{q_0} \qquad (2)$$

where q_e is the amount of solute adsorbed per unit weight of adsorbent (mg/g) and C_e is the equilibrium concentration of solute in the bulk solution (mg/L) while q_0 is the monolayer adsorption capacity (mg/g) and b is the constant related to the free energy of adsorption (L/mg). A linear plot of C_e/q_e versus C_e exhibits that the adsorption obeys the Langmuir isotherm and values of Langmuir constants (q_0 and b) calculated from the slope and the intercept (Figure 5) are presented in Table 2.
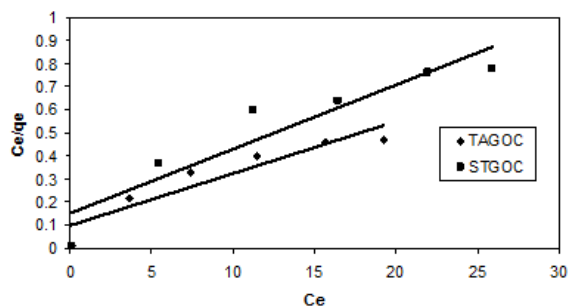

Figure 5. Langmuir adsorption isotherm [Temperature .30±1°C, Cd(II) concentration. (10-60mg/L), equilibration time. 24h, pH. 5.0 ± 0.1, adsorbent dose. 100mg/100mL for TAGOC, 200mg/100mL for STGOC,]

The essential characteristics of the Langmuir isotherm can also be expressed in terms of a dimensionless constant of separation factor or equilibrium parameter, R_L, which is defined as[25]

$$R_L = \frac{1}{1 + b\, C_0} \qquad (3)$$

where b is the Langmuir constant and C_0 is the initial concentration of Cd(II) ion. Separation factor shows the nature of adsorption process and its value indicates the sorption process could be favourable, linear and unfavourable when $0 < R_L < 1$, $R_L = 1$, $R_L > 1$, respectively. The R_L values at different concentrations were found be in the range of 0 to 1 indicated a highly favourable adsorption of Cd(II) ions onto TAGOC and STGOC.

Freundlich isotherm: It is an empirical expression that takes into account the heterogeneity of the surface and multilayer adsorption to the binding sites located on the surface of the sorbent [26]. The logarithmic form of Freundlich model is expressed as follows

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \qquad (4)$$

where C_e is the equilibrium concentration (mg/L) and q_e is the amount of metal ion adsorbed per unit weight of adsorbent (mg/g). The K_F is Freundlich constant related to the adsorption capacity (mg/g) and n shows the adsorption intensity (L/mg). The linear plot of log q_e versus log C_e (Figure 6) exhibits that the

adsorption obeys the Freundlich isotherm and value of Freundlich constants (K_F and $1/n$) calculated from the intercept and slope of the plot are presented in Table 2. The adsorption intensity $1/n$ value was found to be between zero and one which indicate the favourable adsorption of Cd(II) ions onto surface of TAGOC and STGOC.
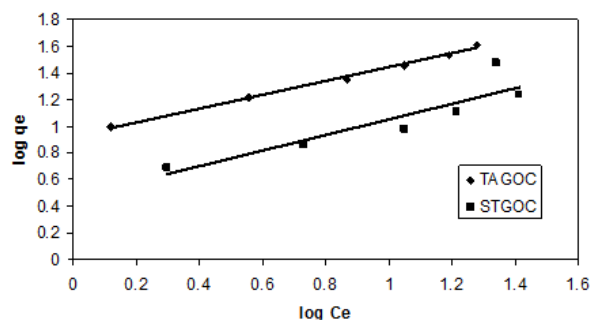

Figure 6. Freundlich adsorption isotherm [Temperature: 30±1°C, Cd(II) concentration: (10-60mg/L), equilibration time. 24h, pH . 5.0 ± 0.1, adsorbent dose. 100mg/100mL for TAGOC, 200mg/100mL for STGOC]

The correlation coefficient (R^2) values of Freundlich model are found to be higher than Langmuir model and closer to unity for both TAGOC and STGOC. These results indicated that the Langmuir model is not able to describe adequately the relationship between the amounts of cadmium(II) ions adsorbed and their equilibrium concentration in the solution. Therefore, it could be concluded that the Freundlich isotherm model was found to be a best fit with the equilibrium data since R^2 values were closer to unity.

Kinetic studies

The study of adsorption kinetics is significant as it provides valuable insights into the reaction pathways and the mechanism of the reactions. Several kinetic models are used to explain the mechanism of the adsorption processes. Two well known kinetic models were applied for this study name pseudo-first-order and pseudo-second-order. A simple pseudo-first order equation was given by Lagergren equation [27]

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303}$$

(5)

where q_e and q_t are the amounts of Cd(II) adsorbed (mg/g) at equilibrium time and any time t, respectively, while k_1 is the rate constant of adsorption (min^{-1}). Plot of $\log(q_e - q_t)$ versus t gives a straight line for first order adsorption kinetics (Figure 7) which allows calculation of the rate constant k_1 and its values are given in Table 3.
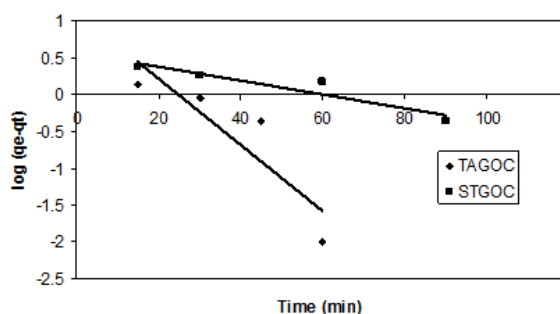

Figure 7. Pseudo-first order kinetic plot for adsorption of cadmium(II) [Temperature: 30±1°C, pH . 5.0 ± 0.1, adsorbent dose. 100 mg/100mL for TAGOC, 200 mg/100mL for STGOC,]

On the other hand, the pseudo-second order equation based on equilibrium adsorption is expressed as [28]

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$$

(6)

where k_2 is the pseudo-second order rate constant (mg g^{-1} min^{-1}), q_e and q_t represent the amount of Cd(II) adsorbed (mg/g) at equilibrium and at any time. The plot of (t/q_t) versus t produces straight line with slope of $1/q_e$ and intercept of $1/k_2 q_e^2$. It indicated the applicability of pseudo-second-order model (Figure 8). The overall rate constants k_2 and other constants of pseudo-second-order kinetics are given in Table 3. The correlation coefficients value (R^2) was also calculated and presented in Table 3.
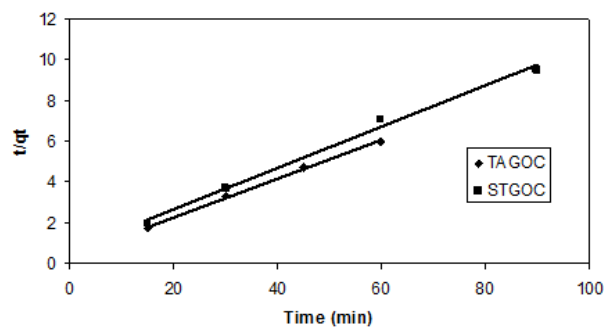

Figure 8. Pseudo-second order kinetic plot for adsorption of Cd(II) [Temperature: 30±1°C, pH . 5.0±0.1, adsorbent dose. 100mg/100mL for TAGOC, 200 mg/100mL for STGOC]

In order to compare the applicability of kinetic models in fitting to data, the percent relative deviation (P) was calculated using the experimental data as given by the following equation [29]

$$P = \frac{100}{N} \left\{ \sum \frac{q_{e(exp)} - q_{e(theo)}}{q_{e(exp)}} \right\}$$

(7)

where $q_{e(exp)}$ is the experimental value of q_e at any value of C_e, $q_{e(theo)}$ the corresponding theoretical value of q_e and N is the number of observations. It is found that lower the value of percentage deviation (P), better is the fit. It is generally accepted that when P value is less than 5, the fit is considered to be excellent[29]. The results were analyzed using equations 5 and 6. The experimental data fitted well in both equations. The values of $q_{e(theo)}$ calculated from these models are compared with experimental values $q_{e(exp)}$ and shown in Table 3. It is found that values of $q_{e(theo)}$ calculated from the pseudo-first-order kinetic model differed appreciably from the experimental values $q_{e(exp)}$. The percent deviation (P) is also very high. On the other hand, values of $q_{e(theo)}$ are found to be very close to $q_{e(exp)}$ when pseudo-second-order rate equation was applied. The percent deviation (P) is well with in the range and values of correlation coefficients (R^2) are very high for pseudo-second-order when compared with pseudo-first-order kinetics. These results indicated that the adsorption of Cd(II) ions onto TAGOC and STGOC was governed mainly by pseudo-second-order kinetics. Thus, it could be inferred that the loading of Cd(II) onto adsorbents appeared to occur by chemical interactions involving valence forces due to sharing or exchange of electrons between Cd(II) and adsorbents [30].

Table 1. Characteristics of adsorbents

Parameter	TAGOC	STGOC
Pore volume ($cm^3 g^{-1}$)	0.04	0.02
BET surface area ($m^2 g^{-1}$)	54.3	36.78
Bulk density ($g cm^{-3}$)	0.84	0.79
pH	11.3	3.7
Matter soluble in water (%)	7.1	0.84
Matter soluble in acid (%)	44.1	4.90
Average pore size (A^0)	117.34	89.56
Decolorizing power ($mg g^{-1}$)	30.0	33.1
Iron content (%)	0.62	0.28
Phenol number	62.0	57.00
Proximate analysis		
Moisture (%)	3.21	2.20
Ash (%)	34.91	4.75
Fixed carbon (%)	46.15	51.75
Volatile matter (%)	18.91	41.30
Elemental analysis		
Carbon (%)	46.90	53.42
Sulphur (%)	1.01	3.26
Nitrogen (%)	0.94	2.72
Oxygen (%)	13.35	15.59

Table 2. Langmuir and Freundlich constants for Cd(II) removal

Adsorbent	Langmuir Model			Freundlich Model		
	q_o (mg/g)	b (L/mg)	R^2	K_F (mg/g)	1/n (L/mg)	R^2
TAGOC	44.92	0.2270	0.874	8.40	0.515	0.994
STGOC	35.97	0.1852	0.847	3.63	0.590	0.932

Table 3. Pseudo – first order and pseudo- second order kinetic constants for the adsorption of cadmium(II)

Adsorbent	Conc. (mg/L)	Expt.q_e (mg/g)	Pseudo-first-order kinetics				Pseudo-second -order kinetics			
			K_1 (1/min)	$q_{e(theo)}$ (mg/g)	R^2	P	K_2 (mg g^{-1} min^{-1})	$q_{e(theo)}$ (mg/g)	R^2	P
TAGOC	10	9.90	0.0168	2.63	0.832	73.43	0.0246	10.20	0.998	3.03
STGOC	10	9.82	0.0940	5.23	0.887	46.74	0.0152	9.92	0.992	1.01

Table 4. Characteristics of electroplating wastewater (synthetic)

	Parameter	Before treatment (mg/L)	After treatment (mg/L)	Removal (%)
TAGOC	Copper(II)	15	14.82	98.8
	Nickel(II)	30	29.71	99.0
	Cadmium(II)	5	4.99	99.8
	Zinc(II)	20	19.88	99.4
STGOC	Copper(II)	15	14.66	97.4
	Nickel(II)	30	29.55	98.5
	Cadmium(II)	5	4.99	99.8
	Zinc(II)	20	19.86	99.3

Thermodynamic studies

The free energy of adsorption (ΔG^0) can be related with the equilibrium constant K (L/mol), corresponding to the reciprocal of the Langmuir constant, b, by the following equation [31-33]

$$\Delta G^0 = -RT \ln b \qquad (8)$$

where R is the universal gas constant (8.314 J/ mol K) and T is the absolute temperature (K). Gibbs free energy changes (ΔG^0) were calculated to be -25.56 kJ/mol for TAGOC and -25.04 kJ/mol for STGOC. Negative values of ΔG^0 indicated the feasibility and spontaneous nature of the adsorption.

Desorption studies

Desorption studies were conducted to recover Cd(II) and regenerate the adsorbent using 0.01 – 0.25 N HNO_3. Results showed that 99% of Cd(II) could be desorbed under optimum concentration of 0.10 N of HNO_3 for TAGOC and 0.15 N of HNO_3 for STGOC. After the desorption of Cd(II), these sorbents were washed thoroughly with distilled water. The adsorption capacities of these sorbents were again tested and five cycles of consecutive sorption-desorption operations were carried out. Results indicated that the adsorption capacity of HNO_3 regenerated TAGOC was decreasing in the range of 99.9 – 28.3% and 99.9 – 55.3% for STGOC. Results indicated that 0.10 N and 0.15 N HNO_3 are suitable for regeneration of TAGOC and STGOC respectively.

Application to wastewater treatment

Experiments were conducted to determine the efficiency of TAGOC and STGOC with respect to treatment of electroplating wastewater (synthetic) [34]. Characteristics of electroplating wastewater before and after treatment are presented in Table 4. Experiments were carried out with 100 mL of cadmium(II) wastewater solution at pH 5.0 in the presence of varying amounts of TAGOC ranging from 100-1000 mg/100 mL and 100-1700 mg/100 mL for STGOC (Figure 9).
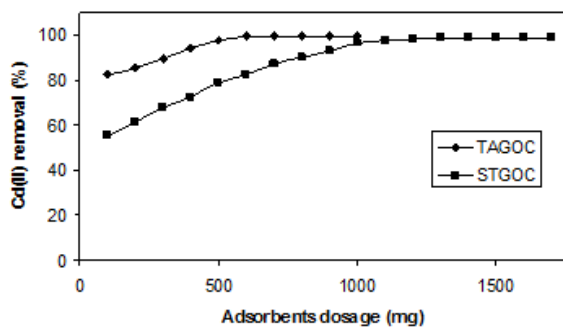

Figure 9. Effect of adsorbent on removal of metal ions from electroplating wastewater [Temperature. 30±1°C, equilibrated time. 1 hr for TAGOC and 2 hrs for STGOC, pH . 5.0±0.1]

Optimum TAGOC dosage was found to be 600 mg/100 mL for the maximum removal (99.8%) of Cd(II) from the wastewater and optimum STGOC dosage was found to be 1300 mg/100 mL for the maximum removal (99.8%). In addition to the removal of Cd(II) ions, the TAGOC and STGOC were able to effectively decrease the concentration of Cu(II), Ni(II) and Zn(II) in the wastewater. Therefore, it could clearly be established that both TAGOC and STGOC can be considered as the effective and alternative adsorbents for the treatment of wastewater containing Cd(II) ions.

Conclusion

The presented study indicated the efficiency of activated carbons such as TAGOC and STGOC obtained from oil cake of *Sesamum Indicum* for the removal of Cd(II) from aqueous solution. The operating parameters such as, contact time, pH,

adsorbent dosage and initial Cd(II) concentration were effective on the adsorption efficiency of Cd(II) ions. Experimental results are good agreement with Freundlich isotherm model and have shown a better fitting to the experimental data. In terms of contact time, adsorbent dosage and adsorption capacity, TAGOC is found to be better adsorbent than STGOC. The kinetics of Cd(II) adsorption onto TAGOC and STGOC were found to follow more reliably pseudo second order kinetics. Negative Gibbs free energy value (ΔG^0) indicated the feasibility and spontaneous nature of the process. Desorption of Cd(II) was effectively be achieved with 0.10 N and 0.15 N HNO_3 from the TAGOC and STGOC respectively. Experiments with wastewater clearly indicated that both TAGOC and SGTGOC are effective adsorbents for the removal of higher concentrations of Cd(II) and other metal ions from wastewater. Based on results, it could be concluded that TAGOC and STGOC can be used as potential adsorbents to treatment of wastewater containing Cd(II) ions since it is efficient, low cost and locally available.

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