



Equilibrium and Kinetic Studies on removal of Cd(II) from Aqueous Solutions by Sulphuric Acid Activated *Sesamum Indicum* Carbon

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Abstract

Activated carbon prepared from oil cake of *Sesamum Indicum* by sulphuric acid treatment was used as adsorbent 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 equilibrium adsorption data were fitted to Langmuir and Freundlich adsorption isotherm models. The equilibrium adsorption isotherms confirmed that activated carbon has high affinity and sorption capacity for Cd(II) with monolayer sorption capacities of 35.32 mg/g. The kinetic study indicated that the pseudo-second order rate equation better described the adsorption process. The adsorbents were also tested for the removal of cadmium (II) from synthetic electroplating wastewater. The results indicated that the prepared activated carbon is an efficient (99.9%), alternative low-cost adsorbent for the removal of cadmium(II) from aqueous solutions.

Keywords: Cd(II) removal, activated carbon, isotherms, kinetics, wastewater.

Introduction

Water resources are being contaminated by heavy metal ions released from various industries. Large volumes of waste generated from a variety of industries are one of the main reasons for the contamination of water and other environmental resources with heavy metals. Heavy metals are harmful pollutants and due to their non-biodegradability and persistence, which is able to accumulate in living organisms causing various diseases and disorders¹. 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 known as a major cause of widespread distribution of the metal at trace levels into the general environment and human foodstuffs². Cadmium can be accumulated in human body, causing erythrocyte destruction, nausea, salivation, diarrhoea and muscular cramps, renal degradation, chronic pulmonary problems and skeletal deformity³. 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 significant in terms of human health.

Various physical and chemical methods have been used for the removal of heavy metal ions from wastewaters. The most widely used methods which comprise ion exchange, chemical

precipitation, reverse osmosis, evaporation, and membrane filtration. Most of these methods suffer from some disadvantages such as deficient 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 economical and viable adsorbent⁴⁻⁶. Many studies have been reported on the increase of low cost activated carbons from cheaper and easily 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 wastewater⁷. There are many studies in the literature regarding preparation of activated carbons from various biomaterials such as coconut shells⁸ fruit stones⁹, pyrolyzed coffee residues¹⁰, pine bark¹¹, neem leaf¹², and olive stones¹³, peanut husks¹⁴, almond tree leaves¹⁵, black gram husk¹⁶, maize cob husk¹⁷, apricot stone¹⁸ 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 activated carbon produced from *Sesamum Indicum* oil cake by sulphuric acid treatment was investigated. The adsorption capacity of adsorbent was investigated 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 activated carbon: 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 °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 °C. The material was sieved (80-120 ASTM size) and used for adsorption experiments. The activated carbon after sulphuric acid treatment was indicated as STGOC. The characteristics of STGOC are given in table-1.

Table -1
Characteristics of adsorbent

| Parameter | STGOC |
|--|-------|
| Pore volume (cm ³ g ⁻¹) | 0.02 |
| BET surface area (m ² g ⁻¹) | 36.78 |
| Bulk density (g cm ⁻³) | 0.79 |
| pH | 3.7 |
| Matter soluble in water (%) | 0.84 |
| Matter soluble in acid (%) | 4.90 |
| Average pore size (Å ⁰) | 89.56 |
| Decolorizing power (mg g ⁻¹) | 33.1 |
| Ion-exchange capacity (m equiv/g) | 0.72 |
| Iron content (%) | 0.28 |
| Phenol number | 57.00 |
| Proximate analysis | |
| Moisture (%) | 2.20 |
| Ash (%) | 4.75 |
| Fixed carbon (%) | 51.75 |
| Volatile matter (%) | 41.30 |
| Elemental analysis | |
| Carbon (%) | 53.42 |
| Sulphur (%) | 3.26 |
| Nitrogen (%) | 2.72 |
| Oxygen (%) | 15.59 |

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 CdSO₄.8H₂O (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 HNO₃ or 0.1 N NaOH solutions. Fresh dilutions were used for each study.

Adsorption studies: Batch mode adsorption experiments were executed 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°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:

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

where q_e, adsorption capacity per unit mass of adsorbent (mg/g); C₀, 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 a significant factor for the successful use of adsorbents for practical applications²⁰. Effect of contact time on the adsorption of Cd(II) by 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 120 min. 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 metals. The removal efficiency was found to be 99.9 % for an initial concentration of 10 mg/L of Cd(II). Therefore, optimum contact time was selected as 120 min for further experiments.

Effect of pH: The pH of the aqueous solution is a central controlling parameter in the heavy metal ions adsorption process²¹. 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 adsorbent over the pH range of 5.0 – 8.0. 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.

At lower pH values (2-4), H₃O⁺ ions compete with Cd²⁺ ions for exchange sites in the adsorbent. Cd²⁺ uptake was decreased because the surface area of the adsorbent was more protonated. Competitive adsorption occurred between H⁺ protons and free Cd²⁺ 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

decrease in Cd(II) removal beyond pH 8.0 and more basic pH conditions, may suggest the possibility of Cd(OH)₂ precipitates reside in the adsorption sites and prevent further removal of Cd(II)²¹. Further experiments were carried out at pH 5.0.

Effect of adsorbent dose: Adsorbent dosage is an important factor because it determines the capacity of an adsorbent for a given concentration of the adsorbate²². The influence of 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 200 mg for an 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 presence of more binding sites on the surface at higher concentration of the adsorbent for binding of metal ions.

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. Cd(II) removal percentage increases when the initial Cd(II) ion concentration decreases. 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: Adsorption isotherm is considered by certain constant values, which states the surface properties and attraction of the adsorbent. It can also be used to compare the adsorptive ability of the adsorbent for different pollutants²³. 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 postulation of the Langmuir method is that adsorption occurs regularly 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 active²⁴.

The linear form of Langmuir equation may be written as

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

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 q₀ 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 (q₀ and b) calculated from the slope and the intercept (figure-5) are presented in table-2.

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

| Metal ion | Langmuir Model | | | Freundlich Model | | |
|-----------|--------------------------|-------------|----------------|--------------------------|---------------|----------------|
| | q ₀ (mg/g) | b (L/mg) | R ² | K _F (mg/g) | 1/n (L/mg) | R ² |
| Cd(II) | 35.32 | 0.1852 | 0.8872 | 3.63 | 0.5907 | 0.8282 |

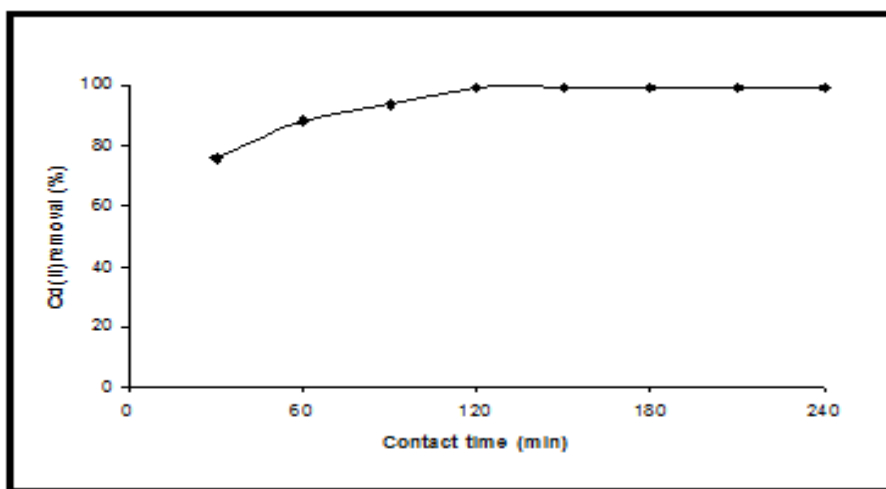


Figure-1
 Effect of contact time [Cd(II) concentration : 10mg/L, adsorbent dose: 200mg/100mL, pH : 5.0 ± 0.1]

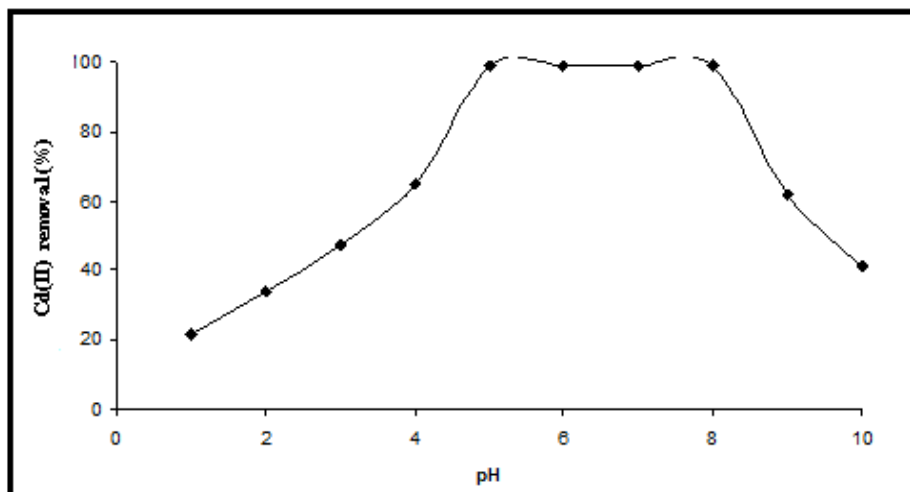


Figure-2

Effect of pH [Cd(II) concentration : 10mg/L, equilibrated time : 2 hrs, adsorbent dose : 200 mg/100mL]

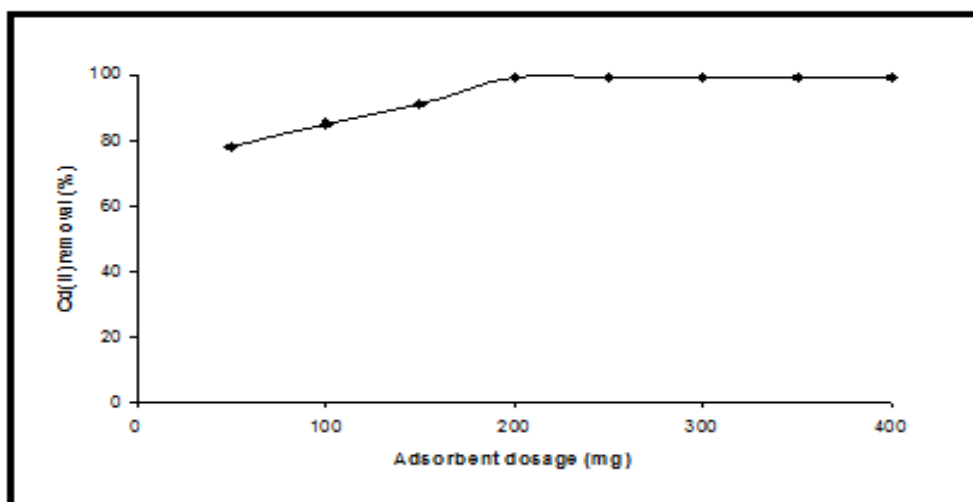


Figure-3

Effect of adsorbent dose [Cd(II) concentration : 10mg/L, equilibrated time:2 hrs, pH : 5.0±0.1]

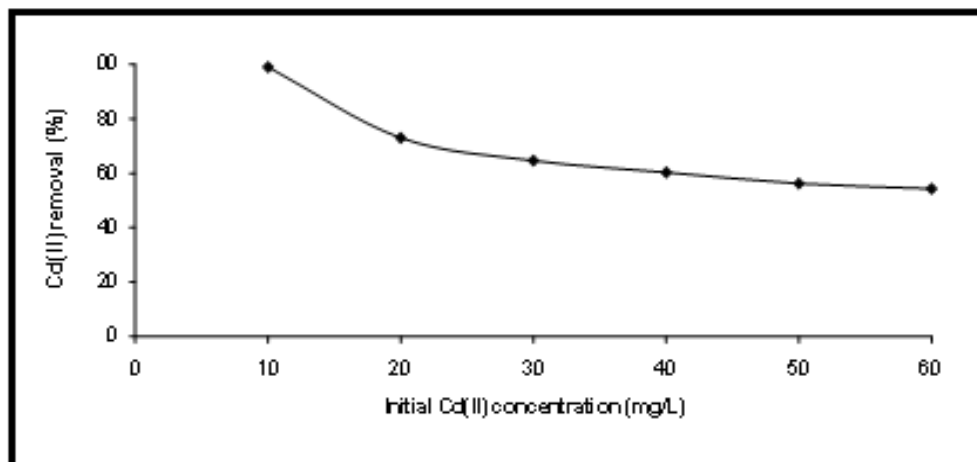


Figure-4

Effect of initial Cd(II) concentration [Equilibrated time : 2 hrs, pH : 5, adsorbent dosage : 200 mg/100 mL]

The vital characteristics of the Langmuir isotherm can also be articulated in terms of a dimensionless constant of separation factor or equilibrium parameter, R_L , which is defined as²⁵:

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

where b is the Langmuir constant and C_0 is the initial concentration of Cd(II) ion. Separation factor demonstrate 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 adsorbent.

Freundlich isotherm: It is an experimental expression that takes into account the heterogeneity of the surface and multilayer adsorption to the binding sites located on the surface of the sorbent²⁶. The logarithmic form of Freundlich model is expressed as follows

$$\log x/m = \log K_F + 1/n \log C_e \quad (4)$$

where C_e is the equilibrium concentration (mg/L) and x/m 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 adsorbent.

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

Kinetic studies: Adsorption kinetics is important as it gives 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 used for this study name pseudo-first-order and pseudo-second-order. A simple pseudo-first order equation was given by Lagergren equation²⁷

$$\log (q_e - q_t) = \log q_e - k_1 t / 2.303 \quad (5)$$

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.

The pseudo-second order equation based on equilibrium adsorption is expressed as²⁸

$$t/q_t = 1/k_2 q_e^2 + t/q_e \quad (6)$$

where k_2 is the pseudo-second order rate constant ($\text{mg g}^{-1} \text{min}^{-1}$), 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.

In order to evaluate 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 equation²⁹

$$P = \frac{100}{N} \left\{ \sum \frac{q_e(\text{exp}) - q_e(\text{theo})}{q_e(\text{exp})} \right\} \quad (7)$$

where $q_{e(\text{exp})}$ is the experimental value of q_e at any value of C_e , $q_{e(\text{theo})}$ the corresponding theoretical value of q_e and N is the number of observations. It is identified 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 excellent²⁹. The results were analyzed using equations 5 and 6. The experimental data fitted well in both equations. The values of $q_{e(\text{theo})}$ calculated from these models are compared with experimental values $q_{e(\text{exp})}$ and shown in table-3. It is found that values of $q_{e(\text{theo})}$ calculated from the pseudo-first-order kinetic model differed appreciably from the experimental values $q_{e(\text{exp})}$. The percent deviation (P) is also very high. On the other hand, values of $q_{e(\text{theo})}$ are found to be very close to $q_{e(\text{exp})}$ 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 STGOC was governed mainly by pseudo-second-order kinetics. Thus, it could be inferred that the binding of Cd(II) onto modified STGOC appeared to occur by chemical interactions relating valence forces due to sharing or exchange of electrons between Cd(II) and STGOC³⁰.

Thermodynamic studies: The free energy of adsorption (ΔG^0) can be connected with the equilibrium constant K (L/mol), corresponding to the reciprocal of the Langmuir constant, b , by the following equation³¹⁻³³.

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

where R is the universal gas constant (8.314 J/ mol K) and T is the absolute temperature (K). Gibbs free energy change (ΔG^0) was calculated to be -25.04 kJ/mol for Cd(II). Negative value of ΔG^0 designated the feasibility and spontaneous nature of the adsorption.

Desorption studies: It was performed to recover Cd(II) and regenerate the adsorbent using 0.01 – 0.25 N HNO_3 . Results showed that 97% of Cd(II) could be desorbed from STGOC under optimum concentration of 0.15 N. 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 successive sorption-desorption operations were carried out. Results indicated that the adsorption capacity of HNO_3 regenerated STGOC was decreasing in the range of 99.9 – 55.8 %. Results indicated that 0.15 N HNO_3 is suitable for regeneration of adsorbent.

Application to wastewater treatment: Experiments were carried out to determine the effectiveness of 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 STGOC ranging from 100-1700 mg/100 mL and the results are presented in figure-9. Optimum dosage was found to be 1300 mg/100 mL for the maximum removal (99.8%) of Cd(II) from the wastewater. In addition to the removal of Cd(II) ions, the STGOC was able to effectively decrease the concentration of other metal ions in the wastewater. Therefore, it could clearly be recognized that the STGOC can be considered as an effective and alternative adsorbent for the treatment of wastewater containing Cd(II) ions.

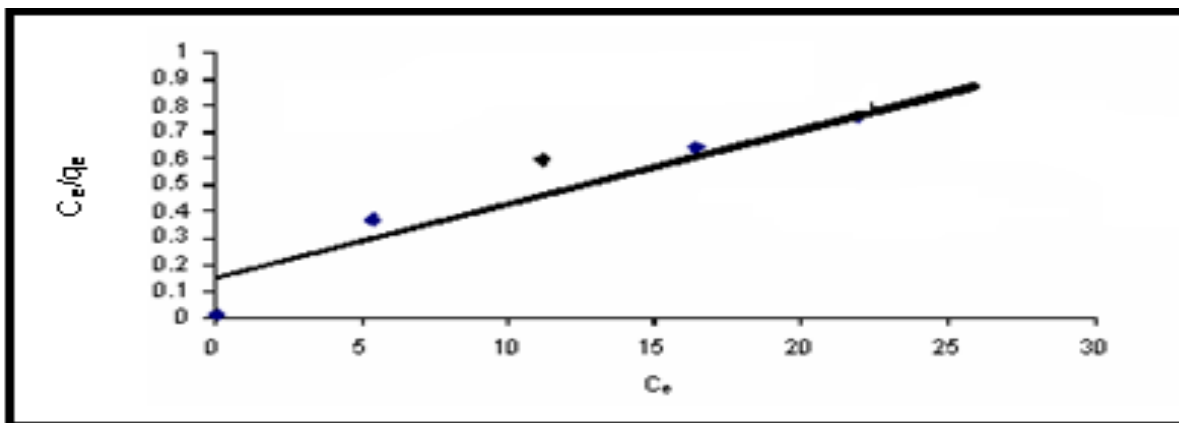


Figure-5
 Langmuir adsorption isotherm

[Temperature : $30 \pm 1^\circ C$, metal ion concentration : (10-60mg/L), equilibration time : 24h, pH : 5.0 ± 0.1 , adsorbent dose: 200mg/100mL]

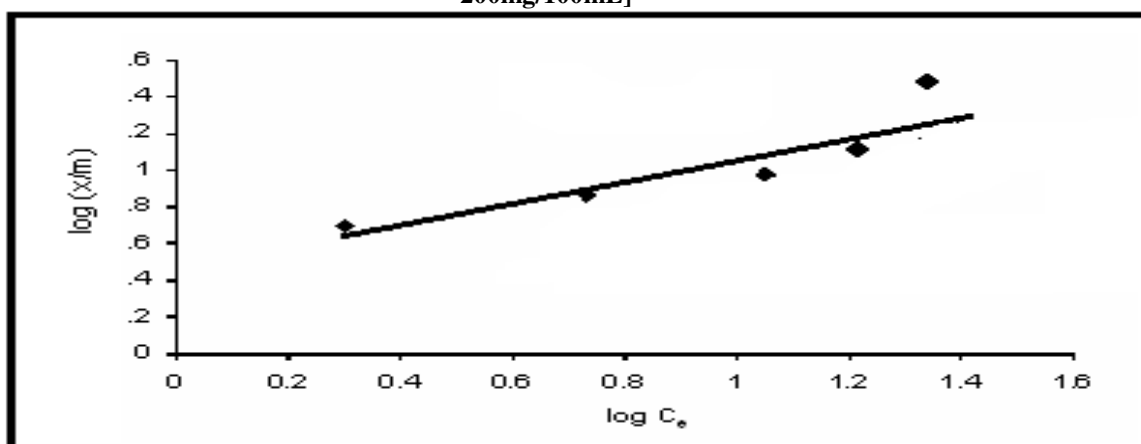


Figure-6
 Freundlich adsorption isotherm

[Temperature: $30 \pm 1^\circ C$, metal ion concentration: (10-60mg/L), equilibration time:24h, pH : 5.0 ± 0.1 , adsorbent dose : 200mg/100mL]

Table -3

Pseudo – first order and pseudo- second order kinetic constants for the adsorption of cadmium(II) onto STGOC

| 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 |
| 3 | 2.98 | 0.0263 | 1.52 | 0.901 | 48.99 | 0.0506 | 3.05 | 0.998 | 2.29 |
| 5 | 4.95 | 0.0232 | 2.00 | 0.956 | 59.59 | 0.0353 | 5.03 | 0.999 | 1.61 |
| 7 | 6.89 | 0.0162 | 3.76 | 0.811 | 45.42 | 0.0268 | 7.07 | 0.996 | 2.61 |
| 10 | 9.82 | 0.094 | 5.23 | 0.887 | 46.74 | 0.0152 | 9.92 | 0.992 | 1.01 |

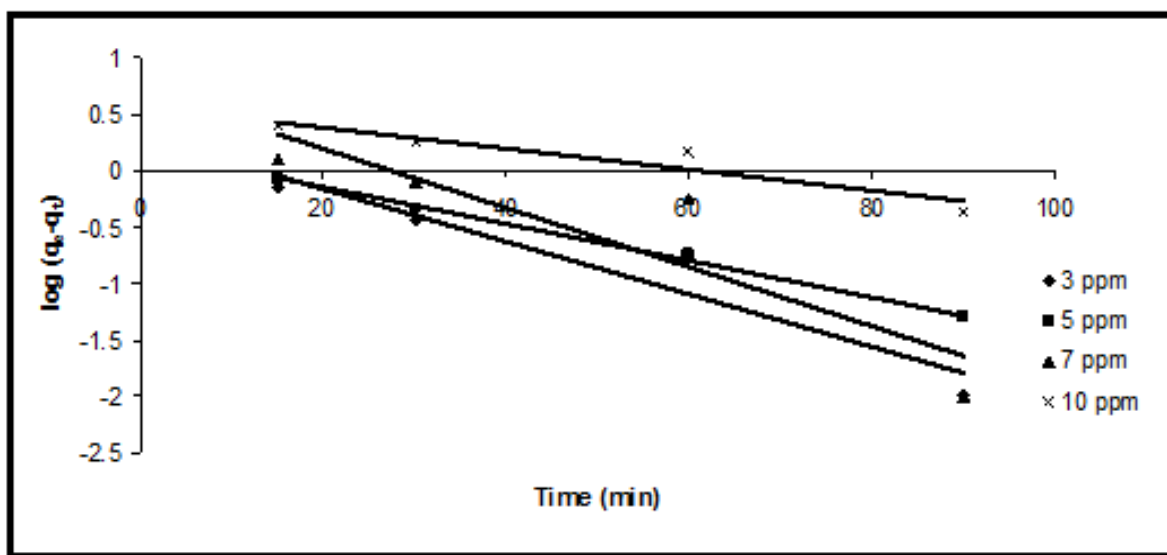


Figure-7
 Pseudo-first order kinetic plot for adsorption of cadmium(II) onto STGOC
 [Temperature: 30±1°C, pH : 5.0 ± 0.1, adsorbent dose : 200mg/100mL]

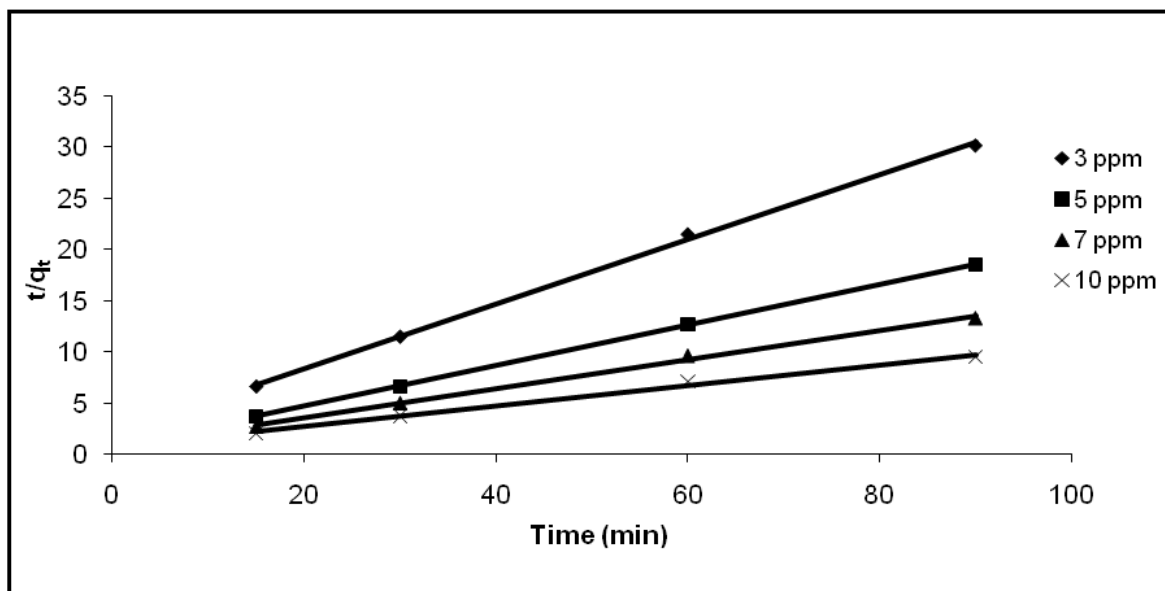


Figure-8
 Pseudo-second order kinetic plot for adsorption of cadmium(II) onto STGOC
 [Temperature: 30±1°C, pH : 5.0±0.1, adsorbent dose : 200mg/100mL]

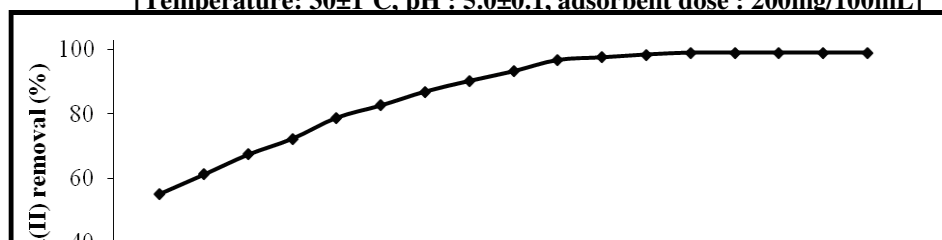


Figure-9
Effect of adsorbent on removal of metal ions from electroplating wastewater
[Temperature: 30±1°C, equilibrated time: 2 hrs, pH: 5.0±0.1]

Table -4
Characteristics of electroplating wastewater (synthetic)

| Parameter | Before treatment (mg/L) | After treatment (mg/L) | Removal (%) |
|-------------|-------------------------|------------------------|-------------|
| 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 |

Conclusion

The presented study signified that the activated carbon obtained from oil cake of *Sesamum Indicum* (STGOC) was employed as an adsorbent 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 Langmuir isotherm model and have shown a better fitting to the experimental data. The kinetics of Cd(II) adsorption onto STGOC was 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 0.15 N HNO₃ from the adsorbent. Experiments with wastewater clearly indicated that the STGOC is an effective adsorbent for the removal of higher concentrations of Cd(II) and other metal ions from wastewater. Based on results, it could be concluded that STGOC can be used as a potential adsorbent to treatment of wastewater containing Cd(II) ions since it is efficient, economical and locally available.

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