Comparative Adsorption Studies of Cd(II) on EDTA and Acid Treated Activated Carbons from Aqueous Solutions

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Abstract

This study plans to functionalize activated carbon with oxygen and nitrogen containing groups to improve removal of Cd(II) ions from aqueous solutions. Activated carbon (AC) was treated with nitric acid giving MC-HNO3 that was pursued by modifying with EDTA to form MC-EDTA. AC, MC-HNO3 and MC-EDTA were analyzed using FTIR, SEM, TEM, Boehm titration, point of zero charge and N2 adsorption-desorption analysis. The batch technique sorption studies of Cd(II) onto sorbents were conducted and the factors controlling the adsorption process of Cd(II) were tested. Langmuir and Freundlich models were used to analyze the isotherm data. The equilibrium data fitted well Langmuir isotherm for all adsorbents. Pseudo-first order, pseudo-second order, intraparticle diffusion and the Boyd equations were used to analyze the kinetic data. The rate constants, equilibrium capacities and related correlation coefficients (R2) for each kinetic model were evaluated and discussed. The second order model is the best fit model for the three sorbents. Though intraparticle diffusion has essential role in rate-controlling step in the adsorption process of Cd(II) onto the investigated sorbents, film diffusion is also governing this process. The thermodynamic parameters ΔG°, ΔH° and ΔS° for the sorption processes of Cd(II) onto the adsorbents were estimated, and spontaneity of adsorption was deduced from the negative sign of ΔG°. Desorption study highlighted the cost saving due to the easiness of regeneration for both MC-HNO3 and MC-EDTA.

Keywords: Water; Activated carbon; Adsorption; Cd(II); Nitric acid; EDTA

Introduction

Heavy metal pollution is a critical environmental issue due to its harmful impacts and accumulation throughout the food chain and therefore in the human body. Cadmium is considered as one of the highly harmful heavy metals pollutants whereas Cd(II) is listed as the 7th most hazardous substance by the Agency for Toxic Substances and Disease Registry [1]. A number of chronic and acute diseases caused by Cd(II) exposure, such as itai-itai disease, renal damage, emphysema, hypertension and testicular atrophy [2]. Cd(II) toxicity is likely related to its high tendency to form bonds with thiol functional groups in some enzymes which lead to the displacement of biologically vital metals [3]. Cd(II) enter the water bodies through diverse ways comprising erosion of natural deposits, metal refinery discharges, and electronic waste runoff [1,4,5]. To keep water healthy, the Cd (II) should be preserved below certain limits. The permissible limit for Cd(II), provided by Environmental Protection Agency (EPA), is 0.005 mg/l and the current guideline value of potable water defined by the World Health Organization (WHO) is 0.003 mg/l [4,6] therefore Cd(II) concentration should not pass these limits to keep water safe. Purification of Cd(II) ions from waste water can be accomplished by applying different conventional techniques that are generally recognized as inefficient and/or expensive [7]. Adsorption by activated carbon is known as one of the extremely efficient methods for the removal of heavy metals [8]. Although the adsorption efficacy of a carbon is essentially related to the pore structure and surface area of the carbon, also the nature and density of surface functional groups have of important role in the adsorption of ionic or polar species [9]. The present work targets to functionalize the surface of activated carbon by oxidation with nitric acid and treatment with EDTA as a chelating agent for the improvement of heavy metals removal from water. The influence of parameters e.g., solution pH, sorbent dose and metal concentration, adsorption isotherms, kinetics modes and thermodynamic parameters of Cd(II) adsorption have been studied and discussed. The experimental equilibrium adsorption data are analyzed by both Freundlich and Langmuir isotherm models. The desorption studies of sorbents were also examined.

Materials and Methods

Materials and apparatus

All activated carbon (Ubichem Ltd., UK) used in the study was in the granular form. The analytical grade reagents and EDTA disodium salt were purchased from Sigma-Aldrich. 1.7909 g of CdCl2.2H2O was dissolved in 1 liter of acidified bi-distilled to prepare 1000 ppm Cd(II) solution that used to prepare the other diluted concentrations. Buffer solution pH=5.5 was adjusted using CH3COOH and NaOH. Glacial acetic acid, nitric acid (65%), hydrochloric acid (36%) were brought from Merck and used without any purification. The concentration of the Cd(II) was analyzed using flame atomic absorption (Analyst 300 Perkin Elmer FAAS). An Analyst 300 Perkin Elmer (FAAS) was used for the quantitative determination. A pH meter (Hi 931401, HANNA Portugal) was used for pH measurements. The adsorbents were weighed using analytical balance. Shaking Water Bath (NE5, Nickel-Electro Ltd., UK) used for adsorption and desorption experiments.

Functionalization of activated carbon

The functionalization of activated carbon was processed based in a...
Characterization of the adsorbents

Fourier transform infrared spectrophotometer (FTIR), Jasco, Model 6100- Japan, was used to investigate the functional groups existed on the sorbents. The oxygen-containing groups were estimated using Boehm titration [11-13]. Also point of zero charge pHpzc, and surface pH were measured [10,14]. Surface Area and Pore Size Analyzer (Quantachrome-Nova 2000 Series) was applied at 77K to investigate N2 adsorption onto the adsorbents and to measure the BET surface areas (SBET) [15]. The χs method was applied to analyze the N2 adsorption isotherms to calculate: S* (total surface area), S′ (non-microporous surface area) and the volume of micropores (V′p) [16]. Also the average pore radius (r) (nm) and the total pore volume (Vt) were estimated [10]. Scanning electron microscope JSE-T20 (JEOL, Japan) at 40 kW and high resolution transmission electron microscope (JOEL JEM2100 HR-TEM) at 200 kV were used to analyze the morphological features of the adsorbents.

Adsorption experiments

Batch adsorption studies of Cd(II) ions onto AC, MC-HNO3 and MC-EDTA were performed using 100 ml to 1 L conical flasks and shaker water bath at 150 rpm. The influence of pH solution on Cd(II) adsorption was investigated by shaking 0.1 g sorbent with 25 ml of 150 ppm Cd(II) solutions for 24 h at 298.15K from 2 to 8. The pH of Cd(II) ion solution was fitted using 0.1M HCl or 0.1M NaOH.

The isotherm studies were executed by shaking 0.1 g of adsorbents with 25 ml solution of various Cd(II) concentrations from 10 to 300 ppm for 24 h at 298.15K. Kinetics studies were performed by agitating 0.5 g of the adsorbents in 500 ml containing 100 ppm Cd(II) solutions at 298.15K. Adsorption capacities were evaluated as follow:

\[ q_t = \frac{(C_0 - C_t)V}{m} \]  

Where, \( q_t \) (mg adsorbate/g adsorbent) is the adsorption capacity at certain time \( t \); \( C_0 \) (mg/L) is the initial concentration of Cd(II) ion; \( C_t \) is the remaining concentration of Cd(II) after adsorption for certain time \( t \) (mg/L); \( V \) (L) is volume of Cd(II) solution and \( m \) (g) is mass of the sorbents. The removal % of Cd(II) ions from solution is estimated as follows:

\[ \text{Removal}\% = \frac{(C_0 - C_t)100}{C_0} \]  

The desorption percentages of Cd(II) from adsorbents were examined by equilibrating 0.1 g of the carbons into 50 ml solution whose concentration is 80 ppm Cd(II) with pH=5.6. After equilibrium, the total adsorbed Cd (II) concentration was calculated, and then the solution was filtrated using a membrane to recover the sorbents. These sorbents were dried for 6 h at 80°C and then placed into 50 ml distilled water. The pH of the dispersed solutions was tuned from 1.5 to 5.5 using suitable amounts of HCl. After equilibrium, Cd (II) concentration was analyzed. These adsorption/desorption procedures were performed for three times, to further ascertain the desorption capability of adsorbents. The Cd(II) desorption % was evaluated by the following equation:

\[ \text{Desorption}\% = \frac{\text{Amount released to solution (ppm)}}{\text{Total Adsorbed (ppm)}} \times 100\% \]  

Results and Discussion

Characterization of the adsorbents

FT-IR: Figure 1 illustrated alike FT-IR spectra for the three sorbents. The wide bands at (3251-3430 cm\(^{-1}\)) appeared for all sorbents were due to stretching model of O-H of hexagonal group. All sorbents possessed shoulders at (2845-2955 cm\(^{-1}\)) that may be assigned to the C-H Aliphatic [17]. The signals appeared around 1700 cm\(^{-1}\) were attributed to stretching vibrations (C=O) of carboxyl groups, ketones lactones or aldehydes [18]. The clear peak appeared at about 1645 cm\(^{-1}\) for the samples may be due to C=O moieties in quinine. Peaks ranging from 1000-1200 cm\(^{-1}\) is problematic due to numerous overlapping broad bands and hence they were very hard to be described as simple motion of precise chemical bonds or functional [19]. Many researchers attributed this interfering band to phenolic and epi-oxide structures and ether stretching vibrations presented in several structural backgrounds [19-21].

Surface acidity and Boehm titration: Boehm titration results are shown in Table 1. The total number of acidic functional groups was increased significantly after treatment with nitric acid and EDTA. The total number of basic functional groups were found to be smaller than that for acidic ones and these numbers were agreed the surface pH values and the pHpzc. The MC-EDTA induced minor increment in the total acidic groups and big increment of basic groups in compared with MC-HNO3.

Nitrogen adsorption-desorption data: The nitrogen adsorption-desorption isotherms for the AC, MC-HNO3, and MC-EDTA are shown in Figure 2. The porous features of the AC, MC-HNO3, and MC-EDTA estimated from the exploration of N2 adsorption isotherms are indicated in Table 2 [22]. The \( S_{BET}, S_{\alpha}, S_{m}, S_{m^*}\) surface areas and pore volumes (\( V_p, V_t, V_m \)) for the activated carbon were declined after treatment with nitric acid and EDTA with widening of the Average pore radius (\( r \)). This could interpreted by the difficult accessibility of nitrogen molecules into the internal adsorption sites because of the increased functional groups existed on MC-HNO3 and MC-EDTA at the pore entrance leading to electrostatic repelling of surface probe molecules (N\(_2\)). Also perhaps by the destruction of some walls with narrow pores that occurred during the oxidation of the AC [23,24]. Additional treatment of MC-HNO3 with EDTA blocked the pore entrance with further functional groups resulting in extra electrostatic repelling and thinner pores thus causing to additional decrement in surface areas as well as the average pore radius with enlarging in micro surface area (\( S_{m^*}\)).

SEM and TEM: Obvious changes in the morphology of the adsorbents were noticed from SEM as shown in Figure 3. MC-HNO3 illustrated a broader pores than that of AC which ensuring the eroding action of nitric acid and collapsing of large grains into small ones and might form a very large micropores as a result of the destruction in the
Figure 1: Fourier transform infrared spectra for AC, MC-HNO3 and MC-EDTA.

Table 1: Surface properties of the adsorbents.

| Adsorbent  | Carboxylic (mmol/g) | Lactonic (mmol/g) | Phenolic (mmol/g) | Total Acidic group (mmol/g) | Basic Groups (mmol/g) | Moisture content % | Ash content % | Surface pH | Point of zero charge |
|------------|---------------------|-------------------|-------------------|-----------------------------|-----------------------|-------------------|--------------|------------|---------------------|
| AC         | 0.078               | 0.0225            | 0.0456            | 0.1461                      | 0.125                 | 10                | 9            | 6.5        | 7                   |
| MC-HNO3    | 0.585               | 0.0476            | 0.2523            | 0.8849                      | 0.084                 | 6.38              | 3.5          | 3.5        | 3.5                 |
| MC-EDTA    | 0.4038              | 0.489             | 0.0966            | 0.9894                      | 0.26                  | 3.7               | 7.2          | 7.45       |                     |

Adsortion and desorption studies

Effect of the solution pH: The pH of the solution governs the charge of the surface charge, ionization extent of the functional groups for the sorbents as well as the form of the metal ions in the aqueous solution. Therefore pH of the solution seems to be the most important parameter affecting the sorption process. The pH of the Cd(II) solutions was altered from 2 to 7.4 which is below the pH necessary for precipitation. It was apparent from Figure 5 that the uptake rate is rapid below pH 5.6 but above this pH the increasing in the uptake became slow and the adsorption capacity is near the maximum one. At lower pH, the adsorption quantity of Cd(II) was quite low that is assigned to the repelling between positive Cd(II) ions and positive function groups on the adsorbents surface. However, with raising the pH, the adsorbents surfaces accepted further negative charges from the ionization of the function groups, that could improve the electrostatic attractions of Cd(II) ions with negatively charged adsorbents surfaces so enhance sorption process. It is noticed that the adsorption capacities for MC-EDTA and MC-HNO3 were larger than that of AC over the studied pH range which indicate the adsorption capacity is increased by the introduction of function groups on the surface of the activated carbon after treatment with HNO3 and EDTA. A pH=5.6 was selected as the peak for further experiments.

Effect of initial concentrations: The equilibrium isotherms for AC, MC-HNO3, and MC-EDTA are shown in Figure 6 indicated that adjacent micropores due oxidation by nitric acid. MC-EDTA showed alike micrographs with that of MC-HNO3 but with smaller number of wider pores. Some slight alterations in the surface are noticed from TEM images as shown in Figure 4 and porous structure of MC-HNO3 and MC-EDTA are demonstrated in comparing with AC.
the adsorption capacities improved with raising the initial Cd(II) concentrations. This is due to the increment in the driving force produced from the concentration gradient [25, 26]. This figure showed that the treated AC seemed to be more efficient under higher and lower Cd(II) concentration whereas the maximum adsorption capacity increased from 42 mg/g in case of AC to 82 mg/g for MC-HNO3 (1.95 times as AC) and 89 mg/g for MC-EDTA (2.12 times as AC). It was observed, the surface treatments with nitric and EDTA had created new sites for binding with Cd(II) ions, which was responsible for enhancing the adsorption.

Effect of contact time: The influence of contact time was investigated for the adsorbents are shown in Figure 7. It was observed that the adsorption of Cd(II) ions increased rapidly until the first 6 hr. The rapid uptake at the initial period may attribute to the sufficient presence of active sites on the surface of the sorbents. After 10 hr, the adsorption was steady therefore it could be selected as the equilibrium time for Cd(II) adsorption.

Effect of adsorbent dose: Figure 8 showed the effect of sorbent dose on the adsorption process. With raising the sorbent dosage from 0.05 g/25 ml to 0.25 g/25 ml, the % of Cd(II) ions uptake improved from 30.2 to 34 for AC, from 51.7% to around 95.1% for MC-HNO3 while increased from 54% to 100% in case of MC-EDTA. It was noticed that the adsorption per unit mass declined by raising the sorbent concentration. The reduction in adsorption density with raising in the adsorbent dosage is mostly because of the unsaturated of adsorption sites during the adsorption process [27, 28]. This behavior could also resulted from the aggregation due the particle interaction and these aggregation might resulted in decrement in total surface area of the carbons and an increment in diffusional path length [28].

Equilibrium adsorption studies: The equilibrium adsorption isotherms are very useful for studying and designing of sorption modules. Langmuir, Sips, Freundlich and Redlich-Peterson models are commonly applied to describe the adsorption of solutes onto solid adsorbents [29]. Langmuir and Freundlich models describe the relation between the concentration of the adsorbate solution at equilibrium and the adsorption capacity at a certain temperature. Langmuir and Freundlich models are used to interpret the adsorption isotherms using regression analysis. The Langmuir equation (linear formula) is indicated as follows:

$$\frac{1}{q_e} = \frac{1}{bq_m} + \frac{1}{C_e}$$

(4)

Where, $q_e$ (mg/g) is the amount adsorbed of Cd(II) per unit mass of adsorbent, $C_e$ is the equilibrium liquid phase concentration of Cd(II), $b$ (l/mg) is Langmuir equilibrium constant, $q_m$ (mg/g) is the monolayer adsorption capacity. Both $b$ and $q_m$ are estimated by plotting $C_e/q_e$ against $C_e$ as shown in Figure 9a. Langmuir isotherm is frequently evaluated by a separation factor, $R_L$, which expressed as follows:

$$R_L = \frac{1}{1 + bC_e}$$

(5)

Where, $C_e$ in that situation is the maximum initial concentration of Cd(II). The type of the isotherm and the nature of the adsorption

### Table 2: Nitrogen adsorption-desorption data.

|          | SBET (m²/g) | $S^\alpha$ (m²/g) | $S^\alpha_0$ (m²/g) | $V_e$ (ml/g) | $V^\alpha_0$ (ml/g) | $\bar{d}$ (nm) |
|----------|-------------|-------------------|---------------------|--------------|---------------------|---------------|
| AC       | 2114.6      | 1765.68           | 1181.25             | 584.43       | 1.7515              | 0.35          |
| MC-HNO3  | 934.4       | 720.944           | 576.332             | 144.611      | 0.87575             | 0.20          |
| MC-EDTA  | 587.8       | 516.874           | 287.196             | 229.678      | 0.5084              | 0.16          |

Figure 3: SEM images (a) and (b) for AC, (c) and (d) for MC-HNO3 and (e) and (f) for MC-EDTA.

Figure 4: TEM images (a) and (b) for AC, (c) and (d) for MC-HNO3 and (e) and (f) for MC-EDTA.
Adsorption ordered as follow: MC-EDTA>MC-HNO₃>AC. Freundlich model is completely empirical and it well interprets the adsorption process on heterogeneous surfaces [31]. Freundlich model (linear formula) is expressed as follow:

$$\log q_e = \log K_f + \frac{1}{n} \log C_e$$

(6)

Where $K_f$ (l/g) is Freundlich constant whereas $n$ is Freundlich exponent. These constants are evaluated by plotting $\log q_e$ against $\log C_e$ as shown in Figure 9b. The isotherm constants for the adsorption of Cd(II) ions onto the adsorbents are illustrated in Table 3. It was observed that the Langmuir adsorption isotherm well fitted the experimental data for AC ($r^2>0.9857$), MC-HNO₃ ($r^2>0.9764$) and MC-EDTA ($r^2>0.9941$).

Adsorption kinetics

Pseudo-first-order and pseudo-second-order: Pseudo-first-order and pseudo-second-order were used to explore the adsorption kinetics of Cd (II) on the surface of the carbons. The pseudo-first-order model is commonly used to analyze kinetic data [32]. Its linear form is given as follows:

$$\frac{t}{q_t} = \frac{1}{k_1 q_e} + \frac{1}{q_e} t$$

(7)

Where $q_e$ and $q_t$ (mg/g) are the adsorption capacities of Cd(II) at equilibrium and at certain time $t$ and $k_1$ (min⁻¹) is the equilibrium rate constant which was estimated from the slopes by plotting $\ln(q_e-q_t)$ against $t$ (as shown in Figure 10a).

The pseudo-second-order kinetic model is defined as follows:

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

(8)

Where $k_2$ (g/(mg min)) is the equilibrium rate constant whereas $q_e$ is evaluated by plotting of $t/q_t$ against $t$ (Figure 10b) [33]. The correlation coefficients for both kinetic models are shown in Table 4. For AC, MC-HNO₃, and MC-EDTA: The second order model provides the best fit for practical kinetic data because the value of the calculated $q_e$ agreed very well with the practical data and $r^2$ is higher than 0.992 for all carbons.

Intraparticle diffusion and Boyd equation: The intraparticle diffusion and Boyd models were used to identify diffusion mechanisms [34-36]. Intraparticle diffusion equation is expressed as follows:

$$q_t = k_3 t^{1/2}$$

(9)

Where $k_3$ (mg/g min⁰.⁵) is the intraparticle diffusion rate constant. The intraparticle diffusion equation is plotted for AC, MC-HNO₃, and MC-EDTA (Figure 11).
Table 3: Langmuir and Freundlich isotherm constants for Cd(II) adsorption on AC, MC-HNO₃, and MC-EDTA.

| Adsorbents  | qₘ (mg/g) | b (L/mg) | R² | R_L | K_F | 1/n | R²  |
|-------------|-----------|----------|----|-----|------|-----|-----|
| AC          | 102.77    | 0.0010   | 0.9857 | 0.5263 | 0.8520 | 0.5755 | 0.9208 |
| MC-HNO₃    | 85.84     | 0.0207   | 0.9764 | 0.0509 | 19.3335 | 0.2193 | 0.9550 |
| MC-EDTA    | 91.91     | 0.0376   | 0.9941 | 0.0287 | 32.8746 | 0.1540 | 0.8720 |

Figure 9: Adsorption isotherm model of Cd(II) on AC, MC-HNO₃, MC-EDTA (a) Langmuir and (b) Freundlich.

Figure 10: Kinetic models for adsorption of Cd(II) (a) Pseudo-first order, (b) Pseudo-second order, (c) Intraparticle diffusion and (d) Boyd plot.


\[ q_t = k_{in} t^{0.5} + C \]  

where \( k_{in} \) (g/mg min^{0.5}) is the intraparticle rate constant for Cd(II) adsorption, \( C \) is the intercept and can be estimated by plotting \( q_t \) against \( t^{0.5} \). Multi-linearity existed in such graphs [38,39], illustrating that two or more stages occurred. The first stage is sharper part and caused by the external surface or instantaneous adsorption. The second part is the gradual sorption stage, while intraparticle diffusion is rate-determined and from it \( K_{in} \) is estimated. The third part is the last equilibrium step while intraparticle diffusion starts to become steady due to extremely small solute concentrations of aqueous solutions.

Also Boyd model was used to investigate the kinetic data [40] to find whether adsorption undergoes to an external diffusion or intraparticle diffusion mechanism, which is defined as follows:

\[
F(t) = 1 - \frac{B}{n} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp(-n^2 B t)
\]

Where \( F \) is the fractional of equilibrium at different periods \( t \), and \( B \) (t) is mathematical function of \( F \). While \( n \) is integer that describes the infinite series solution and \( F \) is the fractional attainment of equilibrium at time \( t \) and is given as follows:

\[
F = \frac{q_t}{q}
\]

where \( q_t \) and \( q \) is the adsorbed amount of Cd(II) ion at certain time \( t \) and equilibrium. Reichenberg [41] gave the next approximations:

When \( F > 0.85; \)

\[
B(t) = -0.4977 - \ln(1 - F)
\]

When \( F < 0.85; \)

\[
B(t) = \left(\sqrt{\frac{\pi}{2}} - \sqrt{\frac{\pi^2 F(t)}{3}}\right)
\]

Figure 10c showed that the intraparticle diffusion plot did not passed through the origin point which indicated that both film diffusion (boundary layer diffusion) and intraparticle diffusion affect the rate-determining step of Cd(II) adsorption process for all the studied adsorbents. Also the same result could be deduced from the Boyd plots (Figure 10d) because the plots did not pass with the origin point.

Thermodynamic studies: The different values of the Langmuir constants \( b \) (1/mol) at different temperature used to calculate the change in the free energy \( \Delta G \) for Cd(II) adsorption using the following expression:

\[ \Delta G = -RT \ln b \]

Where \( R \) is general gas constant (8.314 J/mol/K), \( T \) is the temperature in K. The Standard enthalpy (\( \Delta H \)) and entropy (\( \Delta S \)) for Cd(II) adsorption were calculated from Van’t Hoff equation:

\[ \ln b = \frac{-\Delta H}{RT} + \frac{\Delta S}{R} \]

Figure 11 illustrated the relations between ln b against 1/T were linear and from the slopes the enthalpies \( \Delta H^* \) were evaluated while the entropies \( \Delta S^* \) were estimated from the intercept. Spontaneity of Cd(II) adsorption was deduced from the negative sign of \( \Delta G^* \) for all the adsorbents as shown in Table 5. The amount of the adsorbed Cd(II) at equilibrium was raised with raising the temperature for all cases. The adsorption processes were found to be endothermic due to the positive values of enthalpies \( \Delta H^* \) for all cases. The affinity of Cd(II) adsorption by the carbons were predicted from positive signs of \( \Delta S^* \) also proposed some structural variations in the activated carbons and Cd(II).

Desorption study: The cost saving of the adsorption systems that applied for water treatment is related to both the adsorption capacity and reversibility of the adsorption process. Therefore identical adsorbents should possess high adsorption capacity and easiness for desorption. Figure 12 illustrated the Cd (II) desorption % with regard to solutions at different pH values. It was found that the Cd (II) desorption % improved with decreasing the solution pH. The Cd(II) desorption % raised rapidly from pH=4.5 to pH=1.6 and peaked at pH=1.6 with values above 99.5% for all cases. These results indicated that the adsorbed Cd(II) by the carbons could be simply desorbed and can be applied currently in water decontamination from Cd(II) ions. Moreover, the recycling easiness illustrated that the adsorption mechanism is mainly controlled by ion exchange.

Conclusion

Treatment of AC with HNO 3 and EDTA highly functionalized its surface with oxygen and nitrogen containing groups which accompanied with significant alteration in its textural and morphological features of the activated carbon. Cd (II) adsorption capacities were controlled significantly by pH, metal concentration, equilibration time, sorbent dose, temperature. Functionalization of AC improved the adsorption capacity of AC from 42 mg/g to 82 mg/g in case of MC-HNO 3 and 89 mg/g for MC-EDTA. The adsorption isotherms of the adsorbents were well described by Langmuir model. Pseudo-second-order well fitted the kinetic data AC, MC-HNO 3 and MC-EDTA. Both external and intraparticle diffusions controlled the rate-determining step for Cd(II) adsorption process. The three sorbents adsorbed the

| Kinetic parameters | AC | MC-HNO 3 | MC-EDTA |
|-------------------|----|----------|---------|
| **First-order kinetic** |    |          |        |
| \( q_e, \) exp (mg/g) | 16.85 | 53.6 | 58.1 |
| \( k_1 \) (min\(^{-1}\)) \times 10^3 | 0.91 | 1.5 | 1.92 |
| \( R_1 \) | 0.9501 | 0.9640 | 0.9329 |
| **Second-order kinetic** |    |          |        |
| \( q_e, \) (mg/g) | 11.4256 | 34.659 | 28.17 |
| \( k_2 \) (g/(mg min)) \times 10^1 | 3.01 | 1.02 | 2.03 |
| \( R_2 \) | 0.962 | 0.989 | 0.9974 |
| **Intraparticle diffusion** |    |          |        |
| \( k_{in} \) (mg/g min \(^{0.5}\)) | 0.22248 | 0.48327 | 0.32747 |
| \( C \) | 3 | 20 | 34 |
| \( R_{in} \) | 0.99059 | 0.93791 | 0.89998 |
| **Boyd equation** |    |          |        |
| Intercept | 0.0952 | 0.1059 | 0.3121 |
| \( R^2 \) | 0.9720 | 0.9678 | 0.9528 |

Table 4: Kinetic parameters for the adsorption of for Cd(II) adsorption on AC, MC-HNO 3, and MC-EDTA.
Cd(II) spontaneously that was deduced from negative values of ΔG°. Desorption study illustrated the cost saving due to the easiness of regeneration for both MC-HNO₃ and MC-EDTA.

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