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# Sorption of Bivalent Ions by *Cymbopogon citratus*: Characterisation and Investigation of Biosorptive Capacity and Mechanism

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A B S T R A C T

The main objective of this study was to investigate the removal of cadmium(II) ions from aqueous solution using raw *Cymbopogon citratus* as an adsorbent. It was characterized by FT-IR, XRD, SEM-EDAX and its physical parameters were analyzed. Different factors such as pH, contact time, initial concentration and temperature were studied. Maximum adsorption was taken place at the optimum pH of 6 and the equilibrium data were analyzed by Langmuir, Freundlich and Temkin Isotherm models. Among those isotherm models Langmuir and Temkin were fitted well with good correlation coefficient ($R^2$). The negative values of $\Delta G^0$ for all temperature shows the adsorption process for cadmium(II) ion was spontaneous in nature and feasible. The negative value of enthalpy change $\Delta H^0$ shows the adsorption process is exothermic and the positive value of $\Delta S^0$ indicates the disorderness or randomness process of adsorption. The positive value of Ea indicates the higher solution temperature favors the adsorption of metal ion onto RCC. The experimental data were analyzed by kinetic studies such as pseudo-first order, pseudo-second order and intra-particle diffusion models. Desorption was also studied and the recovery of the adsorbent was found to be 10%. Thus on the basis of these investigations the present study concludes that the raw *Cymbopogon citratus* (RCC) was found to be highly effective, nontoxic, environmental friendly and low cost adsorbent for the removal of toxic Cd(II) ions from aqueous solution.

## 1. Introduction

In the 21st century, environmental pollution has become one of the most important problems faced by the society. To be more specific water pollution significantly plays a crucial role due to rapid industrialization which releases their effluents into the water streams which is mainly composed of heavy metals such as lead, chromium, zinc, cadmium, and nickel generated by industrial activities such as electroplating, mining, battery manufacturing, metallurgical processes, plastics and paint manufacturing, dyes intermediates, textile operation and refining [1] are disposed to water streams without proper treatment which are non-biodegradable and persist for long periods and their accumulation causes harmful effects on the ecosystem. Some conventional methods used for the removal of heavy metals includes chemical precipitation, membrane separation, coagulation and electro-deposition [2]. Most of these methods require high capital investments, non-eco-friendly and not very effective. Therefore, cost effective method is widely needed for the removal of heavy metals [3]. Recently, adsorption was found to be more effective, eco-friendly and versatile method which can be implemented in low cost to remove heavy metals from wastewater due to the usage of low cost adsorbents [4]. Cadmium was found to be one of the toxic heavy metal and the major sources of cadmium are cigarette, tobacco, batteries, plastics, steel coating pans, metal pipes, rubber fertilizers and dental alloys [5]. It is bio-persistent and once absorbed by an organism, remains resident for many years although it has been eventually excreted. According "Environmental Protection Agency" and "WHO" the permissible limit of cadmium in drinking water for humans is 0.005 mg/L [6]. Excessive exposure to cadmium causes severe damage to kidney, renal disorder, high blood pressure, bone fraction and destruction of red blood cells. Toxicological studies have shown that long-term effects from cadmium poisoning include kidney damage and skeletal deformity, liver and some short-term effects include nausea, vomiting, diarrhea, and cramps. Among the various heavy metals, cadmium is considered as extremely toxic and carcinogenic to human beings [7]. The removal of heavy metals from wastewater because of the usage of natural materials and certain waste from agricultural and industrial activity which are considered as low cost adsorbents. The most important characteristic of the good adsorbents is their high porosity and consequent large surface area with more specific adsorption. Some low cost adsorbents banana peel, rice husk and coconut husk etc., [8, 9].

In the present study, lemon grass is used as an adsorbent for the removal of cadmium(II) ions from aqueous solution which is fibrous, non-toxic, easily available, eco-friendly and low cost material. The adsorbent material belongs to poaceae(grass) family and its botanical name is *Cymbopogon citratus*. Thus, the main objective of this study was to investigate the maximum removal of Cd(II) ions from aqueous solution by batch adsorption studies using *Cymbopogon citratus* and its effect on pH, contact time, initial concentration, and temperature were studied. The experimental data is analyzed by kinetic study models such as pseudo-first order, pseudo-second order and intra-particle diffusion. Isotherm models such as Langmuir, Freundlich and Temkin adsorption isotherm were also studied and temperature dependence of adsorption process may be explained on the basis of thermodynamic parameters calculated using standard thermodynamic relationships. The thermodynamic parameters such as free energy, enthalpy and entropy were calculated. Desorption process were also studied to investigate the regeneration of the adsorbent and the percentage removal of metal ion from the adsorbent.

## 2. Experimental Methods

### *2.1 Material*

All chemicals used for this study are AR grade. Cadmium sulphate AR grade chemical was used for preparation of stock solution. The stock solution was prepared by dissolving 2.28 g of cadmium sulphate in 1000 mL of distilled water. Different concentrations of metal ion solution were prepared by dissolving required amount of stock solution.

### *2.2 Preparation of Adsorbent*

Lemon grass (*Cymbopogon citratus*) was collected from the local market. The collected material was washed with tap water and then with

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distilled water to remove dirt and impurity and then it was dried in sunlight. The dried bio-adsorbent was cut into small pieces and powdered. No other chemical treatments were done and then the dried powdered samples were stored in air-tight container. The bio-adsorbent was called as RCC (Raw *Cymbopogon citratus*) for further studies.

### *2.3 The Characterization of Adsorbent*

The physical parameter of the adsorbent was determined by moisture content, ash content, pH, electrical conductivity and bulk density. The pH study was performed using controlled MP plus pH analyzer. The electrical conductivity was measured using digital conductivity meter 611 by adding 1g of the adsorbent in 100ml of water. The RCC is characterized by SHIMADZU FT-IR Spectrometer to investigate the functional group present in raw and treated material. The morphology of the surface site for raw and treated material was examined by Scanning Electron Microscope (SEM) analysis (JEOL Model JSM-6390LV) with an Energy Dispersive X-ray Analyzer (EDAX OXFORD XMX N Model) which shows the elemental detection and identification of heavy metal adsorbed by the adsorbent. X-ray diffraction measurement was obtained using XRD3003TT model to determine the particle size of the adsorbent.

### *2.4 Batch Adsorption Studies*

The adsorption of Cd(II) ion onto the RCC was conducted by batch process. About 0.5 g of RCC is mixed with different known concentrations of Cd(II) ion solution at constant pH then the solution was stirred in mechanical shaker at 120 rpm at room temperature. For the wide range of contact time of 60 minutes, then the solution was filtered and the concentration of the filtrate was analyzed by atomic absorption spectrometer (GBC 932A Atomic Adsorption Spectrometer) at 228 nm in order to determine the adsorption capacity. The amount of adsorbed (mg/g) of Cd(II) ion onto the RCC was calculated by the equation,

$$q= (C_o-C_e) \times V/m \qquad (1)$$

where, "q" is the amount adsorbed (mg/g), "$C_o$" is the initial concentration of metal ions (mg/L), "$C_e$" is the equilibrium concentration of metal ions (mg/L), "V" is the volume of the adsorbate (L) and "m" is the weight of the adsorbent (g). Percentage of removal of metal ion was calculated by the formula,

$$\text{Percentage of removal Cd (II) ions} = C_o-C_e /C_o \times 100 \qquad (2)$$

## 3. Results and Discussion

### *3.1 Physical Parameters*

The physical parameters of the studied adsorbent shown in Table 1.

**Table 1** Physical parameters of RCC

| S.No | Parameters | Results |
|---|---|---|
| 1. | Loss on drying (%) | 5.6 |
| 2. | Ash content (%) | 8.2 |
| 3. | Bulk density (g/cm$^3$) | 0.415 |
| 4. | Tapped density (g/cm$^3$) | 0.554 |
| 5. | Electrical conductivity (μS/cm) | 0.362 |

### *3.2 FT-IR Analysis*

The FT-IR spectrum of *Cymbopogon citratus* was used to investigate functional group present on the surface that may be responsible for the removal of heavy metal species. The spectrum was measured within the range of 4000-500 cm$^{-1}$ using SHIMADZU FT-IR spectrometer and shown in Fig. 1. FT-IR spectrum for before and after adsorption was compared. *Cymbopogon citratus* shows number of absorption peaks which reveal its complex structure by nature. Three peaks between 3440-3552 cm$^{-1}$ corresponds to N-H stretching vibration. A peak at 2920 cm$^{-1}$ corresponds to C-H stretching vibration. The absorption peak at 1734 and 1683 cm$^{-1}$ corresponds to carbonyl group. A peak at 1527 cm$^{-1}$ attributes to C=C stretching and 1045 cm$^{-1}$ assigned for C-C stretching. After adsorption, broad peaks at 3427-3533 cm$^{-1}$ corresponds to the overlapping of N-H peaks and a new peak at 806 cm$^{-1}$ corresponds to C-S stretching. Thus after the treatment of RCC with metal ion solution, due to the binding of adsorbate ($Cd^{2+}$) with adsorbent there exist a change in the peak position indicating change in the environment which in turn attributes the existence of Cd(II) binding onto the surface [10, 11].

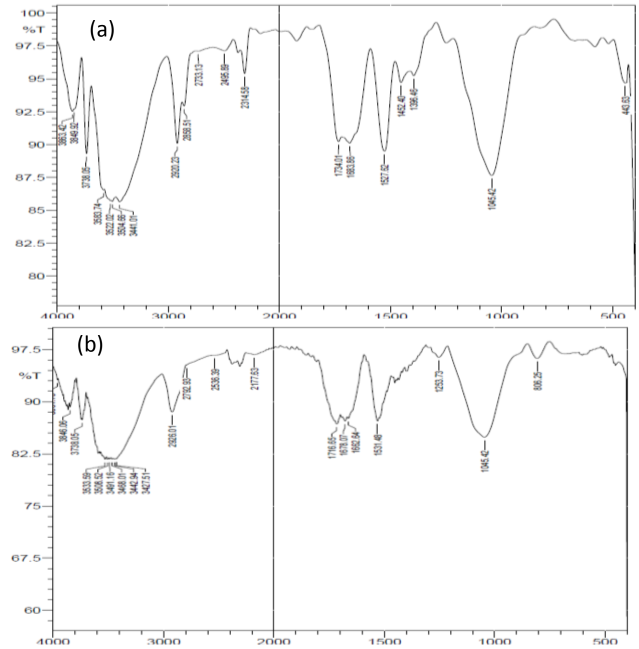


**Fig. 1** FTIR spectra of a) RCC and b) RCC loaded with metal ion

### *3.3 XRD Analysis*

XRD measurement (Fig. 2) is mainly used to determine the particle size of the adsorbent which is calculated using Debye Scherrer's formula, $d=k\lambda/\beta\cos\theta$, where β is the full width (line broadening) at half the maximum intensity (FWHM), 'λ' is the X-ray wave length, θ is the diffraction angle (Bragg's angle) in degrees, k is dimensionless shape factor which is close to unity and 'd' is the average size of the particle. From the XRD analysis particle size was found to be 4.3 nm.

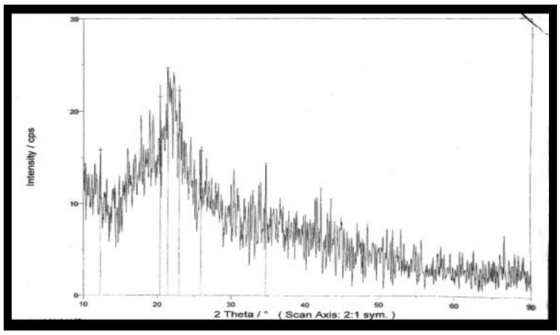


**Fig. 2** XRD pattern for RCC

### *3.4 SEM Analysis*

The scanning electron microscope analysis was mainly used to determine the surface morphology of the adsorbent material. The surface morphological differences of the RCC and metal ion loaded RCC was given in the Figs. 3a and b. These images clearly reveals the surface texture and porosity of RCC adsorbent has holes and small openings found on the surface which shows that these increases the contact area which leads to pore diffusion during the course of the adsorption process [12]. These images also clearly shows the changes in the surface morphologies of RCC and RCC loaded with Cd(II) ions, the pores which is present in the surface of the adsorbent RCC was partly destroyed and this is due to the adsorption of cadmium (II) ions over the pores of the adsorbent surface [13].

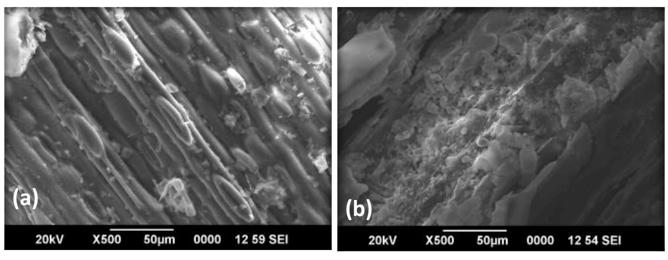


**Fig. 3** a) SEM image for RCC bioadsorbent b) SEM image for metal ion loaded RCC bioadsorbent

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### *3.5 EDAX Analysis*

This is further supported by energy dispersive X-ray analyzer (EDAX) which mainly used to determine the detection of heavy metal ion onto the adsorbent. This provides the direct confirmation of adsorption of cadmium ions onto the RCC adsorbent [14]. Fig. 4 is the EDAX images of RCC and RCC loaded with metal ions. The cadmium peak which is shown in Fig. 4(b) confirms the presence of adsorption of cadmium(II) ions onto the RCC.

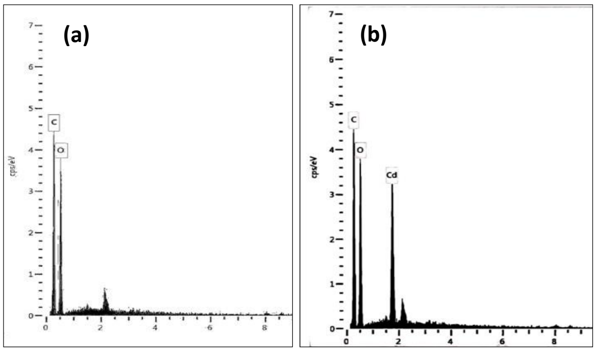


**Fig. 4** a) EDAX for RCC bioadsorbent b) EDAX for metal ion loaded RCC

### *3.6 Effect of pH*

The effect of pH mainly influences the removal of heavy metal ion from aqueous solution by adsorption. It is one of the most important parameter which mainly affects the surface properties of adsorbents, degree of ionization of functional groups and also affects the ionic state of adsorbate [15]. Thus to determine the suitable pH for the effective adsorption of Cd(II) ions from aqueous solution pH study was performed over a pH range of 2.0 to 8.0.

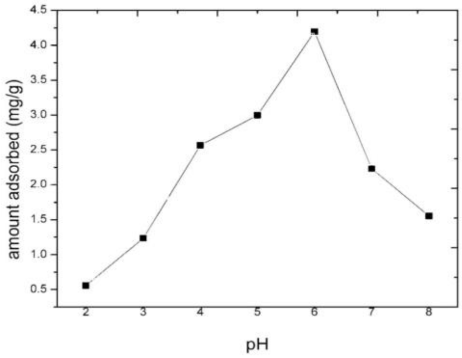


**Fig. 5** Effect of pH on the adsorption of cadmium(II) ions by RCC

Amount of Cd(II) ions adsorbed over a pH range of 2.0 to 8.0 for the concentration of 6 mg/L with adsorbent dosage of 0.5 g at room temperature is given in the Fig. 5 cadmium adsorption increases as pH increase from 2 to 6. It attains maximum adsorption of Cd(II) ions at pH 6 which was considered as an optimum pH and after it decreases with further increase in pH till pH 8. This optimum pH obtained at 6 was used in all subsequent adsorption studies. Under low pH conditions the adsorption of cadmium (II) ions is not significant since the metal binding sites on the RCC surface were closely associated with $H_3O^+$ which restricts the approach of positively charged metal ions ($Cd^{2+}$) due to repulsive forces [16]. Therefore the adsorption capacity increases to optimum pH due to more metal binding sites available with negatively charges which attracts the positively charged Cd(II) ions onto the surface of the adsorbent [17, 18].

### *3.7 Effect of Contact Time*

The contact time is one of the most important factors for the adsorption process to improve as time increases. Fig. 6 shows the effect of contact time on adsorption of Cd(II) onto the RCC adsorbate concentration 2 mg/L, adsorbent dosage 0.5 g, at optimum pH of 6 and at room temperature. To the absorbate added 0.5 g of adsorbent and stirred with a mechanical shaker of 120 rpm after which the solution was filtered and the filtrate was then analyzed by AAS to determine the adsorption capacity. The adsorption rate was found to increase rapidly at the initial stage due to the availability of active sites for the adsorption to occur and maximum adsorption was attained around one hour. On further timings the binding sites become limited and the remaining vacant sites were difficult to be occupied by the cadmium ions due to formation of repulsive forces between cadmium ions and the liquid phase [19]. Hence adsorption of metal ion increases with increase in contact time.

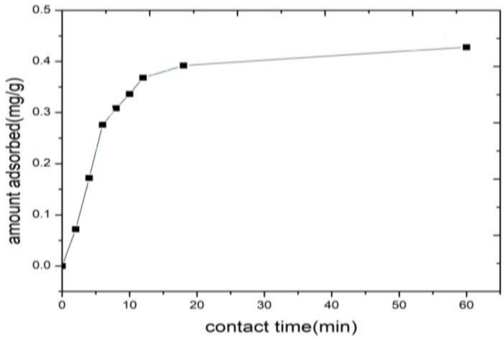


**Fig. 6** Effect of contact time on the adsorption of cadmium(II) ions onto RCC. Conditions: pH 6, Concentration of metal ion 2 mg/L, dosage 0.5 g in 200 mL, particle size 4.3 nm and at room temperature

### *3.8 Effect of Initial Concentration*

Effect of initial concentration of Cd (II) ions were performed over the ranges of 2, 6, 8, 10 and 12 mg/L with the adsorbent dosage of 0.5 g at constant pH and at room temperature. Fig. 7 indicates that as initial concentration increases the uptake capacity of RCC for metal ion increases due to the presence of more surface site available for adsorption. Maximum adsorption has taken place around 20 minutes. Therefore, the uptake capacity of Cd (II) ions by RCC depends on the initial concentration and it can be seen that amount adsorbed increases with increase in the metal ion concentration [20, 21].

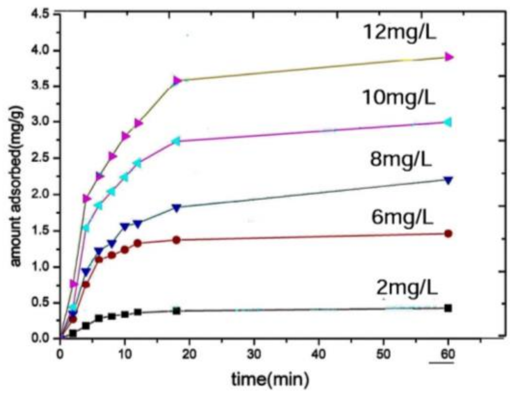


**Fig. 7** Effect of initial concentrations of cadmium(II) ions Conditions: pH 6, dosage 0.5 g in 200 mL, particle size 4.3 nm and at room temperature

### *3.9 Activation Energy and Thermodynamic Parameters*

Generally temperature influences the molecules, functional groups and surface morphology of the adsorbent and adsorbate during adsorption. To determine the thermal effects of adsorption onto RCC, the temperature variation experiments were conducted at 290, 300 and 310 K, with an initial concentration 2 mg/L and adsorbent dosage of 500 mg. The experimental data shows that the adsorption found to be increases with increasing temperature (Fig. 8) which suggest that higher temperature favors the adsorption of metal ion onto the adsorbent [22]. This temperature dependence of adsorption process can be explained on the basis of thermodynamic parameters such as Gibbs free energy $\Delta G^0$, enthalpy change $\Delta H^0$ and entropy change $\Delta S^0$ were calculated from the following standard thermodynamic relationships [23].

$$\Delta G^0 = -RT\ln Kc \quad (3)$$

$$\log Kc = \Delta S^0/2.303R - \Delta H^0/2.303RT \quad (4)$$

$$\ln k = \ln A - Ea/RT \quad (5)$$

where Ce is the equilibrium concentration of metal solution (mg/L), Ci is the equilibrium concentration on the adsorbent (mg/L) and Kc is the equilibrium constant. Gibbs free energy ($\Delta G^0$) for the adsorption of cadmium onto RCC at all temperatures were calculated and are given in the Table 2. The values of $\Delta H^0$ and $\Delta S^0$ were calculated from the slope and intercept values of the plot of logKc against 1/T (figure not given) and the values are listed in the Table 2. Equation 5 is used to determine the activation energy where 'k' is rate constant, Ea is activation energy and 'A' is Arrhenius pre-exponential factor (J/mol) and activation energy was obtained by the plotting 1/T versus logk.

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**Table 2** Thermodynamic parameters for the adsorption of cadmium(II) ions onto RCC

| Temperature (K) | $\Delta G^0$ (kJ/mol) | $\Delta H^0$ (kJ/mol) | $\Delta S^0$ (kJ/mol) | Ea (kJ/mol) |
|---|---|---|---|---|
| 290 | -1719.80 | | | |
| 300 | -1909.80 | -3763.56 | 4432.37 | 16.16 |
| 310 | -2393.83 | | | |

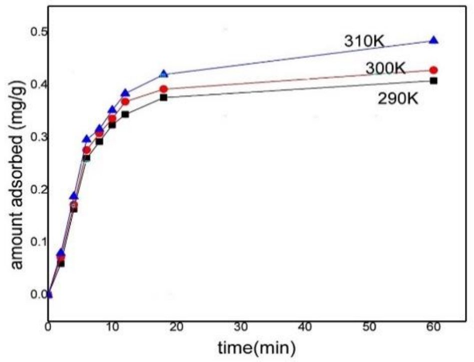


**Fig. 8** Effect of temperature of cadmium(II) ions removed by RCC. Conditions: pH 6, initial Concentration of metal ion 2 mg/L, dosage 0.5 g in 200 mL, particle size 4.3 nm

From the Table 2 the negative values of $\Delta G^0$ for all temperature shows the adsorption process for cadmium(II) ion was spontaneous in nature and feasible [24]. The negative value of enthalpy change $\Delta H^0$ shows the adsorption process is exothermic and the positive value of $\Delta S^0$ indicates the disorderness or randomness process of adsorption. The positive value of Ea indicates the higher solution temperature favors the adsorption of metal ion onto RCC [25].

*3.10 Adsorption Isotherm Studies*

An adsorption isotherm represents the equilibrium relationship between the adsorbate concentration in the liquid phase and that on the adsorbent surface at a given conditions. The equilibrium study is important for an adsorption process as it shows the capacity of the adsorbent. The equilibrium data for adsorption of Cd(II) ion onto RCC bio-adsorbent were evaluated by the Langmuir, Temkin and Freundlich isotherm models.

*3.10.1 Langmuir Adsorption Isotherm*

The Langmuir Isotherm model was mainly used to describe the formation of monolayer sorption occurs on the outer surface of the adsorbent and after which no further adsorption takes place. Thereby, the Langmuir isotherm represents equilibrium distribution of metal ions between the solid and liquid phase [26]. The Langmuir isotherm is valid for monolayer adsorption onto a surface containing a number of identical sites. The linear form of the equation can be written as:

$$C_e/q_e = 1/ Q_o b + C_e/Q_o$$

where, $q_e$ is the amount adsorbed (mg/g), $C_e$ is the equilibrium concentration of metal ions (mg/L), $Q_o$ (mg/g) is the Langmuir constant related to the maximum amount of adsorbed metal ion per unit mass of the adsorbent corresponding to the complete coverage of the adsorptive site, b (L/mg) is Langmuir constant related to adsorption energy respectively. When $C_e$ was plotted against $C_e/q_e$, a straight line is obtained which shows the adsorption of Cd(II) ions. Then the linear isotherm parameters such as b and $Q_o$ were calculated. The plot of specific adsorption ($C_e/q_e$) against the equilibrium concentration ($C_e$) for cadmium (II) ions was shown in the Fig. 9 and the linear isotherm parameters such as $Q_o$, b and the coefficient of determinations are shown in the Table 3. It was observed that the Langmuir isotherm satisfactorily describes the adsorption of cadmium (II) ions from aqueous solution using RCC as indicated by the high correlation coefficient ($R^2$) of 0.9853. Thus it clearly indicates the good monolayer adsorption of cadmium (II) ions on the adsorbent surface [27]. The values of $Q_o$ and b were calculated. It shows that adsorption constant 'b' is related to the affinity of binding sites and the value of 'b' was 6.936 L/mg. Dimensionless constant $R_L$ value indicates the type of Langmuir isotherm its value was found to 0.0672 which shows that the adsorption was found to be favorable. The value of $Q_o$ was 1.310 mg/g for Cd(II) ion. The values indicate the favorable conditions for adsorption.

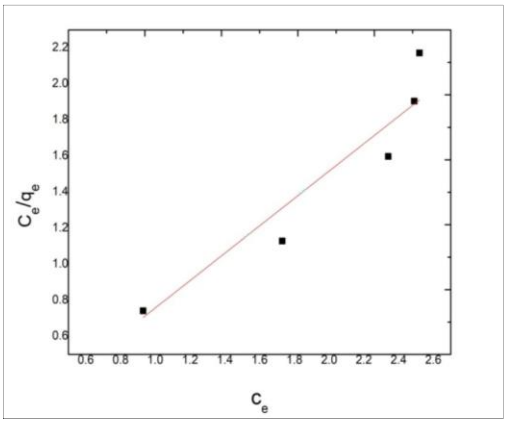


**Fig. 9** Langmuir adsorption isotherm for adsorption of cadmium(II) ions on RCC

*3.10.2 Freundlich Adsorption Isotherm*

The Freundlich isotherm mainly describes the adsorption characteristics on heterogeneous surfaces [28] and the linear form of the isotherm can be represented by the empirical equation proposed by Freundlich.

$$\log q_e = \log K_F + 1/n \log C_e$$

where $K_F$ is the Freundlich constant related to adsorption capacity, n is the Freundlich constant related to adsorption intensity of the adsorbent, 1/n is a function of the strength of the adsorption in the adsorption process. If n=1 the partition between the two phases are independent of the concentration. If the value of 1/n is below one it indicate a normal adsorption. If 1/n being above one it indicates cooperative adsorption [29, 30]. $R^2$ value was found to be 0.9381 (Fig. 10). The values of $K_F$ and n was 1.116 $mgg^{-1}Lg^{1/n}$ and 0.8623 which proves the adsorption tendency of cadmium (II) ions onto RCC.

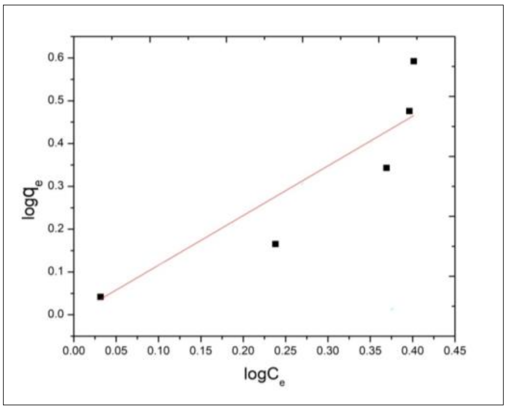


**Fig. 10** Freundlich adsorption isotherm for adsorption of cadmium(II) ion on RCC

*3.10.3 Temkin Isotherm*

This isotherm model assumes that the heat of adsorption of all molecules decreases linearly with the increases in coverage of the adsorbent surface and the adsorption is characterized by a uniform distribution of binding energies up to a maximum binding energy. This isotherm was chosen to evaluate the adsorption potentials of adsorbent for the adsorbate [31]. The Temkin isotherm can be represented by equation,

$$q_e = B_T \ln K_T + B_T \ln C_e$$
$$q_e = RT/ b_T \ln K_T + RT/b_T \ln C_e$$

where T is the absolute temperature (K), R is the universal gas constant (8.314 J/kmol), $K_T$ is the equilibrium binding constant (L/mol) corresponding to the maximum binding energy, $b_T$ is the variation of adsorption energy (kJ/mol), $B_T$ is the Temkin isotherm constant. Plotting $q_e$ against $\ln C_e$ straight line is obtained whose slope and intercept gives the values for $K_T$ and $B_T$. The Temkin isotherm plot for the adsorption of cadmium (II) ions onto RCC was given in the Fig. 11 and the parameters of this isotherm is listed in the Table 3. $K_T$ value was found to be 2.521 and $B_T$ value was found to be 2.852. $R^2$ value was found to be 0.999 which shows the adsorption process has good correlation to this isotherm model.

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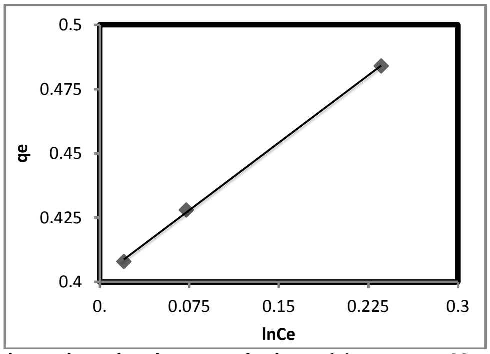


**Fig. 11** Temkin isotherm for adsorption of cadmium(II) ions onto RCC

**Table 3** Parameters of Langmuir, Freundlich and Temkin isotherm models for adsorption of Cd(II) ion onto RCC bio-adsorbent. Conditions: adsorbent dosage 0.5g/200 mL, at constant pH 6, particle size 4.3 nm at room temperature

| Parameters | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Langmuir isotherm | | | | Freundlich isotherm | | | Temkin isotherm | | |
| $Q_0$ | b | $R_L$ | $R^2$ | $K_F$ | n | $R^2$ | $B_T$ | $K_T$ | $R^2$ |
| 1.310 | 6.936 | 0.0672 | 0.9853 | 1.116 | 0.8623 | 0.9381 | 2.852 | 2.251 | 0.999 |

### *3.11 Adsorption Kinetic Studies*

Kinetic study was taken place under the optimized condition of contact time from 0 to 60 minute. The Lagergren first-order reaction rate model (pseudo-first order adsorption kinetics), Ho's second-order reaction rate model (pseudo-second order adsorption kinetics) and intra-particle diffusion model studies were used to describe the adsorption kinetics of cadmium ion onto RCC. Batch kinetic experiments were conducted for cadmium (II) ion solutions at pH 6 with 500 mg/ 200 mL (particle size 4.3 nm) for different concentrations such 2, 4, 6, 8, 10, 12 mg/L at room temperature. Kinetics of adsorption governs the residence time of sorption reaction, is one of the important characteristics which defines the efficiency of sorption. The rate constant of adsorption of the metal ion adsorbents is describes by the Lagergren first-order reaction rate model [32, 33] and Ho's second-order reaction rate model [34].

$$\log(q_e - q_t) = \log q_e - k_{ad}t/2.303$$
$$t/q_t = 1/k_2 q_e^2 + t/q_e$$

where qe is the amount of solute adsorbed (mg/g) at equilibrium per unit weight of the adsorbent, $q_t$ is the amount of solute adsorbed (mg/g) at any time "t" and kad is the pseudo-first order adsorption rate constant. By linear plotting of log ($q_e$-$q_t$) versus time gives the intercept and slope value. From the slope values, the first order rate constants $k_{ad}$ values were calculated. $k_2$ is the pseudo-second order adsorption rate constant, $q_e$ is the amount of solute adsorbed (mg/g) at equilibrium per unit weight of the adsorbent, $q_t$ is the amount of solute adsorbed (mg/g) at any time "t". By linear plotting of $t/q_t$ versus time gives intercept and slope value. From which the second order adsorption rate constant values were calculated. The first-order rate constants kad were calculated from the slope value of Fig. 12 and second-order rate constants $k_2$ and $q_e$ values were calculated from slope and intercept of Fig. 13. By regression modeling, experimental curves were found to be the best fit for the data characterized by the regression coefficient ($R^2$).

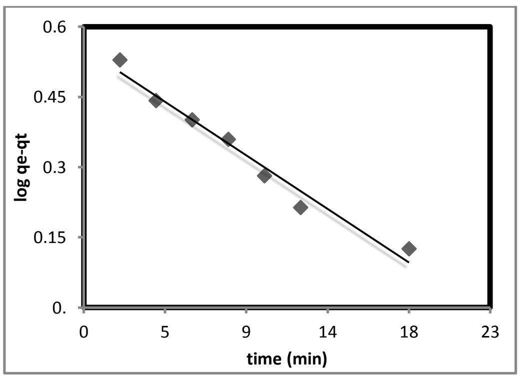


**Fig. 12** Pseudo-first order kinetic plot for the adsorption of Cd(II) ions onto RCC. Condition: Adsorbent dosage: 0.5 g/200 mL, pH 6, particle 4.3 nm and initial concentration 12 mg/L at room temperature

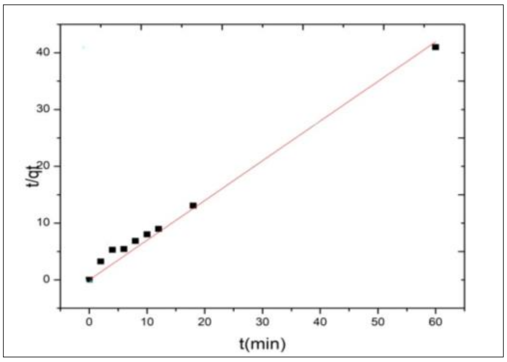


**Fig. 13** Pseudo-second order kinetic plot for the adsorption of Cd(II) ions onto RCC. Condition: Adsorbent dosage: 0.5 g/ 200 mL, pH 6, particle 4.3 nm and initial concentration 6 mg/L at room temperature

Intra-particle diffusion model is characterized by the relationship between specific adsorption and the square root of time [35]. Adsorption kinetic data were further used to define whether the intra-particle diffusion was the rate limiting [36, 37]. The rate constant for intra-particle diffusion $k_{id}$ (mg/g/min$^{1/2}$) is given by the equation, q = $k_{id}$ $t^{1/2}$, where q is amount adsorbed (mg/g) at time "t" (min). $k_{id}$ values were obtained from the linear slope of linear plot of "q" versus $t^{1/2}$. The $k_{id}$ values were obtained from the Fig. 14 which represents the intra-particle plot for Cd(II) onto RCC. The correlation coefficients ($R^2$) and rate constant values for pseudo-first order, pseudo-second order and intra-particle models are shown in the Table 4. And it also clearly shows that equilibrium adsorption capacity ($q_e$) increases with increasing the initial concentration of cadmium (II) ion concentration ($C_0$).

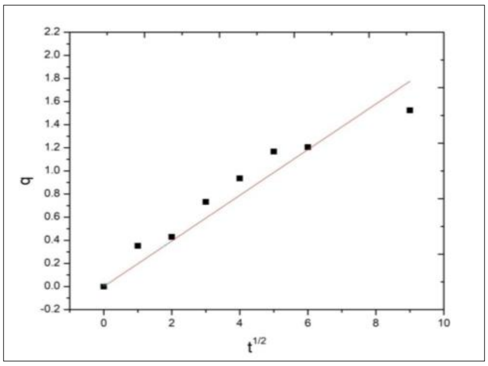


**Fig. 14** Intra-particle diffusion model for the adsorption of Cd(II) ions onto RCC. Condition: Adsorbent dosage: 0.5 g/ 200 mL, pH 6, particle 4.3 nm and initial concentration 8 mg/L at room temperature

**Table 4** Parameters of the kinetic models for the adsorption of Cd(II) ions onto RCC

| Model | Metal ion | Parameter | 2 mg/L | 4 mg/L | 6 mg/L | 8 mg/L | 10 mg/L | 12 mg/L |
|---|---|---|---|---|---|---|---|---|
| Pseudo-first order | Cd(II) ion | kad | 0.1467 | 0.1425 | 0.1685 | 0.1679 | 0.1358 | 0.2260 |
| | | $R^2$ | 0.9884 | 0.9883 | 0.9736 | 0.9922 | 0.9932 | 0.9700 |
| Pseudo-second order | Cd(II) ion | $k_2$ | 0.4636 | 0.0755 | 0.1717 | 0.0578 | 0.0650 | 0.0335 |
| | | $R^2$ | 0.9870 | 0.9692 | 0.9980 | 0.9616 | 0.9836 | 0.9697 |
| | | qe | 0.4647 | 0.1415 | 1.560 | 2.6082 | 3.2594 | 4.5495 |
| Intra-particle diffusion | Cd(II) ion | $k_{id}$ | 0.0104 | 0.0245 | 0.0330 | 0.0638 | 0.0727 | 0.112 |
| | | $R^2$ | 0.9111 | 0.9386 | 0.8690 | 0.9728 | 0.9048 | 0.9579 |

### *3.12 Desorption*

By desorption study, the possibility or regeneration of the adsorbent and recovery of metal ion can be known. Desorption was carried out using batch experiment method. In this study, the adsorbent was regenerated using 100 mL of distilled water and metal ion loaded adsorbent. Desorption rate was found to be very slow and the amount released was also very less. This indicates that the major portions of adsorbate Cd(II) ions were bound to the adsorbent through stronger interaction [38]. The percentage of removal of metal ion from the adsorbent was found to be approximately 10%.

## 4. Conclusion

An overview of this study explains that adsorption of cadmium(II) ion using RCC was highly effective in removing cadmium(II) ions from aqueous solution, cost effective, technically feasible, and environmental-friendly. The adsorbent RCC was characterized by FT-IR, XRD, SEM and EDAX analysis. The adsorption process was also dependent on parameters such as solution pH, contact time, initial concentration and temperature. The amount of adsorption of cadmium ions increases with an increase in the cadmium concentration and also increases as contact time and temperature increases. The maximum adsorption of metal ion was found at pH 6. Equilibrium data fitted very well in the Temkin and Langmuir isotherm models confirming the monolayer adsorption capacity of Cd(II) ion onto RCC. The negative values of $\Delta G^0$ for all temperature shows the adsorption process for cadmium(II) ion was spontaneous in nature and feasible. The negative value of enthalpy change $\Delta H^0$ shows the adsorption process is exothermic and the positive value of $\Delta S^0$ indicates the disorderness or randomness process of adsorption. The positive value of Ea indicates the higher solution temperature favors the adsorption of metal ion onto RCC. The adsorption kinetics followed pseudo-first and pseudo-second order kinetic model with a good correlation coefficient values. Intra-particle diffusion was found to be sole rate controlling or rate limiting factor. Desorption process was also studied in which after the adsorption, the adsorbent was successfully regenerated without using any other chemicals and the extent of desorption was found to be 10%. Therefore, the present study finding suggest that RCC used as an inexpensive, eco-friendly and effective adsorbent without any treatment or any other modification for the removal of cadmium ions from aqueous solution.

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