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Comparative study on removal of cadmium(II) from simulated wastewater by adsorption onto GAC, DB, and PR

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ABSTRACT

This investigation deals with the utilization of granular-activated carbon (GAC), dead biomass (DB) and phosphate rocks (PR) as adsorbents for the removal of cadmium(II) from simulated wastewater. A series of experiments were conducted in a batch system to evaluate the effect of system variables. The effect of pH, initial cadmium(II) concentration, dose of adsorbents, and contact time were considered. The equilibrium data were analyzed using Langmuir, Freundlich and Redlich–Peterson isotherm models at different doses of GAC, DB, and CGA. The Langmuir model was found to fit the equilibrium data very well with high-correlation coefficient (R^2). The maximum uptake capacities were found to be 17.757, 24.677, and 31.379 mg/g onto GAC, DB, and PR, respectively. Adsorption kinetic data were tested using pseudo-first-order, pseudo-second-order, and intra-particle diffusion models. The adsorption process was found to follow a pseudo-first order reaction. The thermodynamic studies showed that the adsorption was spontaneous and exothermic in nature. The study showed that locally available adsorbents, such as DB and phosphate rocks, can be used as efficient adsorbents for the removal of cadmium(II) as compared with commercial GAC.

Keywords: Adsorption; Cadmium(II); Granular-activated carbon (GAC); Dead biomass (DB); Phosphate rocks (PR); Langmuir; Pseudo-first-order

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1. Introduction

Industrial wastewater effluents, bearing heavy metals, pose serious problems for the environment. Cadmium(II), which is usually used and extremely toxic even in relatively low dosage, is one of the principle heavy metals responsible for causing kidney damage, renal disorder, bone fraction, and destruction of red blood cells [1]. Because of toxicity and accumulation, Cd^{2+} is considered as apriority pollutant by the USEPA. The permissible limit for Cd^{2+}, as described by WHO, is 0.01 mg/L. The main anthropogenic pathway through which cadmium enters the water bodies is via wastes from industrial processes such as electroplating, plastic manufacturing metallurgical processes, and industries of pigments and Cd/Ni batteries [2].

Therefore, cost-effective treatment technologies are needed to meet these requirements of recovery and/or removal metal ions. During the last years, increasing attention has been focused on the separation, pre-concentration and/or determination trace metal ions in

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the environment. This field of interest is becoming a real challenge due to specify, accuracy, and sensitivity required by more and more stringent regulations [3]. Conventional technologies for the removal of heavy metals, such as chemical precipitation, electrolysis, ion exchange and reverse osmosis, are often neither effective nor economical [4].

Among the physicochemical treatment process adsorption is found to be highly effective, cheep, and easy to adapt. Activated carbon in most cases has been used as an adsorbent for the reclamation of municipal and industrial wastewater for almost last few decades [5]. But the high cost of activated carbon has inspired the investigation especially in developing countries like Iraq to search for suitable low-cost adsorbents.

Adsorption of metal ions such as cadmium onto activated carbon involves a combination of mechanisms, including physical adsorption caused by Van der Waal's forces, complex formation on the surface after the interaction between metal ions and active groups [6]. Sludge from wastewater systems contains bacteria, fungi, protozoa, yeast, etc. The cell wall of micro-organisms essentially consisting of various organic compounds such as chitin, acidic polysaccharides, lipids, amino acids, and other cellular components could provide a passive uptake of metal ions in a manner of surface adsorption, complexation, chelation, ion exchange, precipitation, etc. Several functional groups are present on the micro-organisms cell wall, including carboxyl and phosphonate. As they are negatively charged and abundantly available, carboxyl groups actively participate in the binding of metal cations [7].

As a result, recent research has focused on the development of cost-effective alternatives using various natural sources and industrial waste [8]. Industrial wastes are potential low-cost adsorbents for metal removal since some of them have high ion-exchange capability. Pre-treatment of adsorbent is also commonly used to increase the adsorption capacity of these materials. Several researches have been made significant contribution in this area, utilizing a number of materials including fly ash [9], sugar beet, rice bran, soy beans and cotton seed hulls [10], reactive polymers [11], grafted cellulose materials [12], natural zeolite [13], etc. The objective of this study was to investigate adsorption characteristics for the removal of Cd^{2+} from simulated wastewater by the use of low-cost abundantly available nonconventional adsorbents such as dead biomass (DB) and phosphate rocks (PR) and comparative with granular-activated carbon (GAC) adsorption capacity.

2. Materials and methods

2.1. Adsorbents preparation

GAC, namely DARCO 20–40 mesh supplied by Sigma-Aldrich.Com., UK was used in this study.

A heterogeneous micro-organism (bacteria, yeast, and fungi) was taken as sludge from drying bed of Al-Rostomia'a sewage treatment plant, third extension in Baghdad-Iraq, dried at atmospheric temperature (37–45°C) for 5 days and sieved through a 1,000 and 600 μm-diameter mesh. Then, the DB was washed with distilled water five times to remove impurities before using in experiments, then drying for 6 h at 70°C to ensure removing the moisture from biomass. There are 14 drying beds each one has a dimension of (300 m × 25 m × 1 m).This means that the volume of sludge produced by each drying bed was about (7,500 m^3).

The PR sample used in this study comes from the Akashat phosphate mines located in the western region of Iraq, about 110 km west of the capital Baghdad. The choice of this material is based on its low cost, considering its abundance in the Iraqi ores. Iraq is one of the major courtiers in phosphate production. The amount of phosphate production in Iraq was about 1,199,343 tons/year [21]. The PR samples were ground in a mortar and sieved into mesh 600, 1,000 μm and geometric mean diameter was taken. Then, the grounded sample was washed with distilled water to remove any nonadhesive impurities and small particles and then dried at 103°C for 24 h to remove moisture. The washing water for DB and PR was analyzed to find whether there is any impurities released (Ca^{2+}, Mg^{2+}, Fe^{3+}, Al^{3+}, F^{-}, and So_3) at pH 4 and 8, respectively. The tests showed no detectable concentrations in leaching solutions.

The physical and chemical properties of adsorbents are measured at the laboratories of the Ministry of Industry and Minerals (Ibn Sina State Company), Ministry of Oil (Petroleum Development and Research Center), Al-Mustansiriya University (College of Engineering, Environmental Department) and according to the data from the supplier and listed in Table 1. The specific surface area and total pore volume were measured using the multi-point-N_2-Brunauer, Emmett and Teller (BET) method (Surface area analyzer, BET method, Quantachrome.com, USA). The functional groups of GAC, DB, and PR was detected by FT-IR analysis. The proportion of adsorbent/KBr is 1/100. The background is obtained from the scan of pure KBr. FT-IR spectrophotometer, IRPRESTIGE-21, SHIMADZU, Japan was used for analysis. Phases present in the samples (chemical analysis) were analyzed

Table 1
Physical and chemical prosperities of GAC, DB, and PR

Properties	GAC	DB	PR
BET surface area, $m^2 g^{-1}$	590	89.87	607.53
Particle porosity	0.48	0.43	0.45
Average particle diameter, mm	0.78	0.78	0.78
Pore volume, $cm^3 g^{-1}$	0.366	0.532	0.422
CEC meq/100 g	–	30.43	–
pH	8.74	7.5	11.49

using an X-ray diffractometer (PAN analytical X-ray, Philips Analytical, Germany) and present in Table 2.

2.2. Preparation of cadmium(II) solution

The aqueous solution of cadmium ions was prepared by using analytical grade chemical. Stock metal ions solution of 1,000 mg/L concentration of Cd^{+2} from Cd $(NO)_3 \cdot 4H_2O$ was prepared. Nitrate is used instead of sulfate to avoid metal precipitation, though the effect of the anion was negligible. This stock solution was used to prepare dilute solutions of cadmium (II) ions by dilution with distilled water. The stock solution was acidified to $4 < pH < 6$ using concentrated HNO_3 in order to prevent the formation of metal hydroxide and to return the metal ion to the dissolve state [14].

2.3. Sample preparation for analysis

Samples (40 mL) were transferred into a micro-centrifuge tube and centrifuged at 3,000 rpm for 5 min, to remove suspended materials in the samples. Supernatant (10 mL) was transferred to 100 mL volumetric flask and acidified with 90 mL of 10% nitric acid (HNO_3) to get a standard solution of 100 mL. These samples were stored in a freezer to terminate the reaction until measurement [15]. These samples were analyzed using Atomic absorption Spectrophotometer (AAS, Buck, Accusys 211, USA).

2.4. Batch adsorption experiments

The specified adsorbent was placed in 250 mL bottles containing 100 mL of cadmium(II) solution. The bottles were then placed on a shaker and agitated continuously at 250 rpm for the desired pH value, contact time, and adsorbent dosage level. Different initial concentration of Cd^{2+} solutions was prepared by proper dilution from stock 1,000 mg/L. pH of the solution monitored by adding 0.1 N HNO_3 and 0.1 N NaOH solutions as per required pH value. Necessary amount of adsorbent material was the added, and contents in the flask were shaken for the desired contact time at ambient temperature (i.e. 30 ± 2°C). The contents of the flask were filtered through filter paper and filtrate was analyzed for Cd^{2+}.

The percentage removal of Cd^{2+} was calculated as follows:

$$\text{Removal of } Cd^{2+}\ (\%) = \frac{C_0 - C_{eq}}{C_0} \times 100 \tag{1}$$

where C_0 and C_{eq} are the initial and final concentration of the metal ion (mg/L).

2.5. Adsorption Isotherms

The equilibrium established between adsorbed component on the adsorbent and unadsorbed component in solution can be represented by adsorption isotherms. The most widely used isotherm equation for modeling equilibrium is the Langmuir equation which is valid for monolayer sorption on to a surface a finite number of identical sites and is given by Eq. (2)

$$q_{eq} = \frac{Q^o b C_{eq}}{1 + b C_{eq}} \tag{2}$$

where q_{eq} is the amount of pollutant bound to per g of adsorbent at equilibrium and C_{eq} is the residual (equilibrium) pollutant concentration left in solution after binding, respectively. Q^o is the maximum amount (maximum loading capacity) of pollutant per unit weight of adsorbent to form a complete monolayer on the surface bound at high C_{eq}, and b is a constant related to the affinity of the binding sites [16].

The Freundlich expression is an empirical equation based on sorption on a heterogeneous surface suggesting (as expected) that binding sites are not equivalent and/or independent. The mono-component Freundlich equation is given below by Eq. (3)

$$q_{eq} = K_F C_e^{1/n} \tag{3}$$

where K_F and n are the mono-component Freundlich constants characteristic of the system [15].

The three-parameter Redlich–Peterson equation was proposed to improve the fit by the Langmuir or Freundlich equation and is given by Eq. (4)

$$q_{eq} = \frac{K_{RP} C_{eq}}{1 + a_{RP} C_{eq}^{\beta}} \tag{4}$$

Table 2
Chemical analysis of GAC, DB, and PR samples

GAC		DB		PR	
Constituent	Weighted average, %	Constituent	Weighted average, %	Constituent	Weighted average, %
C	88.77	Fe_2O_3	48	P_2O_5	21.47
O	10.51	CaO	23.4	CaO	50.98
Si	0.28	MgO	2.5	MgO	0.60
S	0.05	MnO	0.2	CO_2	17.26
K	0.18	SiO_2	12.6	SiO_2	3.845
Ca	0.21	Na_2O	0.7	SO_3	1.70
–	–	K_2O	0.5	F	2.88
–	–	Ash	12	Cl	0.125
–	–	–	–	Fe	0.6
–	–	–	–	Al	0.54

where K_{RP}, a_{RP}, and β are the Redlich–Peterson parameters. The exponent β lies between 0 and 1. For $\beta = 1$, Eq. (4) converts to the Langmuir form [17].

2.6. Adsorption kinetics

The kinetic parameters for the adsorption process were studied on the batch adsorption of 50 mg/L of Cd^{2+} at pH 5. The contact time was varied from 30 to 300 min, and the percentage removal of Cd^{2+} was monitored during the study. The data were fitted to different kinetics adsorption models:

2.6.1. Pseudo-first-order kinetic model

The Lagergren rate equation was the first-rate equation for the sorption of liquid/solid system based on solid capacity and this model represent physical adsorption for pollutants onto adsorbent surface: [18]

$$\log(q_{eq} - q_t) = \log q_{eq} - \left(\frac{k_L t}{2.303}\right) \tag{5}$$

where q_{eq} is the amount of Cd^{2+} adsorbed at equilibrium (mg/g); q_t is the amount of Cd^{2+} adsorbed at time t (mg/g); and k_L is the equilibrium rate constant of pseudo-first sorption (min^{-1}).

2.6.2. Pseudo-second-order kinetic model

If the sorption rate of system is a pseudo-second-order mechanism, the rate-limiting step may be chemical sorption or chemisorption involving valency forces through sharing or the exchange of electrons between adsorbent and adsorbate as covalent forces [18]:

$$\frac{t}{q_t} = \frac{1}{k_s q_{eq}^2} + \frac{t}{q_{eq}} \tag{6}$$

where k_s (g/mg.min) is the rate constant of adsorption.

2.6.3. Intra-particle diffusion model

The intra-particle diffusion model is expressed as [18]:

$$q_t = k_{id} t^{1/2} + C \tag{7}$$

where k_{id} (mg/g $min^{1/2}$) is the rate constant of intra-particle diffusion, C is the value of intercept which gives an idea about the boundary layer thickness, that is, the larger intercept; the greater is the boundary layer effect. The linear plots of q_t vs. $t^{1/2}$ with zero intercept indicates that intra-particle alone determines the overall rate of adsorption. In this case, intra-particle diffusion is not the only determining mechanisms, in addition other mechanisms such as electrostatic interaction, ion exchange may be operating to different extents.

2.7. Thermodynamic parameters

The thermodynamic equilibrium constant for each system was obtained at 30 ± 2°C by calculating the apparent equilibrium constant K_c at different initial concentration (25–100 mg/L) of cadmium(II) and extrapolating to zero [19]:

$$K_c = \frac{C_0 - C_{eq}}{C_{eq}} \tag{8}$$

The Gibbs free energy (ΔG°, kJmol^{-1}) for the adsorption process was obtained at 30 ± 2°C using the formula:

$$\Delta G^\circ = -RT \ln K_c \tag{9}$$

where R is the ideal gas constant ($8.314\,\text{J mol}^{-1}\text{K}^{-1}$) and T is the temperature in K.

3. Results and discussion

3.1. Effect of pH

Experiments concerning the effect of pH on the adsorption were carried out in the range of pH not influenced by the metal precipitation as metal hydroxide which is occurs at pH of 9.7 for cadmium ions [20]. Thus, the uptake of Cd^{2+} as a function of pH was examined over a range of 2–8 as shown in Fig. 1. For GAC with an initial concentration of 50 mg/L of Cd^{2+}, maximum removal was obtain at a pH value of 5 (78.6%). For DB, optimum pH for the adsorption of Cd^{2+} was found to be 5 (89.4%). In case of PR also, maximum sorption of Cd^{2+} from aqueous solution occurred at a pH value around 5 (95.5%). Hence, pH 5 was considered to be the optimum pH for further experiments. The effect of pH can be explained considering the surface charge on the adsorbents material. At low pH (2–4), metal uptake was less and this is due to the fact that adsorbent surface are closely associated with H_3O^+ and access of metal ions to adsorbents surface would be restricted as a result of repulsive forces. Metal uptake increased with pH around 5, and this is due to more ligands with negative charge being exposed with the subsequent increase in attraction sites to positively charged metal ions [21]. On the other hand, at high values of pH (above 5), OH^- ions compete for Cd^{2+} with the active sites on the surface of the adsorbents and thus reduce cadmium adsorption capacity [22–24]. Kalyani et al. showed that at pH over 5, $Cd(OH)^-$ specie was dominate, and therefore, a competition with OH^- ions words functional groups occurred. This fact also supported by several earlier workers [25].

3.2. Effect of initial metal ion concentration

The feasibility and efficiency of a adsorption process depends not only on the properties of the adsorbents, but also on the concentration of the adsorbate. The initial metal concentration provides an important driving force to overcome all mass transfer resistances of the metal between aqueous and solid phase [26]. The effect of initial concentrations of Cd^{2+} was studied and illustrated in Fig. 2. The efficiency values decreases from 86.88 to 51.27% for Cd^{2+} onto GAC, from 93.34 to 70.23% for Cd^{2+} onto DB and from 97.23 to 77.24% for Cd^{2+} onto PR as the initial concentration increased from 25 to 100 mg/L. There are many factors which can contribute to the adsorbate concentration effect. The first and most important one is that adsorption sites remain unsaturated during the adsorption reaction. The second cause is the agglomeration of adsorbent particles at higher concentrations.

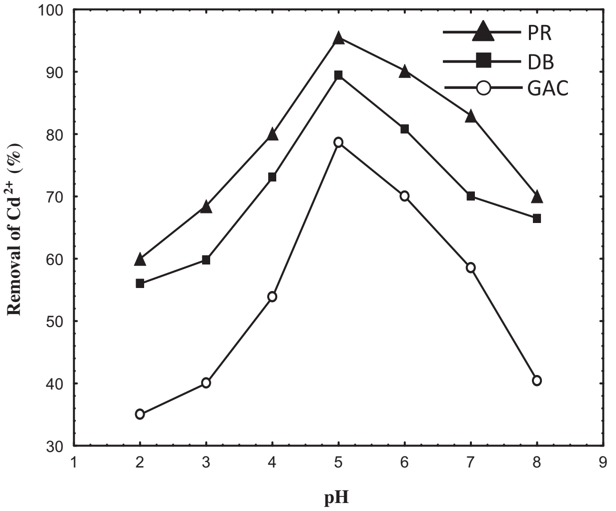

Fig. 1. Effect of pH on the adsorption of Cd^{2+} by GAC, DB and PR, initial concentration 50 mg/L, adsorbent dose 1 g, contact time 5 h and temperature 30°C.

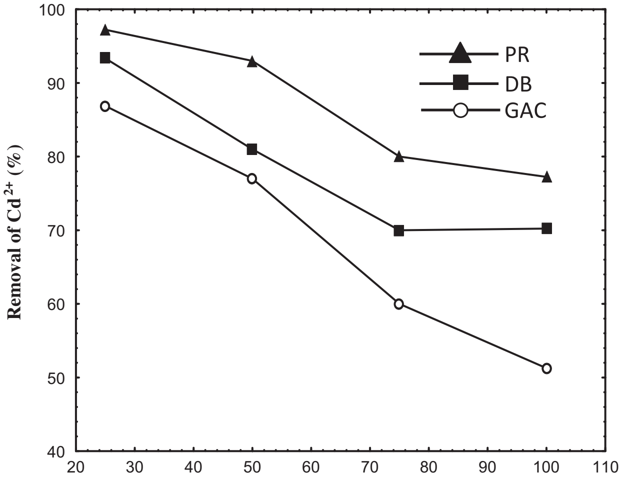

Fig. 2. Effect of initial concentration on the adsorption of Cd^{2+} by GAC, DB and PR, pH 5, adsorbent dose 1 g, contact time 5 h and temperature 30°C.

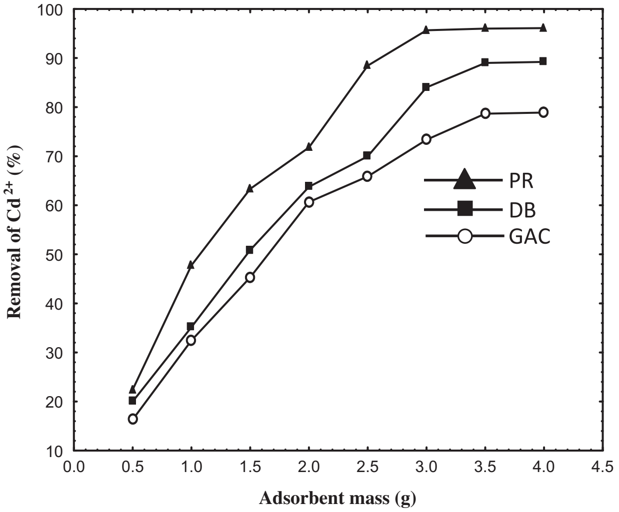

Fig. 3. Effect of adsorbent dose on the adsorption of Cd^{2+} by GAC, DB and PR, pH 5, initial Cd^{2+} concentration 50 mg/L, contact time 5 h and temperature 30˚C.

Such aggregation leads to a decrease in the total surface area of the adsorbent particles available for adsorption and an increase in the diffusional path length [27]. However, Zouboulis et al. [27] explained the effect of initial metal concentration as follows: at low metal ion/adsorbent ratio, metal ion adsorption involves higher energy sites. As the metal ion/adsorbent ratio increase (i.e. at higher initial concentration), the higher energy sites are saturated and adsorption begins on lower energy sites, resulting in decrease in the adsorption efficiency [28].

3.3. Effect of adsorbent mass

The effect of varying the adsorbents mass on the adsorption of cadmium ions is shown in Fig. 3. In each case, increase in adsorbent dosage resulted in an increase in percent removal of Cd^{2+}. After certain adsorbent dosage level, the removal efficiency is not increased so significantly (less than 8%). Removal efficiency increases for cadmium(II) from 16.334 to 78.890% onto GAC, 20 to 89.21% onto DB and 22.44 to 96.1% onto PR as the mass increases from 0.5 to 4 g. The rate of increase gradually decreases with increasing adsorbent mass above 3 g. It is clearly seen that the removal efficiency increases as the adsorbent mass increases. With increasing adsorbent dosage, more surface area is available for adsorption. As the adsorbent mass increases, the number of binding sites for the ions also increases. After some point, sorption capacity was steady or due to a screen effect between adsorbent, this produced a block of the adsorbent active sites by an increase in cadmium ions in the system [29].

3.4. Effect of contact time

Contact time plays an important role in the efficient removal of cadmium ions using different adsorbents. The influence of contact time on the adsorption capacity for different metal ions is shown in Fig. 4. Removal efficiency increases for Cadmium from 20 to 77% onto GAC, 45 to 85% onto DB, and 70 to 93% onto PR as the contact time increases from 30 to 300 min. The results clearly revealed that rate of adsorption is higher at the beginning and this is due to availability of a large number of active sites on the adsorbents. As these sites are exhausted, the uptake rate is controlled by the rate at which the adsorbate is transported from the exterior to the interior sites of the adsorbent particles [30]. Maximum removals were attained within the first 180 min of stirring time. There must not be seemed to be much benefit after 270 min. Therefore, the equilibrium time was set to be 4.5 h.

3.5. Adsorption isotherm models

The parameters for each models were estimated by nonlinear regression using STATISTICA version-6 software. All parameters with correlation coefficient are summarized in Table 3. The adsorption isotherms for Cd^{2+} onto GAC, DB, and PR are shown in Fig. 5.

From Fig. 5 and Table 3, the following conclusions can be drawn: Langmuir model gave the best fit for the experimental data for cadmium(II) adsorption with correlation coefficients of 0.989, 0.993, and 0.988 onto GAC, DB, and PR, respectively. The maximum adsorbed amount (Q^o) for Cd^{2+} onto the selected adsorbents follow the sequence as: $Q^o_{PR} > Q^o_{DB} > Q^o_{GAC.}$ as

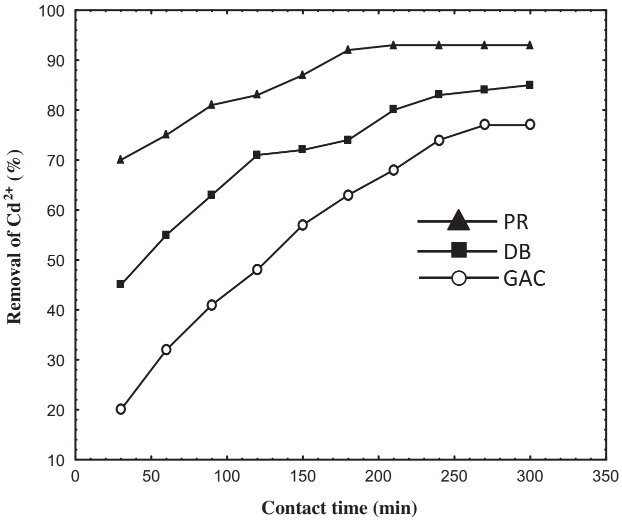

Fig. 4. Effect of contact time on the adsorption of Cd^{2+} by GAC, DB and PR, pH 5, initial Cd^{2+} concentration 50 mg/L, adsorbent dose 3 g and temperature 30˚C.

Table 3
Parameters of adsorption isotherm for cadmium ions onto GAC, DB, and PR

Langmuir model				Freundlich model			Redlich–Peterson			
Adsorbent	Q^o	b	R^2	K_F	n	R^2	K_{RP}	a_{RP}	β	R^2
GAC	17.757	0.194	0.989	4.986	1.286	0.894	3.872	0.164	0.537	0.943
DB	24.677	0.092	0.993	7.983	1.531	0.981	7.212	0.298	0.774	0.988
PR	31.379	0.092	0.988	12.065	1.953	0.972	9.429	0.342	0.976	0.953

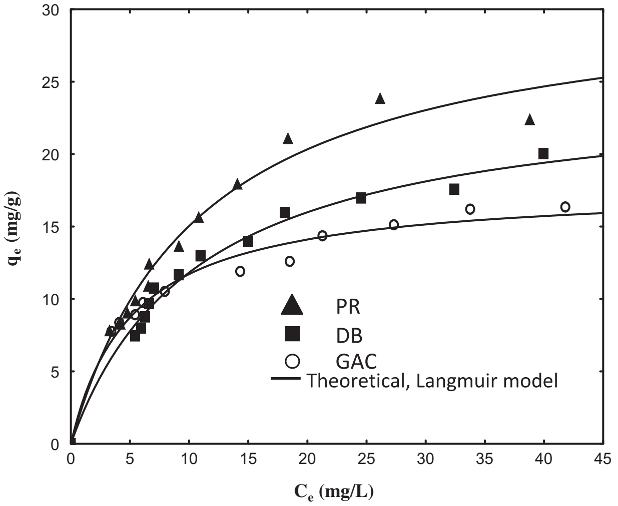

Fig. 5. Adsorption isotherm of cadmium ions onto GAC, DB and PR in single system.

determined in Table 3. PR has more surface area than GAC and DB. Therefore, more adsorption sites are available for cadmium(II) adsorption. However, cation exchange capacity (CEC) for DB represents the total amount of cadmium cation that can be replaced by positive ions (K^+,Na^+,Ca^{2+}, and Mg^{2+}) on DB. CEC for DB used in this study was 30.43 meq/100 g [31]. Thus, adsorption capacity for DB exceeds that for GAC.

A comparison of the maximum adsorption capacity (Q^o) of the GAC, DB and PR sample with that of some other adsorbents reported in the literature is given in Table 4. The adsorption capacity of the PR and DB samples was relatively high when compared with other adsorbents.

Table 4
Adsorption capacities (Q^o, mg/g) for cadmium(II) of various adsorbents

Adsorbent	Cd^{2+}, Q^o (mg/g)	Refs.
Activated sludge	69.2	[26]
Natural zeolite	5.17	[32]
Keratin Powder	25	[33]
Calcite	18.52	[34]
Olive cake	10.56	[35]
Green macroalgae	14.30	[36]

3.6. Adsorption rate kinetics mechanisms

The study of adsorption kinetics describes the solute uptake rate and evidently these rate controls the residence time of adsorbate uptake at the solid–solution interface including the diffusion process. The mechanisms of adsorption depend on the physical and chemical characteristics of the adsorbent as well as on the mass transfer process. The kinetics of cadmium ions adsorption onto GAC, DB, and PR were analyzed using pseudo-first-order, pseudo-second-order, and intra-particle diffusion models. Table 5 demonstrates the results of these models.

The rate of Cd(II) adsorption on the three adsorbents observed to follow the first-order rate law derived by Lagergren Eq. (5). Figs. 6 and 7 show the Lagergren plot of $\log(q_e - q_t)$ vs. time (min) and effluent concentration (C_e) vs. time (min) for all adsorbents. The linearity of these plots indicates that a first-order mechanism is indeed follow in this process and that the process is physical rather than being chemical which represent by second-order kinetic model. However, the value of constant (C) in the intra-particle diffusion model is not equal to zero, suggesting that adsorption proceeds from boundary layers mass transfer across the interfaces to the intra-particle diffusion within the pores of adsorbent. This indicates the mechanisms of cadmium(II) adsorption is complex and both the surface adsorption and intra-particle diffusion contribute to the rate-determining step [37].

3.7. Thermodynamic for adsorption process

The thermodynamic equilibrium constant K_c obtained from calculating the apparent equilibrium constant K_c at different initial concentration of cadmium(II) and extrapolating to zero. The Gibbs free energy for the adsorption process was obtained at 30° C using Eq. (9), Table 6

The Gibbs free energy indicates the degree of spontaneity of the adsorption process, where more

Table 5
Kinetic models parameters for Cd^{2+} ions adsorption onto GAC, DB, and PR

Model	Parameters	GAC	DB	PR
Pseudo-first-order model	q_e (mg/g)	10.342	13.874	16.983
	K_L (min^{-1})	3.56×10^{-2}	4.76×10^{-4}	6.87×10^{-2}
	R^2	0.981	0.977	0.932
Pseudo-second-order Model	q_e (mg/g)	9.1575	10.6270	18.2815
	K_s (g/mg.min)	2.75×10^{-3}	4.98×10^{-3}	8.54×10^{-3}
	R^2	0.910	0.887	0.872
Intra-particle diffusion model	k_{id} (mg/g.min$^{0.5}$)	2.98×10^{-3}	5.32×10^{-3}	7.98×10^{-2}
	C	0.346	0.785	2.875
	R^2	0.911	0.891	0.923

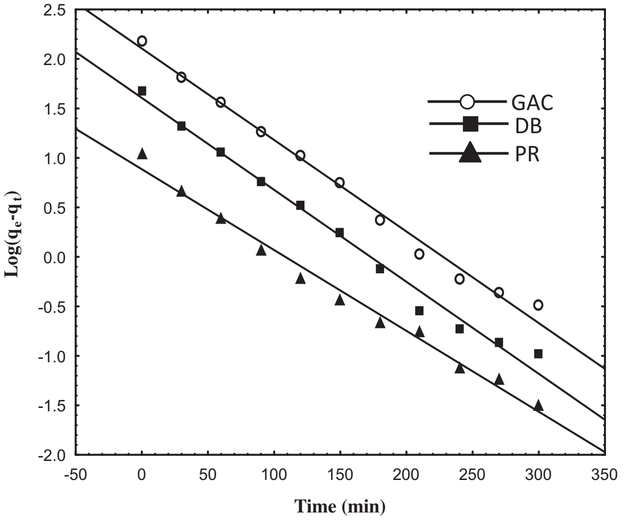

Fig. 6. First-order kinetic model for the adsorption of Cd^{2+} onto selected adsorbents; pH 5, initial concentration 50 mg/L, adsorbent dosage 3 g and temperature 30˚C.

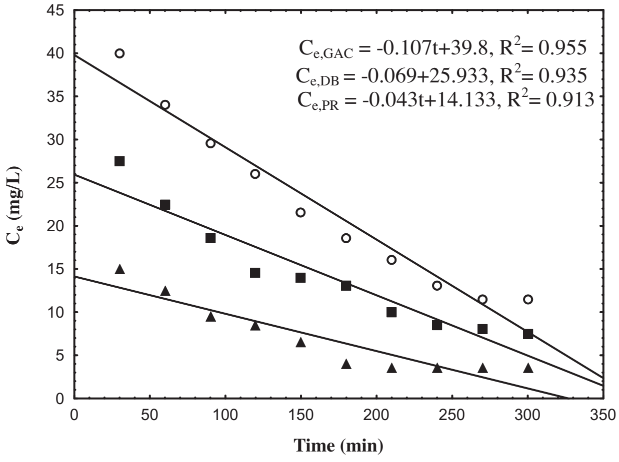

Fig. 7. Effluent concentration vs. time for the adsorption of Cd^{2+} onto selected adsorbents; pH 5, initial concentration 50 mg/L, adsorbent dosage 3 g and temperature 30˚C.

negative values reflect a more negatively favorable adsorption process. The Gibbs free energy values were obtained as −8.324, −11.785, and −17.125 kJmol^{-1} which correspond, respectively, to GAC, DB, and PR. The negative ΔG° values indicated the feasibility of these adsorbents and spontaneity of the adsorption and that the adsorption process is exothermic in nature [18].

Table 6
Thermodynamic equilibrium apparent constant (K_c) and Gibbs free energy (ΔG°) at 30 ± 2˚C

Adsorbent	Equilibrium constant, K_c	Gibbs free energy, ΔG° kJmol^{-1}
GAC	49.432	−8.324
DB	58.652	−11.785
PR	73.872	−17.125

3.8. Mechanism of metal ions adsorption by GAC, DB, and PR

In order to find out which functions are responsible for cadmium(II) adsorption, FT-IR analysis of GAC, DB, and PR was carried out. Figs. 8–10 show the spectra of raw and treated adsorbate samples.

The FTIR spectra of GAC in the range of 500–4,000 cm^{-1} shows less intensity in functional groups that responsible for adsorption process compared with DB and PR. From the results shown in Fig. 8, it can be concluded that the band between 3734.19–2360.87 indicating the presence of OH and NH groups, the C=O stretching of carbonyl in carbonized acid at

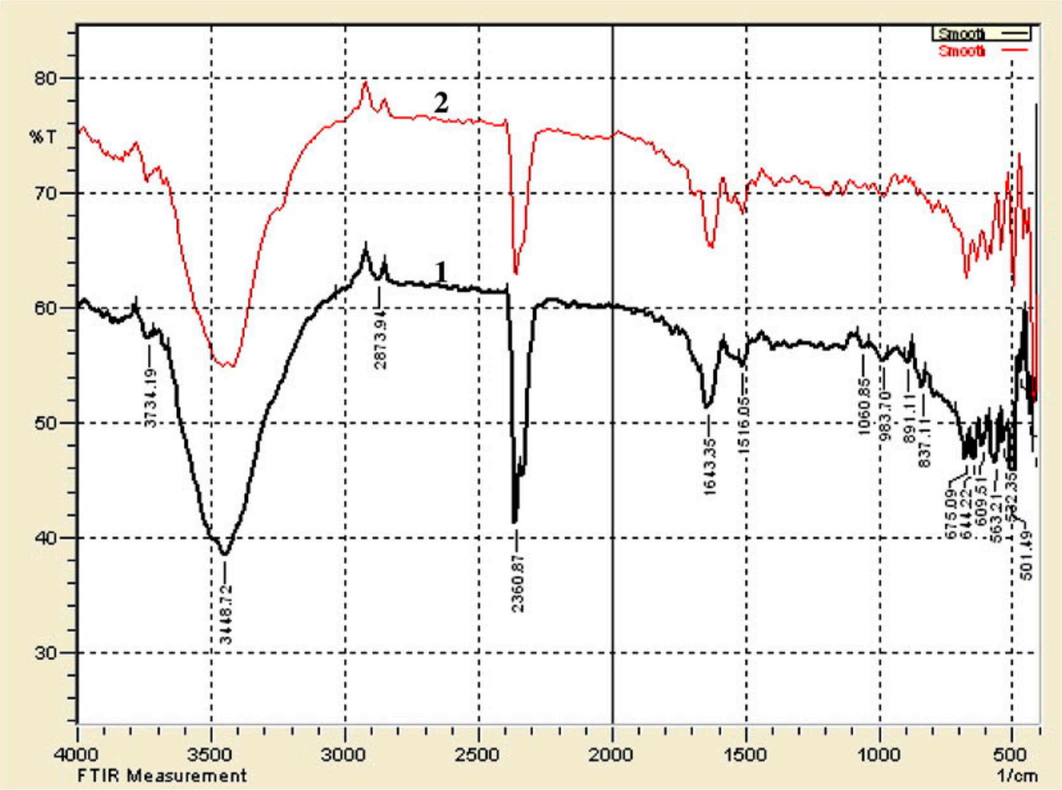

Fig. 8. FTIR spectra of GAC (1) before, (2) after Cd^{2+} adsorption.

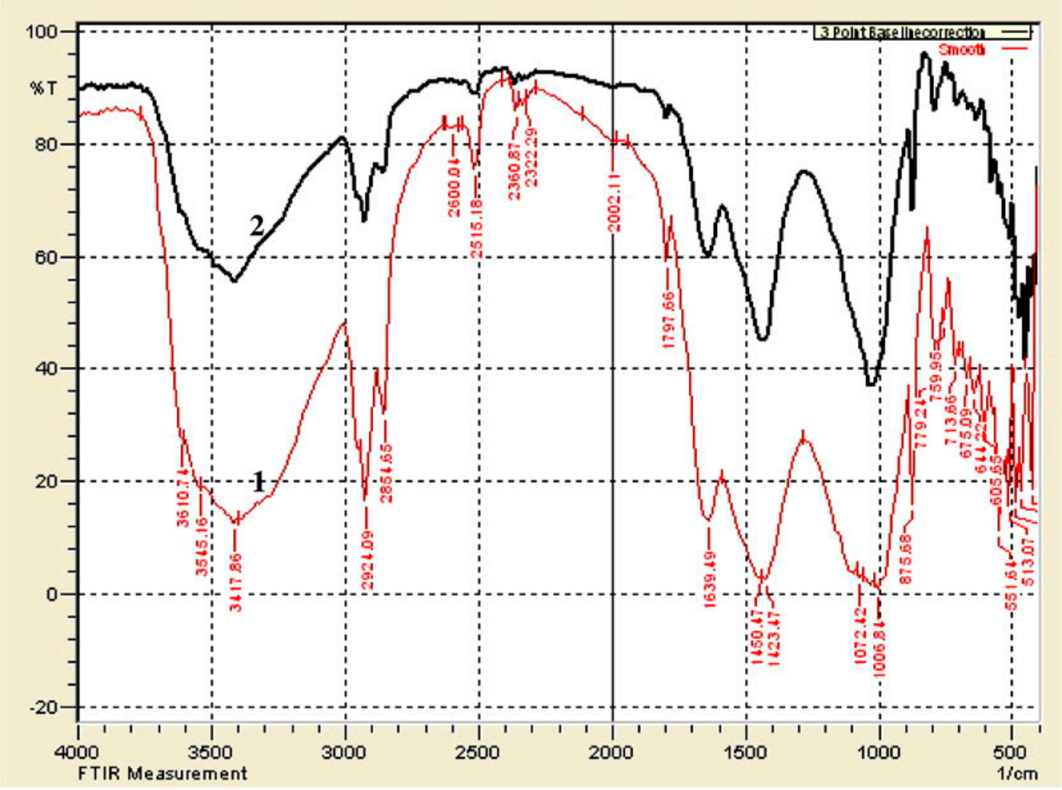

Fig. 9. FTIR spectra of DB (1) before, (2) after Cd^{2+} adsorption.

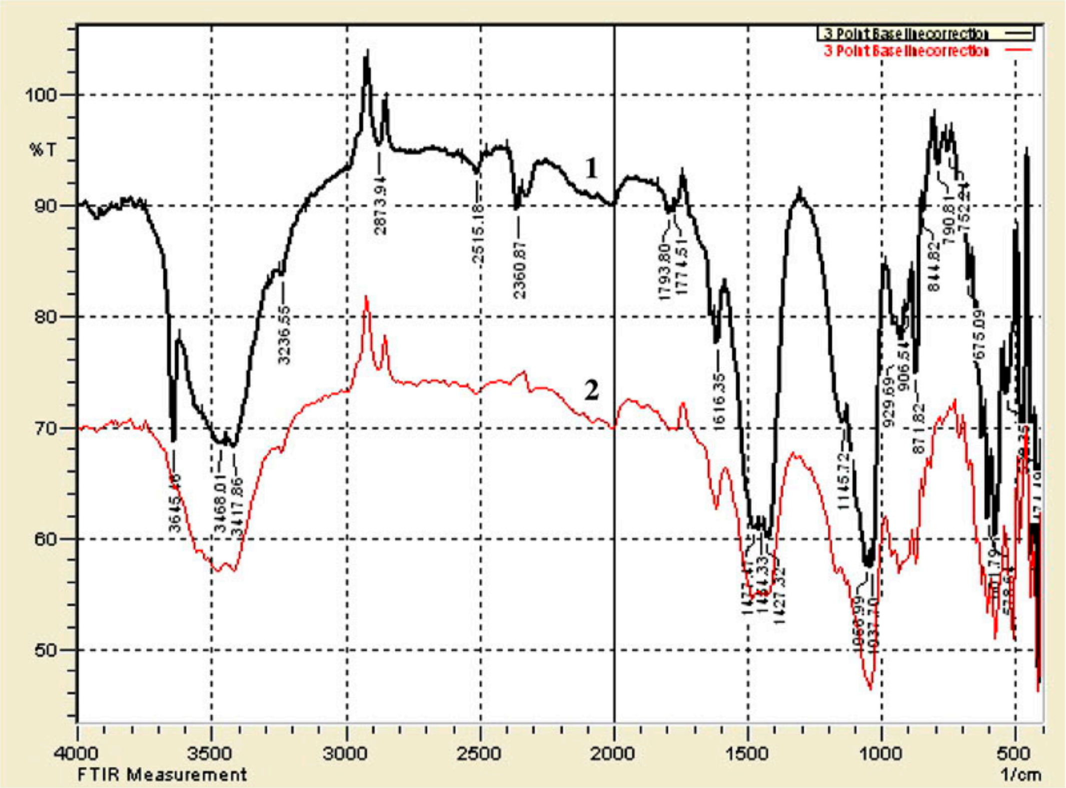

Fig. 10. FTIR spectra of PR (1) before, (2) after Cd^{2+} adsorption.

1643.35 cm^{-1}, C=C stretching of the aromatic compound and alcohol at 1516.05 cm^{-1}, and C–O stretching of carboxylic acid at 16 cm^{-1} and other groups [38]. However, GAC is used efficiently for organic pollutant removal. Ali et al., compare the adsorption capacity of GAC towards lead (metal ion) and phenol (organics). They found that, the maximum loading capacity (qm) of the phenol was 66.8234 mg/g while it was just about 37.0370 mg/g, for lead. These behaviors due to limited functional groups responsible for metals adsorption onto activated carbon surface by electrostatic attraction [39].

According to FT-IR DB Fig. 9, the band between 3610.74–3417.86 cm^{-1} indicating the presence of OH, NH, and NH_2 groups. A 2924.09 cm^{-1} asymmetric vibration of CH, 2854.65 cm^{-1} symmetric vibration of CH and 2600.04 cm^{-1} symmetric vibration of CH. 2515.18, 2360.87 and 1797.66 cm^{-1} vibration of carboxylic acids, 1639.49 and 1562.34 cm^{-1} stretching vibration of C=O and NH peptidic bond of proteins. A 1419.61 cm^{-1} of phenolic OH and CO stretching. The 1080.14 cm^{-1} band is vibration of C–O–C polysaccharides. A 1,029 cm^{-1} band is vibration of C–O–C and OH groups. The <1,000 cm^{-1} is finger print zone which are phosphate and alkyl halides groups [40].

Fig. 10 show the spectra of raw and treated phosphate samples. The sharp bands near 671.82, 929.69, and 1145.72 define the Si–P stretches. The peak at 790.81 cm^{-1} is associated with the PO_{4-3} group. The bands between 1068.99–1037.70 cm^{-1} are Si–O and those at 1427.32, 1454.33, and 1616.35 are C=O, 1774.51–2360.87 is P–H. The sharp peak at 36445.46 and 3468.01 is the O–H stretch. All peaks defined above are related with the mineralogical composition of the sorbent (PO_4, SiO_2, and CO_3). The decrease and increase in intensities at particularly peaks define the change in the structure with Cd^2 and imply the related functional groups to be responsible for the adsorption [41].

4. Conclusions

In batch adsorption system, this study showed that locally available materials, such as PR and DB, can be used as efficient adsorbents as compared by commercial GAC for cadmium ions removal. The pH experiments revealed that the governing factor effecting the adsorption characteristics of the selected adsorbents are competition of the H^+ ions with Cd^{2+} ions at very low pH values, maximum adsorption at pH 5. Increase in mass of adsorbent lead to increase in Cd^{2+}

adsorption due to increase in number of adsorption sites. Maximum uptake of Cd^{2+} obtained at adsorbent dose of 3 g for all the adsorbents. Data showed that PR had considerable potential for the removal of cadmium(II) from aqueous solution. Langmuir isotherm was fitted very well with experimental data. From the Langmuir isotherm, the maximum adsorption capacity for the cadmium(II) ions was found as 17.757, 24.677, and 31.379 mg/g onto GAC, DB, and PR, respectively. Optimum adsorption conditions for cadmium(II) ions removal are as follows: pH 5, contact time 270 min, and adsorbent dose 3 g. The variation in sorption capacities between the various adsorbents could be related to the type and concentration of surface group responsible for the adsorption of cadmium ions from solution. The kinetics of the Cd^{2+} adsorption on the different adsorbents was found to follow a first-order-rate mechanism. Thermodynamic calculations showed that the Cd^{2+} adsorption was spontaneous in nature. The range of Gibbs free energy values ΔG° varies from -8.324 for GAC to -17.125 for PR. More studies are needed to investigate the applicability of these adsorbents under real condition such as industrial effluent treatment.

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