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Equilibrium, kinetics and thermodynamics studies of Cd sorption onto a dithizone-impregnated Amberchrom CG-300m polymer resin

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Abstract Amberchrom CG-300m, a styrene acrylic ester polymer resin, was studied for the first time as sorbent for metal ion sorption in a solid-phase extraction system. The polymer sorbent was modified via impregnation with dithizone to improve its efficiency. Efficiency of the modified sorbent improved by more than 47%. The loading capacity of the resin is 3.2 mg dithizone per gram of sorbent. The mechanisms of Cd(II) sorption from aqueous solutions are presented. Capacity of the modified resin for Cd(II) was investigated in batch experiments as a function of pH, initial metal ion concentration, temperature and time. Maximum capacity of 0.551 mg Cd(II) per gram of sorbent was achieved. The dimensionless separation factor, $0 < R_L < 1$, associated with the Langmuir isotherm (at $T = 294$ K) signifies sorption of Cd(II) was favorable, as do negative values of free energy of sorption (ΔG) at temperatures exceeding 293 K. Sorption was endothermic ($\Delta H > 0$) while $\Delta S > 0$ reflects the affinity of the sorbent towards Cd(II). The pseudo-second order model proved to be the best fit model for Cd(II) sorption kinetics data. Particle-diffusion models suggest sorption follows film as well as pore diffusion mechanisms.

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1. Introduction

The selectivity of any separation system is predominantly associated with the sorption mechanism, which in turn depends on the interactions between the sorbate and sorbent. Chelation is one type of sorbate-sorbent interaction that provides a significantly higher degree of separation selectivity than conventional cation-exchange resins. Chelation has been widely employed in traditional technologies such as solvent extraction to concentrate, quantify and separate metal ions (Nesterenko et al., 2011). However, solvent extraction suffers from many

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drawbacks including labour intensiveness, large scale use of organic solvents, finite aqueous solubility of extractants diluents and modifiers, and associated problems related to waste disposal (Saha et al., 2000). Solid Phase Extraction (SPE) overcomes these drawbacks as it is simple, efficient and cost-effective (Behbahani et al., 2013).

The choice of sorbent is essential to the performance and efficiency of a SPE system; for this reason research into various types of sorbent is ongoing (Cheng et al., 2012). To date, novel sorbents such as chitin (Omar, 2013), coated alumina (Chandio et al., 2013), zeolite (Shirzadi and Nezamzadeh-Ezhieh, 2017; Mudasir et al., 2016), bentonite (Shakerian et al., 2016) and cellulose acetate nanosponges (Zargar et al., 2017) have been modified with dithizone. On the other hand, macroporous resins have proven outstanding as solid phase because of their high surface area, uniform pore size, good sorbent properties and durability. In the last decade, Amberlite® XAD® resins in particular have been extensively used in SPE systems (Dolley and van der Walt, 2014; Meena et al., 2014; Ciopec et al., 2010; Dave et al., 2010). The Amberchrom® line of styrenic polymeric resins (Amberchrom® CG-71, CG-161, CG-300 and CG-1000) are smaller particle versions of Amberlite® XAD® resins, designed for higher performance purifications that are not possible with the larger XAD resins (Sigma-Aldrich Co., 1997). Amberchrom® CG-71 was successfully employed (Dolley et al., 2006) in the production and isolation of Cu-64 and Cu-67 radionuclides from Zn target material and other radionuclides. Literature seems to reveal no instances where Amberchrom CG-300m resin was used as sorbent for heavy metal ion extraction.

The most efficient SPE systems have been demonstrated using sorbents with chelating groups immobilised at the external surface and inside the pores of micro-particles of organic polymers. The chelating group can be attached to the support through chemical bonding or physical sorption (*impregnation*). Impregnation, as opposed to covalent linking of complexing molecules to a polymeric material, is convenient, effective and economical. The incorporation of an ionic liquid extracting reagent into a polymer matrix gives to *Solvent Impregnated Resins* (SIRs). The impregnated extractant can exhibit strong affinity for the polymeric matrix, yet it still behaves as if in the liquid state (Cortina et al., 1997; Cortina et al., 1993; Warsawsky et al., 1981). SIRs are versatile (Kabay et al., 2010) – it is possible to obtain many combinations of polymeric resins impregnated with readily available extractants that are tailor-made for specific applications. SIRs modified with chelating ligands combine the triple action of ion-exchange, chelation and physical adsorption (Saha et al., 2000).

Chelating reagents with thiol groups ($R-SH$, where R represents an alkyl or other organic substituent) are often used in SPE for separation of heavy metals because they form stable complexes with these metals (Chwastowska et al., 2008). For this reason, dithizone has previously been described (White, 1935) as a reagent of the first class and a heavy metal reagent *per excellence* (Koroleff, 1950). Its selectivity and sensitivity make it suitable to prepare sorbents for removal and pre-concentration of a variety of metal ions. Dithizone-impregnated resins have been used for the determination and/or separation of Cu (Dolley and van der Walt, 2014;

Chwastowska et al., 2008; Rajesh and Manikandan, 2008; Dolley et al., 2006); Zn (Dolley and van der Walt, 2014; Chwastowska et al., 2008; Dolley et al., 2006) and Pb (Chwastowska et al., 2008; Rajesh and Manikandan, 2008). Sorption of Cd onto a dithizone-impregnated polymer was reported (Chwastowska et al., 2008).

A review of published literature points to the lack of research into the *mechanisms* of metal sorption onto dithizone-modified polymeric substrates. In the present work on the sorption mechanism of Cd(II), a solvent-impregnated resin (SIR) was prepared by impregnating the Amberchrom® CG-300m resin with dithizone. The impregnation was performed using a method previously employed for the modification of Amberlite XAD-8 (Dolley and van der Walt, 2014). This method was chosen because of its ease and simplicity, and in addition, does not require the use of organic solvents. After evaluating the impregnation capacity of the resin, a preliminary investigation focused on the effect of pH on the extraction of Cd(II).

2. Experimental

2.1. Materials

Amberchrom® CG-300m is a styrene acrylic ester polymer resin supplied as white insoluble beads suspended in isopropyl alcohol. The bead diameter is 50–100 μm with a mean pore size of 300 Å.

All reagents were of analytical or equivalent grade and used without further purification. Dithizone was a product of Sigma-Aldrich.

Cd^{2+} ion was obtained from its oxide, CdO (BDH Chemicals Ltd.). A 1000 $\text{mg}\cdot\text{L}^{-1}$ stock solution was prepared by dissolving 285.6 mg of salt in 250 mL dilute hydrochloric acid. Working solutions in the concentration range 0.1–1.0 mg/L were prepared by serial dilution of the stock solution with de-ionised water.

The pH of the solutions was measured with a Basic 20 + CRISON pH-meter. The following buffers were used to adjust pH: 0.2 M HCl/Cl^- (pH 1–2); 0.1 M $\text{CH}_3\text{COOH}/\text{CH}_3\text{COO}^-$ (pH 3.0–6.0); $\text{H}_2\text{PO}_4^-/\text{HPO}_4^{2-}$ (pH 7) and $\text{H}_2\text{BO}_3/\text{Na}_2\text{B}_3\text{O}_7$ (pH 8–10). Deionised water was obtained from a Milli-Q water-purification system. All glassware was soaked in dilute nitric acid and thoroughly rinsed with de-ionised water before use.

2.2. Conditioning and impregnation of Amberchrom® CG300m

The resin was washed with 0.5 M NaOH, followed by multiple washings with deionised water before use, until the pH of the final washing was in the range 6.5–7.0. The cleaned resin was dried overnight in an oven at 50 °C and stored in a desiccator before use.

The impregnation solution was prepared by dissolving dithizone in 0.5 M NaOH solution to obtain an orange coloured solution. The solution also contained 10% (v/v) isopropyl alcohol for more efficient mixing of the phases. The cleaned resin was added to the solution and the resultant slurry was agitated (at 150 rpm) until equilibrium was established.

Concentrated hydrochloric acid was added drop wise to the equilibrium mixture until the orange coloured solution turned black/deep purple. The impregnated product was filtered using a funnel fitted with a sintered glass, and washed with deionised water to remove excess hydrochloric acid.

The impregnated resin was used immediately due to the proneness of the entrapped dithizone ligand to oxidation when exposed to light or air. Impregnation conditions of dithizone amount, NaOH concentration and agitation time were investigated for optimisation.

The impregnation capacity of the resin was determined by stripping the trapped dithizone from known amounts of impregnated resin with chloroform, and measuring the absorbance of dithizone in the eluate at $\lambda = 605$ nm (Jenway 7305 UV-vis spectrophotometer; 10 mm quartz cell). A calibration curve was constructed to determine the dithizone concentration in the eluate.

2.3. Physico-chemical characterisation of the impregnated resin

The FT-IR spectra of the unmodified Amberchrom® CG-300m (ACG300m) and impregnated Amberchrom® CG-300m-dithizone resins (ACG-DTZ) were recorded on a Spectrum Two® FT-IR spectrometer by Perkin-Elmer.

A Scanning Electron Microscope (Zeiss Auriga FEG-SEM) was used to study the surface morphology of the resin before and after impregnation. Sample preparation was done with a Quorum Q150 T ES sputter coater. The sample was coated with an Au-Pd (60:40) film of 10 nm thickness prior to analysis.

2.4. Sorption equilibrium

The effects of pH, sorbent dosage and initial ion concentration on the sorption of Cd^{2+} ions onto dithizone-impregnated Amberchrom® CG-300m were studied in batch experiments. A known amount of the impregnated resin was mixed at ambient temperature with 50 mL of aqueous solution containing the metal ion and 5% v/v isopropyl alcohol to ensure efficient mixing. Mixtures were initially shaken overnight on an orbital shaker at 150 rpm, but once the time to reach sorption equilibrium had been established, the agitation period was adjusted accordingly. After agitation, the suspensions were filtered and the metal ion content in the filtrate was determined by Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES). The amount of metal sorbed, q_e , was calculated using the formula:

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

The percent metal ion sorption was calculated as follows:

$$\% \text{ Sorption} = \frac{(C_0 - C_e)}{C_0} \times 100 \% \quad (2)$$

[C_0 = initial concentration ($\text{mg}\cdot\text{L}^{-1}$); C_e = equilibrium concentration ($\text{mg}\cdot\text{L}^{-1}$); V = volume of sorbate solution (L); m = mass of sorbent (g)].

To study the effect of sorbent dosage on Cd sorption, the amount of resin was increased from 50 mg to 250 mg at constant pH (6), temperature ($T = 294$ K) and volume ($V = 50$ mL). The concentration-dependence of Cd sorption

was studied in the range $100 \mu\text{g/L} - 2300 \mu\text{g/L}$ at $\text{pH} = 6$. Sorption data was modeled on Freundlich, Langmuir, Temkin and Dubinin-Radushkevich isotherms.

2.5. Sorption kinetics and diffusion mechanisms

The sorption rate from a 200 mL solution containing 400 ± 0.5 mg of resin, $[\text{Cd}^{2+}] = 1.131$ mg/L and $\text{pH} = 6$ was studied over 180 min. 5 mL aliquots of the supernatant solution were drawn at pre-determined time intervals and analysed for metal ion content by ICP-OES.

Data was fitted to pseudo-first order (PFO) and pseudo-second order (PSO) kinetic models. Weber-Morris and Homogeneous Particle Diffusion models were applied to differentiate between film or particle diffusion as rate-determining step. The most suitable model was chosen based on “goodness of fit” using the coefficient of correlation (R^2) as error function. Where appropriate, the agreement between experimental data and calculated values was used as second criterion for “goodness for fit”.

2.6. Thermodynamics studies

Temperature dependence of Cd sorption was studied at $\text{pH} 3.73$ and metal ion concentration $[\text{Cd}^{2+}] = 2.183$ mg/L in the temperature range 283–298 K. Samples were shaken overnight in a shaking incubator (Labcon). 5 mL aliquots of the supernatant were drawn and analysed for its metal ion content. A plot of $\ln K_d$ versus $1/T$ (K^{-1}) was constructed and used to derive the values of the thermodynamic parameters ΔH , ΔS and ΔG .

3. Results and discussion

3.1. Impregnation

Impregnation of Amberchrom® CG-300m with dithizone did not reach the plateau characteristic to most impregnation procedures. A black residue, attributable to possible leaching of dithizone, developed in the impregnation solution when the amount of dithizone in solution exceeded 0.8 mg per 100 mg of resin. A maximum quantity of 0.8 mg H_2Dz per 100 mg resin was maintained in all subsequent impregnation procedures.

Impregnation decreased with increasing concentration of NaOH. However, leaching presented again at $[\text{NaOH}] < 0.5$ M. All impregnation procedures were subsequently done in 0.5 M NaOH. Impregnation was found to reach equilibrium after 30 min of agitation (@ 150 rpm). The average amount of dithizone impregnated onto Amberchrom® CG-300m at optimum conditions was 3.2 mg/g resin ($n = 14$; $\text{RSD} = 6.97\%$). This was more than double the dithizone loading (~ 1.4 mg/g resin) achieved by Dolley et al. (2006) on Amberchrom® CG-71.

3.2. Characterization of Amberchrom® CG-300m-dithizone

Surface morphology studies of the Amberchrom resin (before and after impregnation) as determined using SEM are shown in Fig. 1. In Fig. 1A the varying pore sizes (between 35.62

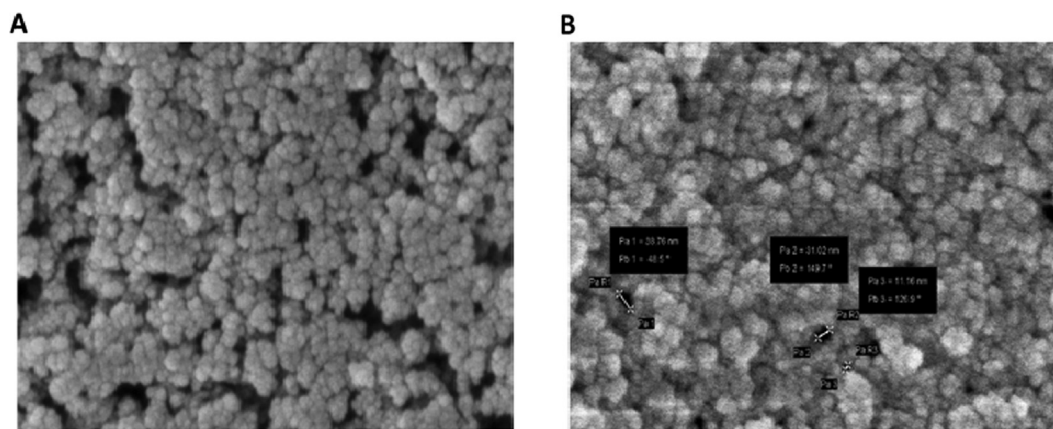


Fig. 1 SEM images of (A) unmodified and (B) impregnated Amberchrom CG-300m resin.

and 94.65 nm) of the unmodified resin are clearly visible. The SEM image of the dithizone-impregnated resin (Fig. 1B) shows a significant decrease in pore size; a pore size as small as 11.16 nm was recorded. This decrease in the pore morphology was indicative of the uptake of dithizone within the resin structure.

Fig. 2 shows the FT-IR spectrum of ACG300m, ACG300m-DTZ and ACG300m-DTZ-Cd. The ACG300m shows peaks at 3387 cm^{-1} , 2924.4 cm^{-1} , 1628.4 cm^{-1} and 1449.5 cm^{-1} corresponding to O—H, C—H, C=O and C—O stretching respectively. The impregnated ACG300m-DTZ (Fig. 2b) exhibited similar bands (3387 , 2924.4 and 1628.4); in addition is observed a shift of the absorption band ν (2961 cm^{-1}) typical of the dithizone molecule to ν (2972 cm^{-1}), development of a broad band around 1362.2 cm^{-1} (C=S) and a weak band at 1122.2 cm^{-1} (—N—N—) (Zargar et al., 2017), indicating the presence of dithizone in the polymer substrate. The latter two bands disappear after coordination with the metal (Fig. 2c), indicating coordination of the metal involved the S,N donor atoms of the ligand.

3.3. Sorption equilibrium

3.3.1. Effect of pH

The pH of the sorption medium plays a critical role in SPE as it influences metal-chelate formation and subsequent metal ion extraction (Wang et al., 2012). Generally, H^+ ions compete with metal ions for reaction sites on the sorbent. An alkali medium favours the formation of the monobasic dithizonate ion (HDz^-) that facilitates complex formation via bi-dentate coordination involving the N- and S-atoms. Conversely, at low pH (acidic medium), protonation of the N-atoms of the dithizone molecule inhibits coordination involving the N donor atom; formation of the metal ion complex via N- and S-atoms subsequently becomes unfavourable.

Sorption from a solution of initial Cd^{2+} concentration ($C_0 = 1.131\text{ mg/L}$) increased rapidly with pH before reaching a maximum capacity of 0.551 mg/g at $\text{pH} = 8$ (Fig. 3). The amount sorbed was equivalent to a percent Cd(II) removal of 97.61%.

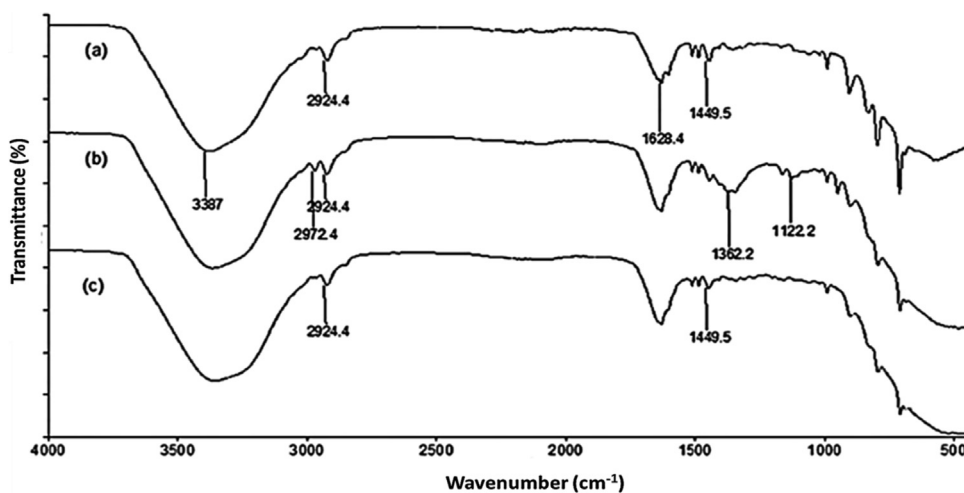


Fig. 2 FT-IR spectra of (a) ACG300, (b) ACG300-DTZ (c) and ACG300-DTZ-Cd.

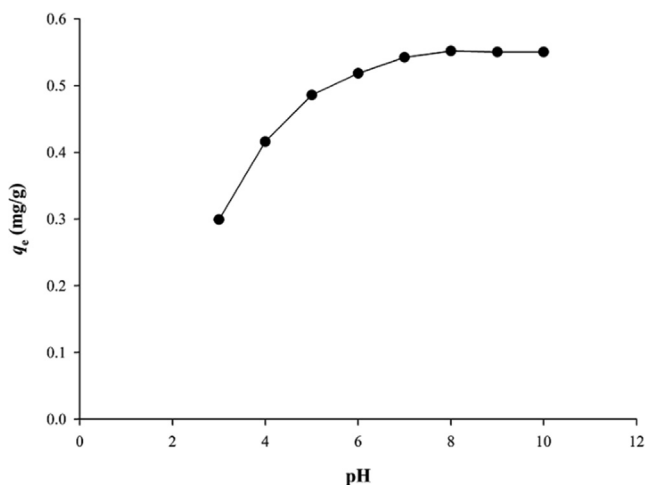


Fig. 3 Variation of sorption capacity (q_e) of Cd(II) with pH.

3.3.2. Sorbent dosage

Cd(II) sorption increased with increasing amount of sorbent until it reached 0.550 mg/g when sorbent dosage was 250 mg, in other words at volume-to-mass ratio (V/m) equal to 0.2 mL/mg.

This value was in agreement with the maximum sorption (0.551 mg/g) attained at pH = 8 using 100 mg sorbent and the same initial concentration. In all subsequent experiments a V/m ratio of 0.2 mL/mg was maintained.

3.3.3. Sorption isotherms

The amount of Cd^{2+} sorbed (q_e) increased with increasing initial concentration (C_0) (Fig. 4). At $[\text{Cd}^{2+}]_0 > 1.131$ mg/L, sorption increased at a slower rate until it reached a maximum value of 0.478 mg/g at $C_0 = 1.131$ mg/L. At $[\text{Cd}^{2+}] > 1.13$ 1 mg/L, sorption ceased as reaction sites were probably depleted. Based on this observation it can be argued that Cd^{2+} sorbed onto the sorbent in monolayer fashion after which no further interaction occurred between sorbed ions and those remaining in the sorbate medium.

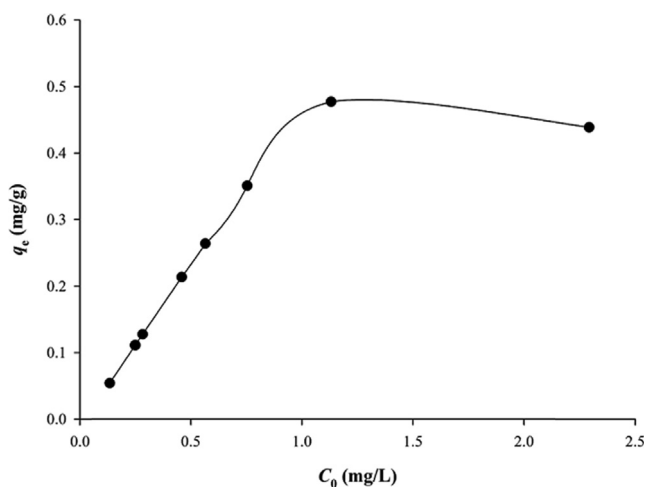


Fig. 4 Variation of sorption amount (q_e) with initial Cd(II) concentration (C_0); pH = 6.

The linearly regressed Langmuir isotherm provided the best fit to the experimental data as its correlation coefficient ($R^2 = 0.9810$). This suggested that Cd(II) ions sorbed onto the resin beads as a monolayer of ions, and that sorption of Cd(II) ions occurred at specific homogeneous sites up to a maximum. Cd sorption data was modeled by the Langmuir isotherm as follows:

$$\frac{C_e}{q_e} = 2.1647 C_e + 0.1413 \quad (3)$$

From Eq. (3), the theoretical maximum monolayer sorption capacity ($Q_0 = 0.462$ mg/g) and binding strength ($K_L = 15.32$ L·mg⁻¹) of the impregnated resin were calculated. The Q_0 -value was in very good agreement with the experimental value, $q_{e,\text{exp}} = 0.478$ mg/g at the given pH, while the relatively large K_L -value attested to the exceptional binding strength of dithi-zone with Cd^{2+} . The separation factor, R_L , was calculated using the formula:

$$R_L = \frac{1}{1 + K_L C_0} \quad (4)$$

The value of the dimensionless R_L predicts the favorability of the sorption process at different initial concentrations (C_0); values between zero and one suggest sorption is favorable. Since the values of R_L over the initial Cd^{2+} concentration range 100–2300 µg/L were between 0 and 1, it implies that Cd sorption onto the modified resin was favorable. A summary of the linear regression equations, constants and correlation coefficients is provided in Table 1:

3.4. Sorption reaction kinetics

Sorption uptake increased with time but equilibrium was not yet attained at $t = 180$ min (Fig. 5).

In experiments that fall outside the scope of this article, it was found that kinetics increased drastically when the resin was used wet; in column experiments, Cd was completely sorbed onto the resin in less than 90 s.

The transient behavior of the batch sorption process of Cd^{2+} from each solution was analysed using Lagergren pseudo-first order and Ho and McKay pseudo-second order models (Ho et al., 2000) respectively. In differential form, the Lagergren pseudo-first order equation can be presented as follows:

$$\frac{dq_t}{dt} = k(q_e - q_t) \quad (5)$$

After integration and applying boundary conditions $t = 0$ to $t = t$ and $q_t = 0$ to $q_t = q_t$, the integrated form of the Lagergren equation (Uzunkavak and Özdemir, 2019) becomes:

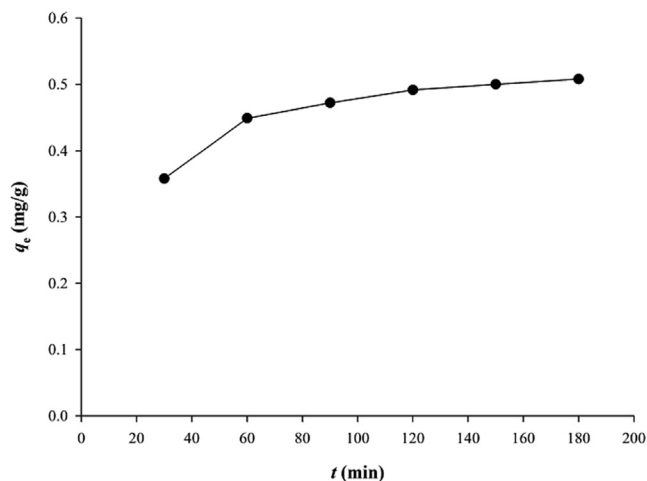
$$\log(q_e - q_t) = \log q_e - \frac{k}{2.303} t \quad (6)$$

[q_e = equilibrium concentration of the sorbed ion (mg·g⁻¹); q_t = concentration of the sorbed ion at time t (min); k is the pseudo-first order rate constant (min⁻¹).]

A plot of $\log(q_e - q_t)$ against t (min) will produce a straight line with slope $-\frac{k}{2.303}$ and intersects the vertical axis at the value of $\log q_e$. However, the experimental value of q_e generally differs from the value obtained from the plot because the parameter q_e does not represent the true number of available sites (Ho et al., 2000). The PFO model is valid only for the initial

Table 1 Summary of sorption isotherms parameters.

Isotherm	Regression equation	Parameters	Correlation coefficient (R^2)
Langmuir	$C_e/q_e = 2.1647q_e + 0.1413$	$Q_0 = 0.462$ mg/g $K_L = 15.32$ L/mg	0.9810
Temkin	$q_e = 0.088 \ln C_e + 0.4951$	$K_T = 277.588$ L/mg $\frac{RT}{b} = 0.088$ J/mol	0.6081
Dubinin-Radushkevich	$\ln q_e = -0.0205 \varepsilon^2 - 0.439$	$E = 4.939$ kJ/mol $X_m = 0.645$ mg/g $\beta = 0.0205$ mol ² /kJ ² (6.984 kJ/mol)	0.6065
Freundlich	$\log q_e = 0.3649 \log C_e - 0.2545$	$K_F = 0.557$ L/mg	0.4458

**Fig. 5** A plot of q_e versus t ; $[Cd^{2+}]_0 = 1.131$ mg/L; pH = 6; $T = 294$ K.

stages of sorption when $q_t \ll q_e$; as q_t approaches q_e , the term $\log (q_e - q_t)$ becomes infinitely large. If sorption data fits the Lagergren pseudo-first order kinetic model, sorption is likely to occur via physical processes.

The pseudo-second order model is based on the assumption that sorption supports second order chemisorption according to the rate law:

$$\frac{dq_t}{dt} = k(q_e - q_t)^2 \quad (7)$$

The driving force ($q_e - q_t$) of sorption is proportional to the available fraction of active sites. For the boundary conditions $t = 0$ to $t = t$ and $q_t = 0$ to $q_t = q_t$, the integrated form of Eq. (7) becomes:

$$\frac{t}{q_t} = \frac{1}{q_e} t + \frac{1}{h} \quad (8)$$

[$h = k_2 q_e^2$ (mg/g·min) is the initial sorption rate; k_2 (g/mg·min⁻¹) is the rate constant of the second order equation.

If sorption data fits the pseudo-second order kinetic model, sorption is likely to occur via chemical processes.

A plot of t/q_t versus t should produce a straight line from the slope of which the sorption capacity can be derived. Fig. 6 shows plots of PFO (6A) and PSO (6B) models respectively.

From the slopes of the respective graphs, the rate constants were derived: $k_1 = 0.018$ min⁻¹ and $k_2 = 0.121$ g/mg·min⁻¹.

A larger correlation coefficient ($R^2 = 0.9998$) suggested Cd sorption was better modeled by pseudo-second order kinetics, thus suggesting chemisorption as driving force. The choice of PSO model as better fit was confirmed by good correlation between empirical sorption capacity value ($q_{e, \text{exp}} = 0.508$ -mg/g) and the value derived from the slope of the graph ($q_{e, \text{calc}} = 0.478$ mg/g). This value was in agreement with values obtained during sorption equilibrium studies reported earlier (see Sections 3.3.1 and 3.3.2).

The sorption capacity of the unmodified resin as a function of initial Cd^{2+} ion concentration was investigated at pH = 8 and found to be only 0.374 mg/g. The comparison of maximum Cd(II) sorption capacities (q_m) by various sorbents is summarised in Table 2.

3.5. Diffusion mechanism

Experimental data was applied to the Weber-Morris model. According to this model, sorbate uptake (q_t) varies almost proportionally with t^0 as opposed to t (Alkan et al., 2007).

$$q_t = K_{ad} \sqrt{t} \quad (9)$$

[K_{ad} is the rate constant of intra-particle transport (mg/g·min^{0.5}).

A linear graph of q_t vs. $\sqrt{t}$ that passes through the origin implies intra-particle diffusion is the sole rate-determining step. However, the graph may not always pass through the origin as sorption diffusion kinetics may be controlled by film diffusion and pore diffusion simultaneously (Qiu et al., 2009). The presence of both diffusion regimes lead to multi-linear plots (Saha, 2010). In cases of absorbents whose pore sizes were extensive (micro-, meso- and macropores) up to three linear sections have been obtained (Nawar and Doma, 1989). Doke and Khan (2012) extended the Weber-Morris equation by including a constant (I) which is related to the boundary layer thickness (mg·g⁻¹):

$$q_t = K_{ad} \sqrt{t} + I \quad (10)$$

A plot of q_t versus t^0 (Fig. 7) suggests intra-particle diffusion was not the only diffusion mechanism that controlled the rate of Cd migration from the bulk solution into the resin pores. Failure of the graph to pass through the origin could be attributed to external resistance to mass transfer by the liquid film surrounding the resin particles. Multi-linear plots suggest varying pore sizes influenced the diffusion of Cd^{2+} ions through the resin interior.

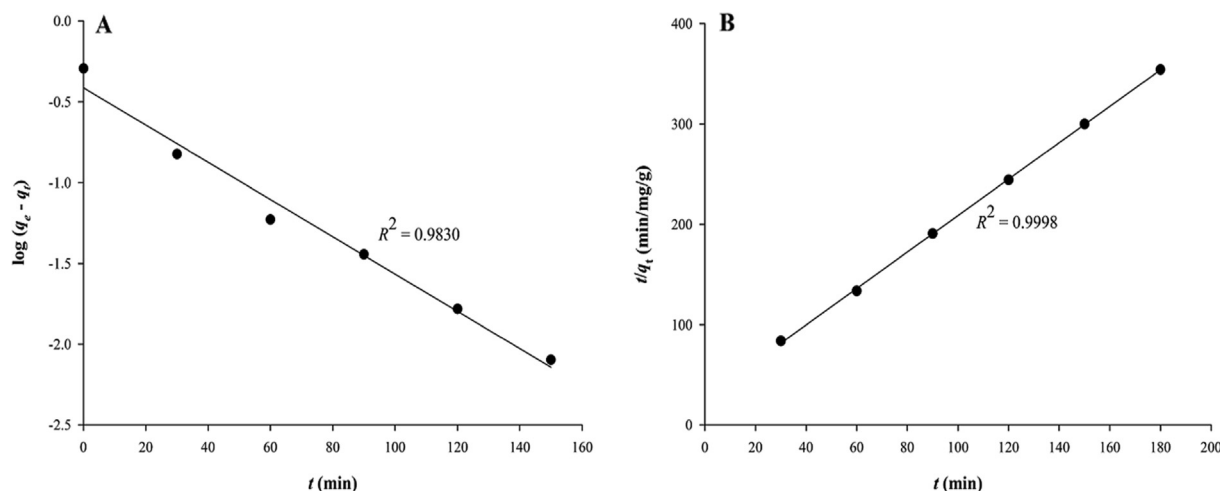


Fig. 6 Pseudo-first order (A) and pseudo-second order (B) plots of Cd sorption.

Table 2 Comparison of maximum Cd sorption capacity, q_m , by various dithizone-modified sorbents.

Sorbent	Sorption capacity, q_m (mg/g)	Modification	Technique	References
Amberlite XAD-2	83.2	Chemical rxn	Column	Wu et al. (2006)
Naphthalene	0.5	Impregnation	Batch	Costa et al. (2002)
Styrene-DVB copolymer	5.6	Chemical rxn	Batch	Chwastowska and Kosiarska (1988)
Poly (EGDMA-HEDA) microbeads	18.3	Chemical rxn	Batch	Salih et al. (1998)
Cellulose acetate nanospheres	195	Impregnation	Batch	Zargar et al. (2017)
Styrofoam	29.1	Impregnation	Batch	Memon et al. (2006)
Nanoporous fructose	101	Impregnation	Column	Behbahani et al. (2013)
Amberchrom CG-300m	0.6	Impregnation	Batch	This study

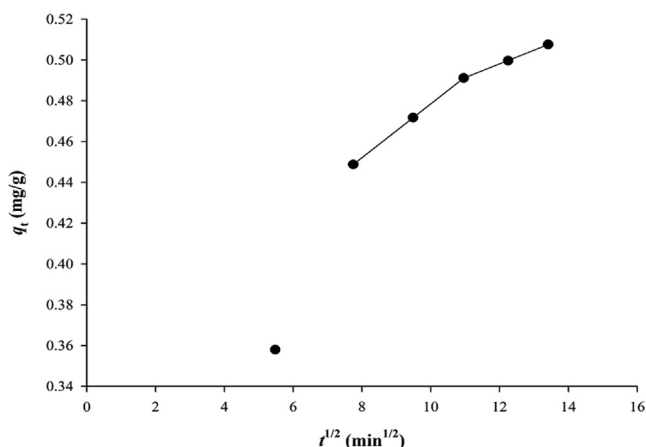


Fig. 7 Weber-Morris plot for intra-particle diffusion of Cd.

According to the HPD model, mass transfer in an amorphous and homogeneous sphere is represented by the differential equation (Qiu et al., 2009):

$$\frac{\partial q}{\partial t} = \frac{D_s}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial q}{\partial r} \right) \quad (11)$$

[D_s is the intra-particle diffusion coefficient, r = radial position and q the sorption quantity of solute in the solid varying with radial position at time t .]

Assuming that film resistance is negligible, the solution to Eq. (11) is:

$$\frac{\bar{q}}{q_\infty} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left(-\frac{D_s n^2 \pi^2 t}{R^2}\right) \quad (12)$$

[R = total particle radius; q_∞ represents the average concentration in the solid at infinite time.]

Assuming short-time data where the fractional attainment of equilibrium, $X = \frac{\bar{q}}{q_\infty} < 0.3$ the solution to Eq. (12) is:

$$X = 6 \left(\frac{D_s}{R^2 \pi} \right)^{1/2} t^{1/2} \quad (13)$$

If data is recorded over a long time, i.e. $q_e = q_\infty$, the higher terms of the summation in Eq. (12) become small and are negligible and it then becomes:

$$\ln(1 - X) = \ln \frac{6}{\pi^2} - \left(\frac{D_s \pi^2}{R^2} \right) t \quad (14)$$

The intra-particle diffusion coefficient (D_s) can be derived from the slope of a linear plot of $\ln(1-X)$ versus t . The magnitude of D_s is dependent upon the nature of the sorption process. If the value of D_s is in the range 10^{-6} – $10^{-8} \text{ cm}^2 \cdot \text{s}^{-1}$, then film diffusion is most likely to control the sorption mechanism. A value of D_s in the range 10^{-11} – $10^{-13} \text{ cm}^2 \cdot \text{s}^{-1}$ suggests pore diffusion controls the sorption mechanism. The two diffusion mechanisms may not always be clearly distinguishable (Doke and Khan, 2012).

Fractional attainment of equilibrium (X) of Cd ion sorption in this study was greater than 0.3, hence a plot of $\ln(1 - X)$ versus t was constructed (Fig. 8).

The value of the intra-particle diffusion constant, D_s , was calculated as follows:

$$\frac{D_s \pi^2}{R^2} = 0.0285 \quad (15)$$

Assuming a mean pore diameter value, $R = 75 \mu\text{m}$, the value of D_s was found equal to $2.7 \times 10^{-9} \text{ cm}^2 \cdot \text{s}^{-1}$, confirming that neither film- nor pore-diffusion could be distinguished with certainty as rate-determining mechanism.

3.6. Thermodynamics

Cd sorption increased with increasing temperature. The free energy of sorption (ΔG^0) is related to the distribution coefficient, K_d , by the classical van't Hoff equation (Saha and Chowdurry, n.d.):

$$\Delta G = -RT \ln K_d \quad (16)$$

[K_d = distribution coefficient (q_e/C_e); R = ideal gas constant ($8.314 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$); T is the absolute temperature (K)].

This relationship can be expressed in differential form as follows:

$$\frac{d \ln K_d}{dt} = \frac{\Delta H^0}{RT^2} \quad (17)$$

After integration, Eq. (17) becomes:

$$\ln K_d = -\frac{\Delta H^0}{R} \left(\frac{1}{T} \right) + \frac{\Delta S^0}{R} \quad (18)$$

[ΔH^0 = change in enthalpy ($\text{kJ} \cdot \text{mol}^{-1}$); ΔS^0 = change in entropy ($\text{J} \cdot \text{mol}^{-1}$)].

Substituting Eqs. (16) and (18), ΔG^0 can be calculated as follows:

$$\Delta G^0 = \Delta H^0 - T \Delta S^0 \quad (19)$$

A plot of $\ln K_d$ versus $1/T$ produced a linear graph (Fig. 9). From the slope and intercept of the graph the values of ΔH^0 and ΔS^0 were derived and found equal to $\Delta H = 54.02 \text{ kJ} \cdot \text{mol}^{-1}$

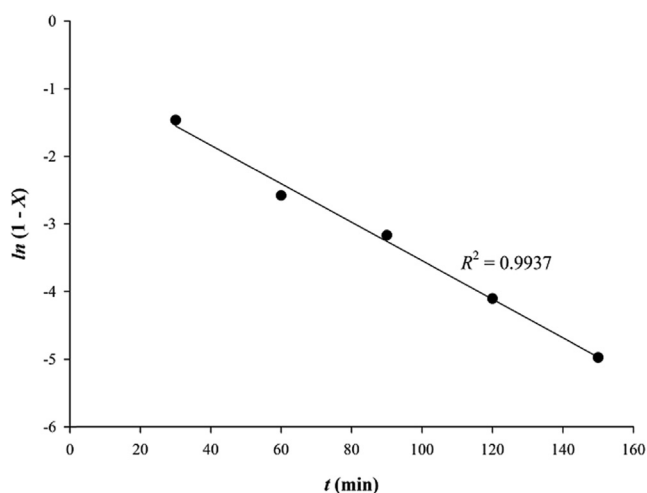


Fig. 8 Plot representing pore diffusion according to the HPD model.

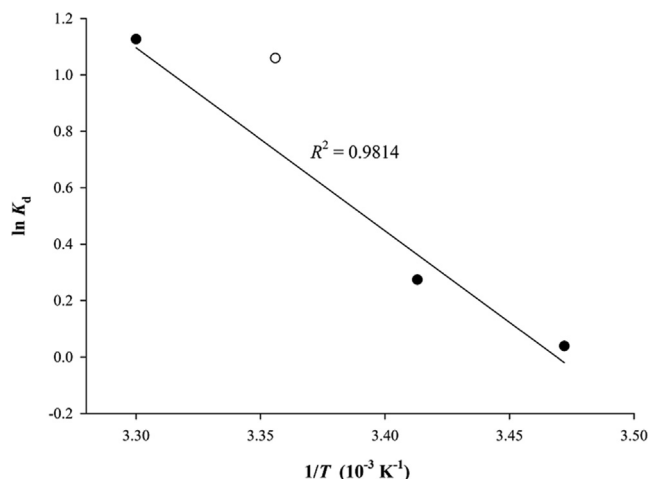


Fig. 9 Plot of $\ln K_d$ vs $1/T$ for Cd sorption; the data point denoted by (o) considered an outlier.

and $\Delta S = 0.187 \text{ kJ} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ respectively. The values of ΔG^0 were subsequently calculated over the temperature range by using Eq. (19). The values of all parameters are listed in Table 3.

The heat of physisorption is normally in the range 2.1–20.9 $\text{kJ} \cdot \text{mol}^{-1}$, whereas sorption associated with chemical processes generally falls in the range 80–200 $\text{kJ} \cdot \text{mol}^{-1}$ (Saha and Chowdurry, undated). More specifically, the energy associated with coordination exchange is in the range 40–60 $\text{kJ} \cdot \text{mol}^{-1}$ (Huang et al., 2007). The value of ΔH obtained in this study suggests Cd sorption is most likely as a result of coordination between Cd(II) and the S, N donor atoms of the dithizone ligand, and is attributed to a physico-chemical sorption process rather than pure physical or chemical processes. $\Delta H > 0$ implies that Cd sorption is endothermic. Values of the free energy of sorption (ΔG) became increasingly negative at $T > 293 \text{ K}$. As a rule of thumb, an increase in the negative value of ΔG with increasing temperature signifies more favourable sorption at higher temperatures. The positive ΔS value reflects the irreversibility of sorption (Anantha and Kota, 2016) and affinity of the sorbent towards the sorbate species. It further suggests randomness exhibited by the sorption system at the liquid–solid interface, accompanied by structural changes in the sorption system.

4. Conclusions

This studied demonstrated that impregnating Amberchrom® CG-300m resin with dithizone improved its capacity for Cd

Table 3 Thermodynamic parameters of Cd sorption by dithizone impregnated Amberchrom resin.

Temperature (K)	ΔG ($\text{kJ} \cdot \text{mol}^{-1}$)	ΔH ($\text{kJ} \cdot \text{mol}^{-1}$)	ΔS ($\text{kJ} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$)
288	0.164	54.02	0.187
293	−0.771		
298	−1.706		
303	−2.641		

(II) by 47.3% under optimal conditions. More than 97% of Cd(II) was removed from a 1.131 mg/L solution at pH 8. Sorption was best modeled by the Langmuir isotherm; the Langmuir monolayer sorption capacity was 0.478 mg/L at pH 6. Maximum capacity for Cd(II) was 0.551 mg/g at pH = 8.

Sorption kinetics reveals that the pseudo-second order model fitted sorption better than the pseudo-first order model, suggesting coordination between Cd(II) and the dithizone ligand was the driving force behind the sorption process as opposed to weak forces of interaction between Cd(II) and the unmodified resin skeleton. Intra-particle diffusion models showed Cd(II) sorption was controlled by both film and pore diffusion. Thermodynamic data suggested sorption was random, feasible and endothermic. The study shows that the modified Amberchrom CG-300m is effective for the removal of Cd(II) ions from dilute aqueous solutions; however, sorption capacity for Cd was much less compared to other dithizone-impregnated sorbents.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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