**Synthesis of Core-Shell Structured Microspheres and their Application in Separation of Cadmium from Aqueous Solutions**

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**ABSTRACT**

A simple process to fabricate magnetic porous microspheres of calcium hydroxyapatite was demonstrated. The magnetic microspheres were synthesized by utilizing calcium hydroxyapatite as a core and iron oxide nanoparticles as a shell. The properties of the prepared magnetic microspheres were characterized by BET surface area measurements, Fourier transform infrared spectroscopy (FTIR), X-ray powder diffraction (XRD) analysis, scanning electron microscopy (SEM) and energy dispersive analysis system of X-ray (EDS). Furthermore, the microspheres were applied to remove cadmium from aqueous solutions using batch technique. The influence of different sorption parameters, such as equilibration time, initial concentration of metal ion, pH value of solution, temperature and ionic strength on the separation of cadmium were studied and discussed. It was found that the amount of Cd(II) ion sorbed at equilibrium was 61.22 mg g\(^{-1}\) with 75% removal occurring at the first 5 hrs. The removal was pH and ionic strength dependent and was hypothesized to be achieved through an ion exchange process and surface complex mechanism in neutral medium. Meanwhile, precipitation was the relevant mechanism in removal of cadmium at pH > 9. The isotherm models of Temkin, Dubinin–Radushkevich (D–R) and Redlich–Peterson (R–P) were used to describe the sorption at the solid-liquid interface. Data suggest that there may be variation in the physicochemical phenomena involving metal adsorption. The mean adsorption energies evaluated using the D–R model indicated that the separation of Cd(II) was taken place by chemisorption. The thermodynamic parameters (\(\Delta G^\circ\), \(\Delta H^\circ\) and \(\Delta S^\circ\)) showed that the removal of cadmium ions was feasible, spontaneous and endothermic process at 30–60 °C.

**Keywords:** Synthesis /Core-shell structure /Microspheres / Cadmium separation.

**INTRODUCTION**

Heavy metals are major pollutants in marine, ground, industrial and even treated wastewaters \(^1\). They are non-biodegradable and their concentration gets accentuated through bioaccumulation via food chain in living tissues, causing various diseases and disorders. Heavy metals such as lead, mercury, cadmium and chromium are hazardous materials for environment \(^2, 3\). Cadmium is one of the major heavy toxic elements which may be found in surface and underground waters. The main sources of contamination are industrial wastes and phosphate fertilizers. Further, cadmium has many radioisotopes of them cadmium-109 that has a half-life of 462.9 days and decays by electron capture to \(^{109}\)Ag with emission of a \(\gamma\)-ray of 88.03 keV. It is using as a calibration source for X-ray and \(\gamma\)-ray spectrometry \(^4\). Accelerator-based production of \(^{109}\)Cd is achieved via nuclear reactions \(^{109}\)Ag (p, n) \(^{109}\)Cd \(^5\). Cadmium is also a common impurity found in natural phosphates used for the manufacture of fertilizers \(^6\). Several harmful effects have been attributed to cadmium in living systems. One of them is the interaction with the biological apatites of bones, leading to a disease producing effects similar to
osteoporosis (7). Cadmium intake at over amounts causes malfunction of the kidneys and spilling proteins in the urine and deducting protein metabolism (8,9).

Increasingly strict discharge limits on removal of heavy metals have directed to develop high effective and economically attractive methods. Numerous processes have been used for the removal of heavy metal ions from aqueous solution (10,11). In this concern, magnetic microspheres have attracted much attention due to their extensive applications in many fields such as biology, biomedicine (12), wastewater treatment (13), catalyst (14), magnetic resonance image (15), and hyperthermia (16). Recently, the most interest in magnetic microspheres has focused on microspheres containing iron oxide, because of their chemical stability, biological compatibility, low toxicity and the relative ease of fabrication of magnetite (Fe₃O₄) and maghemite (α-Fe₂O₃) nanoparticles. Furthermore, iron oxide-based materials are very effective in the removal of heavy metal ions (17), arsenic (14) and dyes (18,19) from water.

Additionally, preparation and design of composite particles consisting of cores covered by shells of different chemical compositions have attracted much interest due to their superior catalytic, optical, magnetic and electrical properties, which are different from those of single-component materials (20,21). These interesting properties of core-shell materials are due to structure, size, morphology, composition of their shells and cores (22). Among core-shell particles of various compositions, those made of core with inexpensive compounds and a reactive shell has received particular interest because of the functional and economic advantages that they can provide (23). Arranging of reactive materials as thin shells on proper low cost cores greatly magnifies their use, and can also significantly enhances their properties via the so-called strain and ligand effects of the core substrate on the shell compound (24,25).

This study deals with the preparation of a core-shell structure composed of iron ferrite coated calcium hydroxyapatite. The fabricated magnetic composite will be subjected, in batch reactor, with Cd(II) ions to investigate their sorption characteristics in aqueous solution under different experimental conditions.

**EXPERIMENTAL**

**Chemicals and Reagents :**

All chemicals used were of analytical grade purity and were used without further purification. Ferric chloride (FeCl₃, 162.21 g mol⁻¹) and ammonia solution (NH₄OH, 35.04 g mol⁻¹) were supplied from Redel, Germany. Ferrous chloride (FeCl₂.4H₂O, 198.81 g mol⁻¹) was purchased from Aldrich, US. Cadmium nitrate (Cd(NO₃)₂.4H₂O, 308.47 g mol⁻¹) was a product of Merck, Germany. Calcium nitrate (Ca(NO₃)₂.4H₂O, 263.15 g mol⁻¹) was supplied from WinLab, UK while di-ammonium hydrogen phosphate ((NH₄)₂HPO₄, 132.7 g mol⁻¹) was a product of VEB, Germany. Both hydrochloric acid and sodium hydroxide were obtained from Adwic, Egypt. A stock solution of 1000 mg L⁻¹ Cd(II) ions was prepared by dissolving the required amount of cadmium nitrate (Cd(NO₃)₂.4H₂O) in definite volume of bidistilled water and was used to prepare the desired concentrations of adsorbate solution by appropriate dilution.

**Composite Preparation :**

Iron ferrite particles (RS1) were prepared by co-precipitating Fe²⁺ and Fe³⁺ ions with ammonia solution in an inert atmosphere. Ferric and ferrous chlorides (molar ratio 2:1) were dissolved in bidistilled water, mixed together and stirred in N₂ atmosphere. Chemical precipitation was achieved at 29 °C under vigorous stirring by adding NH₄OH solution (29.6 %) and the pH value was maintained at
about 11 during precipitation process. Thereafter, the precipitate was separated, dried at room temperature in presence of N₂ gas, to prevent product oxidation, and finally sieved to the desired mesh size.

The magnetic microspheres (RS2) were decided to be constructed by applying calcium hydroxyapatite as a core and iron ferrite as an active shell. They were prepared by firstly dropping a solution of 0.387 M (NH₄)₂HPO₄ into an equal volume of 0.5 M Ca(NO₃)₂ solution with continuous stirring at room temperature and under N₂ atmosphere. The mixture was stirred and purged with N₂ for additional 30 min at room temperature. After that, ammonium hydroxide was dropped into the mixed solution to precipitate hydroxyapatite (HAP) and the reaction was terminated at pH 11 which could produce the stoichiometric Ca/P ratio of 1.67. After further stirring for 30 minutes, HAP precipitate was filtered and washed repeatedly to remove the unwanted ions. Secondly, a solution of 0.5 M FeSO₄ was added slowly to an equal volume of 1 M FeCl₃ with continuous stirring and nitrogen gas flow. Further, the mixture was stirred and purged with N₂ for an additional 30 min at room temperature. Then, it was added to HAP slurry at 5 ml min⁻¹ rate with continuous stirring in N₂ atmosphere. A shell of ferrite was then precipitated on HAP surface by adding NH₄OH till pH attained a value of 10. The mixture was let to complete settling wherein the supernatant was separated. The precipitate was then washed thoroughly with distilled water until constant pH value was sequentially attained. Finally, the composites were dried, pulverized, sieved and stored in a desiccator for further usage.

Characterization:

The surface characteristics of the synthesized resins were characterized using Fourier Transform Infrared (FTIR) spectrophotometer of type Nicolet iS10, Thermo, USA. The powder X-ray diffraction patterns were recorded with Philips x-ray diffractometer model PW1710 equipped with monochromatized Cu-Kα radiation (λ = 0.154 nm, 40 kV and 25 mA) employing a scan rate of 0.02° s⁻¹ in the range from 10 to 70°. Samples morphology was analyzed using Scanning Electron Microscope (SEM) model JSM-6510A from JEOL, Japan. The specific surface area was determined from N₂ adsorption isotherm by the BET method using Nova 3200, Version 6.08 High Speed Gas Sorption Analyzer. The concentration of cadmium was determined using an Atomic Absorption Spectrometer (AAS). Analysis was performed using Solaar-II M5 atomic absorption spectrometer from Thermo Fisher Scientific Inc., Cambridge, UK. The measurements were carried out using Air-C₂H₂ flame with a fuel flow rate 1.2 L min⁻¹ and the absorbance reading was detected at a wavelength of 228.8 nm.

Sorption Procedures:

The change in Cd(II) uptake with time was studied by shaking a definite weight of prepared samples with 10 mL of 200 mg L⁻¹ Cd(II) solution in sealed glass bottles. The mixture was shaken in a thermostatic shaker at 30 ±2 °C with V/m ratio 200 mL g⁻¹. Aliquots were taken at appreciate time intervals as necessary, centrifuged and the concentration of Cd(II) was determined by atomic absorption spectrophotometer. The effect of hydrogen ion concentration on Cd(II) uptake was studied by equilibrating 0.05 g sample with a set of 10 mL Cd(II) solutions. The initial pH value of these solutions was adjusted to different values ranged from 1 to 11 using 0.1 M HCl and/or 0.1 M NaOH solutions. Similar experiments were carried out by contacting a fixed amount of samples with 10 mL of Cd(II) solutions have varying concentrations cover the range of 100-800 mg L⁻¹ and agitated till equilibrium. Then, the samples were separated and cadmium concentration was determined by AAS.

Additional set of experiments were performed as previously described at different ionic strengths ranging from 0.001 to 0.2 mol L⁻¹ using NaCl as a background electrolyte. An additional set of experiments were also performed at different temperatures ranged from 30 to 60 °C. The apparent sorption capacity (mg g⁻¹) was determined by repeated equilibration of a definite weight of prepared materials with 10 ml of 200 ppm Cd(II) solution. The equilibration was repeated until no further
uptake of Cd(II) took place. All experimental data were the average of two replications of each experiment.

RESULTS AND DISCUSSION

CHARACTERIZATION

Surface area measurements:

Nitrogen adsorption and desorption isotherms were followed in measuring the specific surface area and pore size for the prepared samples and the corresponding results are presented in Table (1). The samples were degassed before nitrogen adsorption measurements. The Brunauer-Emmett-Teller (BET) surface area was determined by a multipoint BET method using the adsorption data in the relative pressure ($P/P_0$) range of 0.05–1.05. The nitrogen adsorption volume at the relative pressure ($P/P_0$) of 0.9502 was used to determine the pore volume and average pore size for the synthesized samples. The prepared core-shell hybrid composite (RS2) exhibited a type H3 hysteresis loop according Brunauer–Deming–Deming–Teller (BDDT) classification, indicating the presence of mesopores (2–50 nm) and the pore can be assumed as a cylindrical pore mode (26). This classification indicates the existence of textural larger pores formed between plate-like particles (27). According to the BET method, the specific surface area of RS1 and RS2 is 51.72 and 48.64 m² g⁻¹, respectively. The adsorption cumulative pore volume is 0.052 and 0.039 cm³ g⁻¹ for RS1 and RS2, respectively. The decrease in the effective surface area value of RS2 compared with that of RS1 could be assigned to the reorganization of iron oxide particles in apatite structure during shell formation process, which may lead to closing of some opened micropores in the coating process. This is in accordance with the fact that the total pore volume of RS2 is also decreased.

<table>
<thead>
<tr>
<th>No.</th>
<th>Samples Codes</th>
<th>Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Iron ferrite RS1</td>
<td>S_BET (m² g⁻¹)</td>
</tr>
<tr>
<td>2</td>
<td>HAP @ Iron ferrite RS2</td>
<td>51.72</td>
</tr>
<tr>
<td>2</td>
<td>HAP @ Iron ferrite RS2</td>
<td>48.64</td>
</tr>
</tbody>
</table>

FT-IR spectroscopy

The infrared spectra of prepared samples are shown in Fig. (1). The spectra show that the samples exhibit a broad absorption bands around 3429 cm⁻¹ that could be due to the presence of structural hydroxyl groups stretching band. The peak observed at about 1635 cm⁻¹ might be assigned to the binding mode of H₂O. The absorption bands detected at 626 and 556 cm⁻¹ could be ascribed to the stretching vibration of Fe-O bond of Fe₃O₄ while the band revealed at 416 cm⁻¹ might be attributed to Fe³⁺–O₂⁻ vibration (28). The peaks observed at 1095 and 1034 cm⁻¹ for HAP are due to the stretching vibration of phosphate (PO₄³⁻) groups. The bands detected at 689 and 595 cm⁻¹ imply the bending vibration of O–P–O bond of phosphate group (PO₄³⁻). These bands are characteristic to hydroxyapatite structure (29).

Comparing the spectra of RS1 with that of RS2 clarifies that the absorption band due to the O–Fe stretch (at 556 cm⁻¹) was hardly changed in the synthesized composite, but a weakness in its intensity was observed. Further, four resolved weak adsorption peaks within 690–550 cm⁻¹ was detected and appeared obviously in the synthesized composite. These data clarify that there was an interaction of the hydroxyl groups of HAP and the surface hydroxyl groups of Fe₃O₄ particles. This could be attributed to the depletion of these groups in the binding reaction during incorporation of iron
ferrite into apatite structure. This demonstrates clearly the attachment of Fe$_3$O$_4$ onto the surface of hydroxyapatite during RS2 synthesis.

X-ray analysis

The phase structure of the synthesized samples was investigated by XRD and some of data are given in Fig. (2). The diffractogram of RS1 indicated main peaks at 2θ = 30.22° (2 2 0), 35.48° (3 1 1), 43.14° (4 0 0), 53.44° (4 2 2), 57.04° (5 1 1) and 62.58° (4 4 0). These peaks are characteristic of Fe$_3$O$_4$ and clarifies that RS1 are pure Fe$_3$O$_4$ with a spinel structure $^{30}$. The XRD patterns of prepared calcium hydroxyapatite exhibited sharp peaks corresponding to 2θ = 26.12° (0 0 2), 29.39° (2 1 1), 30.62° (1 1 2), 32.11° (3 0 0), 39.18° (3 1 0), 47.65° (2 2 2) and 50.21° (3 1 2) that confirm a hexagonal hydroxyapatite structure $^{31}$. The diffraction patterns of RS2 showed diffraction lines of both iron ferrite and hydroxyapatite implying the presence of admixture of ferrite and hydroxyapatite and confirm the incorporation of iron oxide in the interlayer region of hydroxyapatite in a core-shell structure.

Using XRD diffraction data, the crystal thickness of the prepared composite was calculated using the following Debye-Scherrer Equation $^{32}$:

$$L = \frac{K\lambda}{B_2\cos\theta_B} \quad (1)$$

where: $L$ is the thickness of crystallite, $K$ is a constant dependent on crystallite shape (0.89), $\lambda$ is the X-ray wavelength (0.154 nm), $B$ is the full width at half max (FWHM) or integral breadth and $\theta_B$
is the Bragg angle. The line broadening measurements were calculated from the half-width of the most intense peak of XRD patterns revealed at 20 = 35.6° (line 311) that is common for iron ferrite. The calculated average crystallite thickness value was 54 and 50 nm for RS1 and RS2, respectively.

**Crystal morphology**

The SEM micrograph of HAP–ferrite hybrid particles are shown in Fig. (3). The figure indicates that the core-shell hybrid particles are asymmetry and ruleless agglomerates. The morphology of the particles is observed to be almost plate-like irregular hexagonal with particle size in the range 50–75 nm. The particles surface was loosen and smoothless and had lots of tiny interspaces structure so the metal ions, in the solution, can be adsorbed easily by such materials. Furthermore, EDS analysis revealed that the ferrite-coated hydroxyapatite particles were found to be deposited on the surface of hydroxyapatite microspheres with increasing the weight ratio of the magnetic iron oxide. The distribution of the Fe$_3$O$_4$ particles is comparatively uniform and the ferrite-coated hydroxyapatite are easily to aggregate forming microspheres have core–shell hybrid and porous structure. In addition, the diameter of the microspheres decreased markedly with coating process. Meanwhile, the weight ratio of apatite to magnetic fluid was a rolling factor in controlling the particle size.

![Figure (3): SEM photograph of RS2 sample.](image1)

![Figure (4): EDS spectrum of RS2 sample.](image2)

The energy dispersive spectroscopy (EDS) analysis of the synthesized hybrid microspheres is shown in Fig. (4). The spectrum clarifies that only oxygen, phosphorus, calcium and iron are present in RS2 sample. The presence of Fe K peaks with high intensity in the EDS spectrum confirmed that Fe$_3$O$_4$ was successfully embedded on the apatite surface. The elemental molar ratio of the applied materials is presented in Table (2). It was found that Ca/P ratio of RS2 is consistently lower than the hydroxyapatite stoichiometric value (1.67). An explanation for this observation was given by Chusuei et al. (33), who pointed out that this might be due to the instability of the compounds and prolonged exposure of the composite powder to X-ray source, leading to selective ejection of calcium. The decrease in Ca/P ratio could also be ascribed to the loss of calcium from the surface of hydroxyapatite after iron embedding process. The values of Fe/Ca and (Ca+Fe)/P ratios were relatively higher than unity indicating that there was a massive weight of iron was embed on the surface of HAP. Data argues that Fe ions have hybrid with hydroxyapatite particles and a core–shell hybrid structure of HAP@Fe$_3$O$_4$ composite was successfully synthesized.
Table (2): EDS chemical analysis of the prepared microspheres and their elemental ratios.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Atomic percentages</th>
<th>Elemental ratios</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>O %</td>
<td>P %</td>
</tr>
<tr>
<td>RS1</td>
<td>54.06</td>
<td>–</td>
</tr>
<tr>
<td>RS2</td>
<td>33.81</td>
<td>16.72</td>
</tr>
</tbody>
</table>

Separation Studies:

The uptake of Cd(II) ions from aqueous solutions by the synthesized materials was carried out using batch technique. The different parameters affecting the uptake process were investigated individually.

Contact time

The results of cadmium separation study carried out as a function of contact time on both RS1 and RS2 are presented in Fig. (5). The plots clarify that the rate of Cd(II) uptake was initially quite fast, followed by a much slower subsequent removal rate leading gradually to an equilibrium condition. About 50 % of the Cd(II) was removed by RS2 during the first one hour of the reaction, while only a small part of the additional removal occurred during the rest of contact. The necessary time to reach the equilibrium was about 5 hrs. A further increase in contact time had a slight increase on the quantity separated of cadmium up to 48 hrs, where it did not bring any remarkable effect. Accordingly, the agitation time was fixed at 10 hrs for the rest of the batch experiments to make sure that the equilibrium was reached. Similar two-phase removal has been reported in sorption of Cd onto other sorbents (3, 34). Generally, efficiency amounted to 17 and 75 % for Cd(II) removal using RS1 and RS2 was attained after ~ 5 hrs of contact. These results reflect the efficiency of the used composite for removal of Cd(II) from aqueous solution.

Figure (5): Effect of contact time on Cd(II) uptake onto the prepared samples.
(Cₐ=200 ppm, V/m=200, pH = 5.95, temp.= 30 °C)

The rapid uptake of Cd(II) by the applied samples could be attributed to that the surface site initially available for Cd(II) removal is very large compared to the concentration of Cd(II) ions and consequently, the rate of uptake was very high. However, with increasing coverage, the fraction of active sites in beads surface rapidly diminished and Cd(II) ions had to compete among themselves for the active sites. This results in a slowing down of the interaction progress and the rate of uptake becomes predominantly dependent on the rate at which Cd(II) ions transport from the bulk to the
sorbent–adsorbate interface. The kinetic of interaction was thus likely to be dependent on different rate processes as the interaction time increased. Further, the maximum sorption capacity (\(Q\)) was experimentally determined and exhibited the values 9.4 and 61.22 mg g\(^{-1}\) for cadmium sorption onto RS1 and RS2, respectively. The data clarify that RS2 exhibited a sorption capacity much higher than that of RS1 and evaluate the participation of HAP in the overall removal of Cd(II) although it was used as a core in the hybrid microspheres. This result authenticates the constructive core-shell structure synthesis of RS2 to introduce a novel and promising candidate for the treatment of hazardous aqueous solutions.

**Solution pH value**

The influence of initial pH value of the aqueous solutions on cadmium uptake was studied in the range of 1–11, using 200 mg L\(^{-1}\) Cd(II), 5.0 g L\(^{-1}\) sample and temperature 30 °C. The relationship between initial pH value and the quantity of Cd(II) sorbed on RS1 and RS2 is presented in Fig. (6). The results show that the uptake increased as pH increased up to ~ 4. The removal was nearly unaffected with rising pH up to 8 after which separation increased dramatically, which could be attributed to the precipitation of Cd(II) ions at higher pH value. It was noted that, final pH values attained a constant value around 5 corresponding to the initial pH values ranged from 4-8. This behavior could be ascribed to the buffering properties of HAP that were a result of the acid–base reactions of the reactive surface sites. Therefore, it would be incorrect to conclude that the Cd(II) separation from its aqueous solution using RS1 and RS2 was independ on the pH value. Only, It can be said that the Cd(II) sorption was independent of the initial pH value in the investigated pH range.

![Figure (6): Effect of pH value on Cd(II) uptake onto the prepared samples.](image)

\(C_0=200\) ppm, \(t_{eq}=10\) hrs, \(V/m=200\), temp.= 30 °C

![Figure (7): Speciation diagram of Cd(II) in aqueous solutions at different pH values.](image)

The distribution of various hydrolyzed cadmium ionic species as a function of pH at 298 °K was calculated using visual MINTEQ software \(^{(35)}\) and data are given in Fig. (7). The formation constants of cadmium hydroxo-complexes \(^{(36)}\) are listed in Table (3). The figure clarifies that cadmium presents in aqueous solution mainly in the form Cd\(^{2+}\) up to pH ~8. The positively charged Cd(OH)\(^+\) hydrolytic products appear in pH range 8–12, while the neutral Cd(OH)\(_2\) particles start to precipitate at pH 8.5 and become predominant at pH 11. The negatively charged species Cd(OH)\(^{-}\);\(_3\) predominates at pH value of 13 while the species Cd(OH)\(^{-}\);\(_4\) appeared at pH > 12.
Table (3): Equilibrium constants (log $K$) for cadmium hydrolysis reactions

<table>
<thead>
<tr>
<th>Equation</th>
<th>log $K$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Cd}^{2+} + \text{H}_2\text{O} = \text{Cd(OH)}^+ + \text{H}^+$</td>
<td>7.9</td>
</tr>
<tr>
<td>$\text{Cd(OH)}^+ + \text{H}_2\text{O} = \text{Cd(OH)}_2 + \text{H}^+$</td>
<td>10.6</td>
</tr>
<tr>
<td>$\text{Cd(OH)}_2 + \text{H}_2\text{O} = \text{Cd(OH)}_3^+ + \text{H}^+$</td>
<td>14.3</td>
</tr>
</tbody>
</table>

In acidic solution, the protonated oxide site $\text{–FeOH}_2^+$ and $\equiv\text{P}-\text{OH}_2^+$ are tentatively the dominating surface species giving raise a high surface positive charge density. This surface positivity made $\text{Cd}^{2+}$ separation electrically unfavorable in this region due to the strong electrostatic repulsion. At these conditions, retention of $\text{Cd}^{2+}$ was hypothesized to be achieved through an ion exchange process according to the following interactions:

$$2 \text{–Fe–O} + \text{Cd}^{2+} (\text{aq.}) \rightarrow (\text{–Fe–O})_2\text{Cd} + 2 \text{H}^+ (\text{aq.}) \quad (2)$$

$$2 \equiv\text{P–OH} + \text{Cd}^{2+} (\text{aq.}) \rightarrow (\equiv\text{P–O})_2\text{Cd} + 2 \text{H}^+ (\text{aq.}) \quad (3)$$

The removal of Cd(II) occurred in neutral medium up to pH 8 suggested that Cd(II) was removed from aqueous solution by single Cd$^{2+}$ species through equimolar exchange with either Ca$^{2+}$ or Fe$^{2+}$ and/or surface complexation interactions.

$$\text{HAP-Ca} + \text{Cd}^{2+} (\text{aq.}) \rightarrow \text{HAP-Cd} + \text{Ca}^{2+} (\text{aq.}) \quad (4)$$

$$\text{HAP@FeO-Fe}_2\text{O}_3 + \text{Cd}^{2+} (\text{aq.}) \rightarrow \text{HAP@Cd-Fe}_2\text{O}_3 + \text{Fe}^{2+} (\text{aq.}) \quad (5)$$

With further increase in pH value $> 9$, precipitation of cadmium as Cd(OH)$_2$ was the relevant mechanism in removal of cadmium. Different researchers have observed different pH values at which cadmium precipitates as Cd(OH)$_2$. Bhattacharya and Venkobachar (37) observed that cadmium precipitated at pH values $> 10$ while Sharma (38) observed cadmium precipitation beyond pH 6.5. Singh et al. (39) have reported maximum adsorption of cadmium at pH 8.6. To confirm the possibility of Cd(OH)$_2$ precipitation at the pH 9, blank study had been performed and the results showed that cadmium precipitation had obviously initiated at pH 8 and highly increased with rising pH value. Thus the removal at the range pH $> 9$ was mainly due to precipitation.

It is pertinent to note that the previously proposed removal mechanisms should be accompanied with a release of Ca$^{2+}$ and Fe$^{2+}$ ions into the reaction solution. To demonstrate this supposition, some experiments were carried out to investigate whether Ca$^{2+}$ and Fe$^{2+}$ were released in the reaction solution after the completion of Cd(II) sorption. The concentration of Ca$^{2+}$ and Fe$^{2+}$ ions released from the synthesized beads after Cd$^{2+}$ sorption was experimentally determined and the values are listed in Table (4). The results show that different concentrations of both Ca(II) and Fe(II) were detected in the solution after Cd(II) sorption. Also, the ratios Cd/Ca and Cd/Fe exhibited values for RS2 greater than that for RS1 and this illustrated that the ion exchange capacity of RS2 towards Cd(II) was substantially greater than that of RS1.
Table (4): Ion exchange of the prepared microspheres with Cd(II) ions.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Cd²⁺ sorbed (mg L⁻¹)</th>
<th>Released [M²⁺]</th>
<th>Exchange %</th>
<th>Ratios</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Ca²⁺</td>
<td>Fe²⁺</td>
<td>Ca²⁺</td>
</tr>
<tr>
<td>RS1</td>
<td>32.0</td>
<td>0.0</td>
<td>4.0</td>
<td>0.0</td>
</tr>
<tr>
<td>RS2</td>
<td>146</td>
<td>64.0</td>
<td>6.0</td>
<td>43.8</td>
</tr>
</tbody>
</table>

It is well known that the Ca²⁺ ions in HAP can be easily exchanged with many other metal ions (40). The ionic radius of Cd²⁺ (0.95 Å) is smaller than that of Ca²⁺ (0.99 Å) and greater than that of Fe²⁺ (0.65 Å), so it could be thought that Cd²⁺ easily substituted Ca²⁺ in the HAP core. Contrary, Fe²⁺ ions weren’t easily substituted with Cd²⁺ although they were easily reached because they found as a shell formation in RS2 structure. Comparing with XRD pattern of the original HAP, Zhu et al. (34) indicated that the lattice parameters (a and c) of original HAP slightly decreased after cadmium sorption, which could be considered as a direct indication of isomorphic Cd substitution. In addition, they reported that the intensity of XRD pattern was apparently lower than that of the original HAP, which clarified the decrease in degree of HAP crystallinity after cadmium sorption. These results support the ion-exchange as a main mechanism participating in Cd(II) separation.

Ionic strength

The effect of ionic strength on cadmium separation was investigated using NaCl as a background electrolyte and the solution ionic strength was set to have values ranged from 0.04 to 0.2 mol L⁻¹. Figure (8) clarifies that the removal of cadmium decreased with increasing the electrolyte concentration. It was noted that, cadmium uptake decreased from 16.6 % to 8.9 % and from 74.6 to 53.5 % with increasing the solution ionic strength from 0.04 to 0.2 mol L⁻¹ for RS1 and RS2, respectively. The decrease in cadmium removal with increasing the electrolyte concentration could be attributed to a competition between cadmium species and Na⁺ ions at the binding sites of the beads matrix. In addition, Cd(II) would form CdCl⁺ and/or CdCl₂ species in chloride medium which would reduce the possibility of both cadmium substitution, with Ca²⁺ ions, and surface complexation interactions with the electron-pair donating function groups (such as: phosphate (–ÖPO₃)). Further, these species are less strongly adsorbed compared to Cd²⁺ ions because they have lower affinities to microsphere surface. Therefore, the coexistence of Cl⁻ ions depressed the removal of cadmium from aqueous solutions containing NaCl electrolyte. The pH independent and ionic strength dependent sorption behavior could be referred to the small contribution of electrostatic adsorption compared to surface complexation in the overall cadmium removal.
Adsorption Isotherm Models:

Sorption equilibrium data are very important to optimize the design parameters of a decontamination system. They are also helpful to provide sufficient physicochemical information to understand the mechanism of separation process. The sorption capacity of an adsorbent can be also described by equilibrium sorption isotherm, which is characterized by definite constants whose values express the surface properties and affinity of this adsorbent. In this study, three different isotherm models namely Temkin, Dubinin–Radushkevich (D–R) and Redlich–Peterson (R–P) isotherm models were selected to fit the revealed experimental results.

Temkin model:

Temkin sorption isotherm model was applied to evaluate the sorption potentials of the applied sorbents for adsorbate ions. The logarithmic form of the isotherm equations may be written as:

\[ q_e = \frac{RT}{b_T} \ln k_T + \frac{RT}{b_T} \ln C_e \]  

Figure (8): Variation of Cd(II) uptake onto the prepared samples with the concentration of background electrolyte (\(C_o=200\) ppm, \(t_{eq}=10\) hrs, \(V/m=200\), pH=5.95, temp.= 30 °C).

where \(C_e\) is the equilibrium concentration of Cd(II) in the liquid phase, \(q_e\) is the corresponding concentration of the adsorbate in the solid phase (mol g\(^{-1}\)), \(b_T\) is a constant related to the heat of sorption, \(k_T\) is Temkin isotherm constant indicates the sorption potential of used microspheres. The different isotherm parameters for sorption of Cd(II) ions on prepared samples were evaluated by plotting \(q_e\) versus \(\ln C_e\) and data are presented in Figs. (9). The corresponding isotherm parameters along with correlation coefficients are given in Table (5). The values of Temkin sorption potential constant \((k_T)\) are 0.049 and 0.024 L g\(^{-1}\) for sorption of Cd(II) onto RS1 and RS2, respectively. The value of Temkin constant \((b_T)\) that related to the heat of cadmium sorption was estimated to be 1.147 and 0.195 kJ mol\(^{-1}\) respectively. These low values indicate a weak interaction between Cd(II) ions and the sorbents surface supporting an ion exchange mechanism to predominate the sorption process. This evidence reinforces the emphasis stemmed from the role of solution pH that indicated that cadmium separation was mainly attributable through an ion-exchange process.
Dubinin–Radushkevich (D–R) isotherm model is the popular model that used to estimate the characteristic porosity of a sorbent and the apparent free energy of sorption process and to determine the sorption type (physical or chemical). The D–R isotherm equation is expressed as:

\[ q_e = Q_m e^{-k_{DR} \varepsilon^2} \]  

\[ \ln q_e = \ln Q_m - k_{DR} \varepsilon^2 \]  

where \( q_e \) is the amount of cadmium sorbed at equilibrium per unit weight of sample (mol L\(^{-1}\)), \( Q_m \) is the maximum sorption capacity (mol g\(^{-1}\)), \( k_{DR} \) is the activity coefficient related to mean adsorption energy (mol\(^2\) J\(^{-2}\)), \( \varepsilon \) is a Polanyi potential constant which equal to:

\[ \varepsilon = RT \ln \left(1 + \frac{1}{C_e} \right) \]  

where \( R \) is the universal gas constant which equals to 8.3145 J mol\(^{-1}\)K\(^{-1}\), \( T \) is the absolute temperature (K). Figure (10) shows a plot of ln \( q_e \) vs. \( \varepsilon^2 \) and exhibits linear relations for sorption of Cd(II) on both samples. The values of \( Q_m \) and \( k_{DR} \) were estimated using intercept and slope values and results are listed in Table (5). The maximum sorption capacity attained the values of 0.067 and 0.299 mol g\(^{-1}\) for sorption of Cd(II) onto RS1 and RS2, respectively. The values of porosity factors \( (k_{DR}) \) for RS1 and RS2 are 1.51 x 10\(^{-4}\) and 1.77 x 10\(^{-4}\) mol\(^2\)kJ\(^{-2}\), respectively. These values are less than unity and so imply the synthesized samples to have fine micropores and indicate a surface heterogeneity which may be arisen from the pore structure as well as adsorbate-adsorbent interactions.
The mean energy of sorption ($E_a$, kJ mol$^{-1}$), which is the free energy change when one mole of cadmium ions was transferred to the surface of the used beads from infinity in solution, was calculated using the relationship (43):

$$E_a = \frac{1}{\sqrt{-2k_{DR}}}$$  \hspace{1cm} (10)

The $E_a$ value (kJ mol$^{-1}$) gives information about adsorption mechanism, physical or chemical. The mean adsorption energy was calculated as 57.5 and 53.1 kJ mol$^{-1}$ for Cd(II) sorption onto RS1 and RS2, respectively. These results indicate that the sorption of cadmium may be taken place by chemical ion exchange.

Table (5): Isotherm model parameters for sorption of Cd(II) onto the prepared samples.

<table>
<thead>
<tr>
<th>Isotherm Models</th>
<th>Model</th>
<th>Parameters</th>
<th>Samples</th>
<th>RS1</th>
<th>RS2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temkin</td>
<td>$k_T$ (L g$^{-1}$)</td>
<td>0.049</td>
<td>0.024</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$b_T$ (kJ mol$^{-1}$)</td>
<td>1.147</td>
<td>0.195</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$R^2$</td>
<td>0.997</td>
<td>0.988</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>SD</td>
<td>$\pm 0.247$</td>
<td>$\pm 2.58$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dubinin -Radushkevich (D–R)</td>
<td>$Q_m$ (mol g$^{-1}$)</td>
<td>2.99</td>
<td>6.72</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$k_{DR}$ (mol$^2$ kJ$^{-2}$)</td>
<td>1.51x10$^{-4}$</td>
<td>1.77x10$^{-4}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$E_a$ (kJ mol$^{-1}$)</td>
<td>57.5</td>
<td>53.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$R^2$</td>
<td>0.953</td>
<td>0.939</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>SD</td>
<td>$\pm 0.0079$</td>
<td>$\pm 0.0168$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Redlich - Peterson (R–P)</td>
<td>$k_{RD}$ (L g$^{-1}$)</td>
<td>1.02</td>
<td>0.979</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$a$ (L mg$^{-1}$)</td>
<td>1.69</td>
<td>1.43</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$g$</td>
<td>0.61</td>
<td>0.37</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$R^2$</td>
<td>0.985</td>
<td>0.955</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>SD</td>
<td>$\pm 0.153$</td>
<td>$\pm 0.146$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Redlich–Peterson model:

Redlich–Peterson isotherm model assumes that monolayer formation and multi-site adsorption occur simultaneously, exhibiting characteristics of Langmuir and Freundlich isotherms. It was applied to represent cadmium sorption data under surface heterogeneity conditions that revealed from Dubinin–Radushkevich isotherm model. The non-linear and linear forms of Redlich–Peterson isotherm are given as (44):

\[ q_e = \frac{k_{RP} C_e}{1 + a C_e^g} \]  \hspace{1cm} (11)

\[ \ln \left( \frac{k_{RP} C_e}{q_e} - 1 \right) = \ln a + g \ln C_e \]  \hspace{1cm} (12)

where \( k_{RP} \) and \( a \) are Redlich–Peterson isotherm constants, \( g \) is an empirical constant which varies from 0 to 1 (i.e. \( 0 < g < 1 \)). The linearized form of the Redlich–Peterson isotherm may not be evaluated without trial-and-error optimization. A general trial-and-error procedure was used to determine the isotherm parameters \( (k_{RP}, a \text{ and } g) \) by employing Microsoft Excel 2010. The linear regression of Redlich-Peterson isotherm plot is presented in figure (11) and the values of the different isotherm constants were determined and given in Table (5). The values of Redlich-Peterson constant \( (k_{RP}) \) are 1.2 and 0.979 L g\(^{-1}\) for Cd(II) sorption onto RS1 and RS2, respectively while that of \( a \) are 1.69 and 1.43 L g\(^{-1}\). The empirical constant \( (g) \) has the values 0.61 and 0.37 for Cd(II) sorption on RS1 and RS2, respectively.

Generally, Redlich–Peterson isotherm model becomes a special case of Langmuir isotherm model when the value of \( g \) equals to 1, while it becomes a special case of Freundlich isotherm model when \( (C_e)^g \gg 1 \), and \( 1/n = 1 – g \) (45). Therefore, it could be affirmed that the applied isotherm models are appropriate in their merits in describing the ability of prepared beads to separately remove Cd(II) from wastes solutions. However, Temkin isotherm model mostly provide a better fit of experimental data, the other two models produce a satisfactorily fit over the entire range of concentration.

**Figure (11):** Redlich–Peterson isotherm plots for sorption of Cd(II) onto the prepared samples (\( C_0=200 \text{ ppm}, t_{eq}=10 \text{ hrs}, V/m=200, \text{ temp.}=30 \degree C \)).
Thermodynamic Results:

Thermodynamic parameters are important assessments to evaluate efficiency of cadmium separation at different temperatures. Hence, the values of the thermodynamic parameters were calculated at different temperatures and listed in Table (6). The positive values of \( \Delta H^o \) indicate the endothermic nature of Cd(II) ions separation using the synthesized samples and suggest that a large amount of heat is consumed to transfer the Cd(II) ions from aqueous into the solid phase. The negative values of the Gibbs free energy change (\( \Delta G^o \)) showed that the adsorption process was feasible and spontaneous thermodynamically. The decrease in \( \Delta G^o \) values with increase in temperature showed that the adsorption was favorable at higher temperatures. The positive values of \( \Delta S^o \) indicate that Cd(II) ions are less hydrated in the composite layers than in the aqueous solution.

Table (6): Thermodynamic parameters for sorption of Cd(II) onto the prepared samples.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Thermodynamic parameters</th>
<th>( \Delta H^o ) (kJ mol(^{-1}))</th>
<th>( \Delta S^o ) (J mol(^{-1})K(^{-1}))</th>
<th>( \Delta G^o ) (kJ mol(^{-1})) at 30 °C</th>
<th>40 °C</th>
<th>50 °C</th>
<th>60 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>RS1</td>
<td>74.19</td>
<td>0.25</td>
<td>1.87</td>
<td>4.38</td>
<td>6.89</td>
<td>9.40</td>
<td></td>
</tr>
<tr>
<td>RS2</td>
<td>30.23</td>
<td>0.15</td>
<td>14.6</td>
<td>16.08</td>
<td>17.56</td>
<td>19.04</td>
<td></td>
</tr>
</tbody>
</table>

Further, \( \Delta S^o \) values announce the increased disorder in the system with changes in the hydration of the adsorbing Cd(II) cations. Therefore, the distribution of rotational and translational energy among a small number of molecules will increase with increasing sorption producing a positive value of \( \Delta S^o \) and randomness will increase at the solid–solution interface during the sorption process.

CONCLUSION

Novel magnetic porous microspheres were synthesized. The synthesis procedures were adapted to have a core-shell structures composed from calcium hydroxyapatite in core and iron oxide nanoparticles as a shell. This work contributed to a better understanding of the mechanisms of cadmium separation using the synthesized core-shell microspheres and to the use of such material for the decontamination of hazardous wastewaters. Further, experiments are planned to elucidate the involved sorption mechanisms, speciation of cadmium ions and the fitting to different isotherm models. The calculated thermodynamic parameters indicated the feasibility, endothermic and spontaneous nature of the adsorption process at 30–60 °C. Since the physiochemical properties of synthesized composite, could be modified to a great extent by conditions of its preparation procedures, the conditions can be optimized for different practical applications in the future emphasizing its versatility. Thus the novel composite designed in the above study is distinguished by significantly higher adsorption capability and versatile application. Furthermore, it can be evaluated as an alternative adsorbent for treatment of wastewater.

REFERENCES

(8) A. Sari, M. Tuzen; Desalination; 249, 260 (2009).