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The kinetics of cadmium sorption by polyelectrolyte-coated fly ash from aqueous solution

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ABSTRACT

In this study, the sorption efficiency of different layers of polyelectrolyte-coated fly ash (PEFA) on cadmium (Cd) ions adsorption from aqueous solution was investigated. Using layer-by-layer technique, PEFA materials were synthesized in which fly ash treated with acid was coated with 5 and 20 layers of polyelectrolyte. The morphology of the modified fly ash was characterized using field-emission scanning electron microscope equipped with energy dispersive X-ray spectroscopy and Brunauer–Emmett–Teller surface area analysis. The synthesized PEFA materials were then tested for their efficiency to remove cadmium, Cd(II) ions from aqueous solution under different number of PEFA layers, pH, adsorbent dosage, shaking speed, and treatment time. The results revealed that 5-layer PEFA had better efficiency in removing Cd than the 20-layer PEFA. At pH 7, more than 96% removal of Cd(II) ions was achieved using 5-layer PEFA compared with 58% removal using the 20-layer PEFA within 15 min. Langmuir, Freundlich, Dubinin–Radushkevich, and Scatchard plot isotherm models were used to assess the Cd sorption data at equilibrium. The equilibrium adsorption isotherm models showed good fit to the experimental data for both 20 and 5 layers PEFA followed pseudo-second-order kinetics. The study also indicated a favorable sorption process between the adsorbents and Cd(II) ions in aqueous solution. On the other hand, the Scatchard plot analysis revealed the presence of multiple binding sites on PEFA surface, which confirmed the good fit in the Freundlich model.

Keywords: Polyelectrolytes; Fly ash; Adsorption; Cadmium; Scatchard plot; Kinetic study

1. Introduction

The demand and consumption of water is on the increase. As a result, it has been tagged a precious commodity and regarded to be the 21st century oil. Due to progressive population growth, declining precipitation, urban civilization, and stringent health regulations, water available for supplies is on the low side [1]. Consequently, researchers are seeking alternative water sources that include wastewater, storm water, and seawater, among others. Quite a number of industries generate massive volumes of wastewater. Recycle, recovery, and reuse of water have been confirmed to be successful and active in producing fresh and dependable water supply without undermining the health of the populace [2]. Toxic substances removal, such as cadmium, and reclaim of treated water would make available substantial drop in labor, charges, time and cost to industry and lead to enhanced environmental control. Cadmium (Cd) is regarded as a hazardous

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and toxic metal of environmental concern and work related such as smelting, alloy manufacturing, and pesticide [3]. Exposure to Cd can be teratogenic or carcinogenic to human. As per the World Health Organization (WHO), the required contaminant level for Cd ions in drinking water is 3 ppb [4]. Remediation techniques such as screening, membrane separation, reverse osmosis, ion-exchange, coagulation, softening, solvent extraction, and adsorption have been used in treating such contaminant [5]. However, when compared with other techniques, adsorption remains the most worthwhile because of the possibility of obtaining highly efficient, costless, and environment-friendly adsorbents that would be easy to apply [6–8]. However, efficient adsorption is reliant on the use of an effective adsorbent, thus the continuing need for research in this area [9–11]. One candid condition for toxic metals remediation in aqueous solution through the means of adsorption mechanism is producing a novel adsorbent [12]. Activated carbon derived from numerous agricultural waste (rice, peanut, wheat bran, and the likes) were successfully used for heavy metals removal from aqueous solution [13,14]. Maleki et al. [15] investigated barley hull ash and barley hull sorption efficiency at pH solution of 9 for Cd(II) ions and obtained 99.9% and 95.8% removal, respectively. Several adsorptive studies have been conducted on fly ash (FA). The sorption features of Cd and Ni using various particle sizes of bagasse FA from sugar industry were reported by Gupta et al. [16]. In another study, El-Sherif et al. modified the adsorptive features of bagasse FA for Cd(II) ion uptake in aqueous solution. They observed a 97.5% removal at pH 5 after 30 min [17]. Al-Khaldi et al. conducted a comparative study on Cd adsorption using activated carbon, carbon nanotubes, carbon nanofibers, and FA. They found that at pH 7, 120 min, with 50 mg adsorbent and 150 rpm speed, a removal of 95%, 27%, 34%, and 38% was attained for FA, CNT, CNF, and activated carbon, respectively [7]. These studies indicate the importance of FA as an efficient adsorbent material. One way by which FA removal efficiency can be increased is via polyelectrolyte coating. Modifying through alternating the poly cationic and anionic charges depends on the study. Polyelectrolytes are soluble in water and applicable in different areas such as paper making, and drug production, and these include: polyacrylic acid, poly styrene sulfonate (PSS), poly diallyldimethylammonium (PDAD). Brian [18] demonstrated that interchanging the deposition of polyelectrolytes on a support that is permeable can produce nanofiltration membranes that permit the influx of water at higher transition rate alongside ion transport that are selective with the aid of PSS/PDAD on porous alumina.

In this work, industrial waste FA surface morphology was modified by depositing alternating charges of cationic PDAD and anionic PSS, via layer-by-layer (LBL) deposition, and used to study the removal of Cd(II) ions from polluted water via adsorption mechanism. The influence of pH, dose of adsorbents, shaking speed, time of contact, initial concentration, and number of layers on the removal efficiency was investigated.

2. Materials and methods

2.1. Adsorbent preparation

Electrostatically precipitated FA collected from a power plant located in the Eastern Province of Saudi Arabia was used in this research. In order to remove trace metal impurities, the raw FA was first washed with 1 M HNO_3 and then dried as described by Abulaiwi et al. [19].

Homogeneous mixture of PDAD chloride was prepared by stirring 3 mL PDAD aqueous solution in 1,000 mL deionized water. Similarly, PSS aqueous solution was prepared. The LBL coating technique has been described in a previous work by Refs. [20–22]. The desired layer was prepared as shown in Fig. 1 and the procedure was repeated as many times as required.

2.2. Adsorbent characterization

Surface morphology of the prepared adsorbents was studied to identify the pore sizes, elemental, functional groups, and thermal stability. Scanning electron microscope (SEM) from JOEL, Japan (Model JSM-5900LV) coupled with energy disperse X-ray (EDX) spectroscopy detector model X-max was used to acquire the micrographs and the elemental composition, respectively. Brunauer–Emmett–Teller (BET) surface area analysis was also performed using surface area and porosity analyzer (ASAP 2020) to examine the pore volume, pore size, and surface area of prepared adsorbents

2.3. Preparation of stock solutions

Cadmium stock solution of 2.0 mg/L was prepared by dissolving 2.0 mL of 1,000 mg/L anhydrous cadmium nitrate $Cd(NO_3)_2$ in 1,000 mL of deionized water produced by Milli Q Ultra-pure water system. Analytical grade reagents were used in this research work. PDAD (Mw: 200×10^3 to 350×10^3 kg/mol) and PSS (Mw: 70×10^3 kg/mol) were used in this work. 1.0 M HNO_3 and 1.0 M NaOH solutions were used for pH adjustment.

2.4. Experimental procedures

Batch sorption experiments were conducted at room temperature to examine the adsorption of Cd(II) ions by polyelectrolyte-coated fly ash (PEFA). Adsorption parameters (i.e., pH, uptake time, dose of adsorbent, mixing rate, initial Cd ions concentration, adsorbents stability, and layers) were examined at various levels by adding 50 mL aqueous solutions of Cd ions to PEFA adsorbents in 100 mL Erlenmeyer flasks. The flasks were placed on an orbi-shaker at certain speed and left to reach equilibrium. Analysis of initial and final concentrations of Cd ion was carried out using Perkin Elmer Optima 7300 inductively coupled plasma optical emission spectrometry (ICP/OES).

Eqs. (1) and (2) were used to calculate the removal efficiency of Cd ions in % as well as the sorption capacity, respectively.

$$\%\ \text{Cd ion removal} = \frac{C_i - C_e}{C_i} \times 100 \tag{1}$$

$$\text{Adsorption capacity, } q_e\left(mg/g\right) = \frac{C_i - C_e}{M_s} \times V \tag{2}$$

where C_i, C_e, V, and M_S depict the initial and final metal ion concentrations (mg/L), volume of Cd ion aqueous

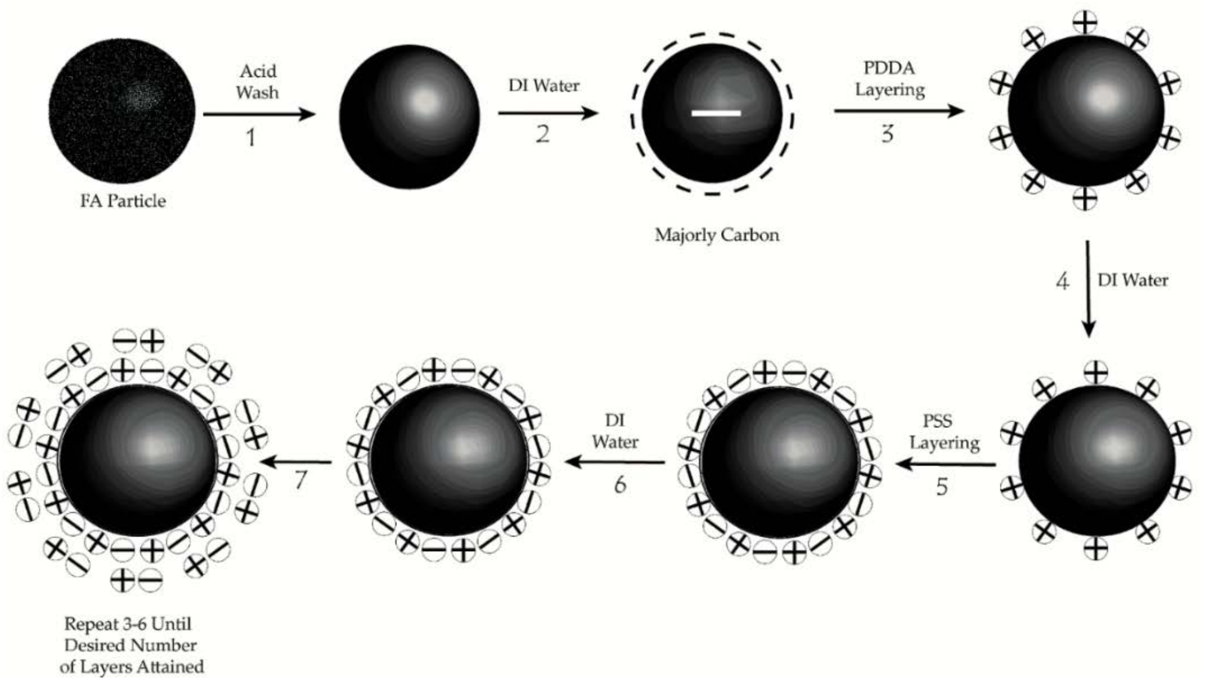

Fig. 1. Schematic illustration of acid treatment and polyelectrolyte coating of FA (PEFA).

solution (L), and adsorbent quantity, respectively. Average values of five (5) replicates were used for data analysis to ensure reproducibility with a relative standard deviation (%RSD) ranges from ±3% to 5%.

2.5. Desorption studies

Desorption experiment was conducted by stirring 4 g/L of the adsorbents (PEFA$_5$ and PEFA$_{20}$) in 50 mL Cd(II) ion solutions for 60 min. The loaded adsorbents were then filtered, dried to constant weight, and subsequently dissolved in 50 mL 0.1 M nitric acid after which the mixture was mounted on an orbi-shaker and agitated for 24 h. The suspension was filtered with 0.45 μm millipore filter paper and 2–3 mL of the filtered solution was analyzed with ICPOES to determine the quantity of Cd(II) ions desorbed in the filtrate. The percent desorption of Cd(II) ions was calculated by Eq. (3) as follows:

$$\%\ \text{Cd}\left(\text{II}\right)\text{ion desorbed} = \frac{C_d V_d}{q_e W} \times 100 \tag{3}$$

2.6. Adsorption isotherms model

Mathematical models often describe the behavior of adsorption which is known as the adsorption isotherm models [7]. The sorption isotherm illustrates an equilibrium state between exchange of adsorbate particles among liquid and solid phase [23]. In this study, Langmuir, Scatchard, Freundlich, and Dubinin–Radushkevich (D-R) isotherm models were used to assess the capabilities of (PEFA)$_5$ and (PEFA)$_{20}$ for the removal of Cd ion in aqueous solution.

2.6.1. Langmuir isotherm model

The Langmuir isotherm models explain sorption on a monolayer surface, indicating finite capacity on the materials [24]. The adsorbent has definite homogeneous sites within which adsorption occurs [6]. The Langmuir isotherm is expressed in the following equation:

$$Q_e = \frac{Q_{\max} K_L C_e}{1 + K_L C_e} \tag{4}$$

Eq. (4) can be linearized as follows:

$$\frac{1}{Q_e} = \frac{1}{Q_{\max} K_L C_e} + \frac{1}{Q_{\max}} \tag{5}$$

where C_e represents Cd equilibrium concentration (mg/L); Q_e represents quantity of Cd adsorbed (mg) per gram of the sorbent at equilibrium (mg/g); $Q_{\max}$ is the theoretical maximum adsorption capacity (mg/g), and K_L is the Langmuir isotherm constant (L/mg). When Eq. (5) is plotted as $\frac{1}{Q_e}$ against $\frac{1}{C_e}$ a straight line which passed through an origin is obtained. Both values of the slope and intercept can be extracted from $Q_{\max}$ and K_L, respectively. Using the key features of Langmuir parameters, the connection between the sorbate and sorbent can be predicted with the aid of dimensionless separation parameters (R_L) as shown in the following equation:

$$R_L = \frac{1}{1 + K_L C_i} \tag{6}$$

where Langmuir constant is denoted as K_L and the initial concentration of Cd is denoted as C_i. The value of R_L gives vital information on the nature of sorption. $R_L = 0$, means an irreversible reaction, a favorable reaction means $R_L > 0$ but <1 (i.e., $0 < R_L > 1$), the reaction is linear if $R_L = 1$ while the reaction becomes unfavorable if $R_L < 1$.

2.6.2. Freundlich isotherm model

The main application of this isotherm model is heterogeneous surface sorption with interface between adsorbate molecules [25] also explains the adsorptive behavior of the adsorbent material [26]. Eq. (7) can be used to explain Freundlich isotherm.

$$Q_e = K_f C_e^{1/n} \tag{7}$$

The linear form of Eq. (6) is written as follows:

$$\ln Q_e = \ln K_f + \frac{1}{n}\ln \mathrm{C}_e \tag{8}$$

where C_e (mg/L) from Eq. (8) represents Cd equilibrium concentration; Q_e (mg/g) represents quantity of Cd (mg) adsorbed per gram of the sorbent at equilibrium; K_f ((mg/g) (L/mg)) represents sorption constant for Freundlich. When Eq. (8) is plotted as ln Q_e against ln C_e, a straight line which passed through the origin can be obtained.

2.6.3. D-R isotherm model

An empirical correlation that can be used to infer the non-uniformity of the actual energy of sorption on the adsorbent surface is known D-R model [27]. This type of model does not support sorption surface with uniform layers [28]. Eq. (9) explains the D-R model.

$$\ln Q_e = \ln Q_m - \beta\varepsilon^2 \tag{9}$$

In Eq. (9) Q_m represents a hypothetical sorption capacity at its optimum level (mg/g), R measured in kJ/mol/K denotes the gas constant, β represents D-R constant analogous to mean energy of adsorption measured in mol^2/kJ^2, T measured in K denotes absolute degree temperature, ε denotes the Polanyi sorption potential which can be expressed as follows:

$$\varepsilon = RT\ln\left(1 + \frac{1}{C_e}\right) \tag{10}$$

A linear plot of ln Q_e against ε^2 was used to extract the slope and intercept which are Q_m and β, respectively. The value of mean sorption free energy E (kJ/mol) [29] could be gotten from the relationship in Eq. (11).

$$E = \frac{1}{\sqrt{-2\beta}} \tag{11}$$

E offers information about sorption mechanism whether it is chemical or physical sorption. If the value of E is between 8 and 16 kJ/mol, then the sorption mechanism is chemically dictated. If $E > 16$ kJ/mol, then a chemical particle diffusion governs the reaction mechanism [29]. But if $E < 8$, then the adsorption mechanism is physically dictated.

2.6.4. Scatchard analysis

The conventional Langmuir equation can be modified into a more simplified isotherm description known as Scatchard analysis. Sorption mechanisms are commonly studied using this form of model. The affinity of the sorbent binding sites can be more elucidated with a Scatchard analysis. The following equation gives more explanation [30]:

$$\frac{Q_e}{C_e} = Q_s b - Q_e b \tag{12}$$

where Q_S (mg/g) and b (L/mg) are the Scatchard isotherm constants. A straight-line plot of Q_e/C_e versus Q_e can be used to obtain the values of Q_S and b from intercept and slope, respectively. The types of interaction in the solute phase of a sorption process can be known through the shape type of a Scatchard plot [31]. A heterogeneous straight line in this plot type often suggest multiple binding sites presence, while a homogeneous straight line in this plot specifies uniform binding site that is not aligned. Consequently, a linear plot with a negative slope in a Scatchard plot means it aligns with Langmuir model, thereby confirming binding sites of the sorbent and its interaction with metal ion solution [32]. This model provides a comprehensive information on active sites nature which make it an all-inclusive model than other isotherm model [33,34].

2.7. Kinetic modeling studies

The sorption of Cd ion was evaluated via various kinetic models like pseudo-first order, second order, and Weber intraparticle diffusion expressed in the following equation:

$$\frac{\log\left(q_e - q_t\right)}{q_e} = \frac{-K_L t}{2.303} \tag{13}$$

$$\frac{1}{\left(q_e - q_t\right)} = \frac{1}{q_e} + Kt \tag{14}$$

$$\frac{t}{q_t} = \frac{1}{\left(2K_s q_e^2\right)} + \frac{t}{q_e} \tag{15}$$

$$q_t = K_{id} t^{1/2} + C \tag{16}$$

where q_e and q_t represent the equilibrium quantities of adsorbed Cd ions (mg/g) and at a given time, t (min) respectively. K_L (min^{-1}) represents the pseudo-first-order sorption rate constant. K and K_S (g/mg/min) are second-order sorption rate constant and pseudo-second order. C, $t^{1/2}$, and K_{id} are intercept, square root of time, and intraparticle diffusion rate constant measured in (mg/g/min) and (min)$^{1/2}$, respectively. The above-mentioned constants (K_S, K_L, and K) can be obtained from the slopes of straight-line plots of $\frac{t}{q_t}$ against t, log($q_e - q_t$) against t, and $\frac{1}{\left(q_e - q_t\right)}$ against t, where q_e was obtained from the intercept of second-order rate and pseudo-second-order equations. Data obtained for this study were incorporated into Weber intraparticle diffusion, pseudo-first-order and pseudo-second-order equations [35].

3. Results and discussions

3.1. PEFA surface and chemical composition modification

Morphological and chemical composition of the raw fly ash (RFA), acid-treated fly ash (AFA), and PEFA surface were studied using SEM/EDX system. The SEM/EDX results were discussed in a previous work by Olabemiwo et al. [20,23,24] which clearly revealed that most of the heavy metal impurities were removed from the RFA after treatment with nitric acid (HNO_3). Comprehensive characterization of PEFA material using Fourier transform infrared, X-ray diffraction, thermogravimetric analysis, and X-ray fluorescence were also discussed in a previous work by Olabemiwo et al. [20,36,37]. However, in this paper, the SEM/EDXs and BET surface area analysis are presented to elucidate more on the adsorbent properties.

3.1.1. SEM and EDX spectroscopy analysis

Both modifications and chemical composition of as received FA, AFA, and PEFA surface were studied and characterized using *FESEM* coupled with *EDX*. Table 1 indicates the EDX analysis of the prepared adsorbents.

The micrograph obtained from the FESEM as shown in Figs. 2(a) and (b) indicates that as received FA and AFA have hollow shapes with heterogenous pore structures. The diameter of these materials varies from 50 to 500 µm with an average diameter of 100 µm having surface pores of varying sizes (i.e., mesoporous). Fig. 2(c) shows PEFA micrographs which confirm the presence of a thin pore linen coating with PDAD-PSS aqueous solutions. The microchemical analysis of the prepared adsorbents (as received FA, AFA and PEFA) was also investigated with EDX spectroscopy. Table 1 displays EDX analysis of the prepared adsorbents, as received FA contain about 75.9% composition of carbon, and oxygen at 10.97%, in addition to this there were elements like silicon, copper, vanadium, iron, zinc, nickel, and sulfur with percent composition of 0.17%, 1.74%, 2.21%, 1.24%, 0.05%, 1.49%, and 6.23%, respectively. Also, it can be deduced from Table 1 that there was an increase in percent carbon composition from 75.9% to 91.03% as well as increased silicon content from 0.17% to 0.35%. At this stage, there were no impurities like heavy metals as a result of acid treatment of as received FA with nitric acid. This was essential to ensure there was no metal impurities like Cd to avoid cross contamination of sample during adsorption study. Additionally, the data in Table 1 confirms as well the presence of polylelectrolyte as there was increase in sulfur content from 4.24% to 7.39% for PEFA due to the presence of polymer that has a styreno-sulfonate compound (i.e., PSS) in its composition. Although a deduction of the sulfur contents in the AFA might be due to the concentration of the acid that was used for acid treatment [38].

3.1.2. BET surface area analysis

BET analysis was conducted to examine the modifications that have occurred as a result of PE layering of the FA adsorbents. The results obtained were translated based on the adsorption–desorption of N_2 at 77 K for all the prepared adsorbents. Table 2 shows the summary report of BET surface area analysis of each adsorbents prepared (RFA, AFA, and PEFA). It can be observed from Fig. 3(a) that the adsorbents exhibited mesopore size which is supported by a type III isotherm. More so, the hysteresis loop of the isotherms

Table 1
EDX analysis of prepared adsorbents

	% Elemental composition									
	C	O	S	Si	V	Fe	Ni	Cu	Zn	Total
As received FA	75.90	10.97	6.23	0.17	2.21	1.24	1.49	1.74	0.05	100.0
Acid-treated FA	91.03	4.38	4.24	0.35	–	–	–	–	–	100.0
PEFA	88.73	3.88	7.39	–	–	–	–	–	–	100.0

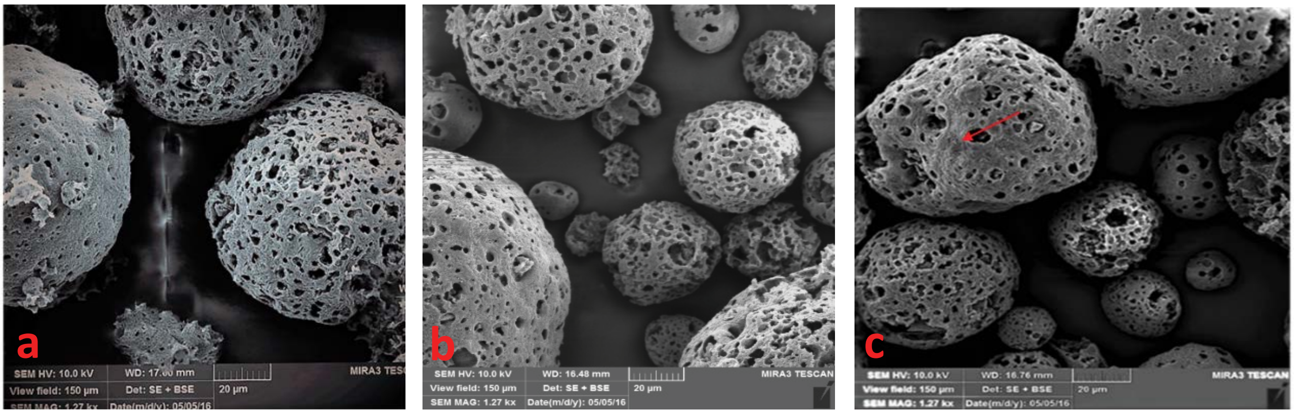

Fig. 2. SEM micrograph of (a) as received FA, (b) acid-treated FA, and (c) PEFA.

Table 2
Summary report of BET analysis for prepared adsorbents

	As received FA	Acid-treated FA	PEFA
Surface area (m^2/g)			
BET	7.60	32.08	14.39
BJH			
Adsorption cumulative	7.24	27.75	10.58
Desorption cumulative	7.41	30.74	11.11
Cumulative pore volume (cm^3/g)			
BJH adsorption	0.04	0.10	0.05
BJH desorption	0.04	0.11	0.05
Average pore size (Å)			
BET	96.84	81.10	67.25
BJH desorption	208.48	137.59	166.30

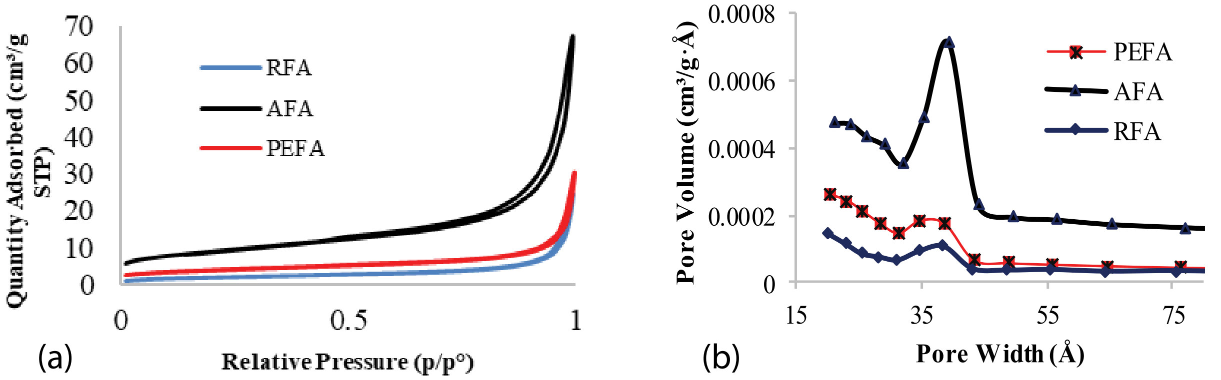

Fig. 3. (a) Adsorption–desorption isotherm plot showing hysteresis loop for as received FA, AFA, and PEFA (b) Pore size distribution of as received FA, AFA, and PEFA.

indicated that the rate of desorption is close to adsorption, an indication of large pore sizes on the surface of the adsorbents [39,40]. Also, from the data obtained for average pore sizes reported in Table 2, indicate that AFA gave the highest BET surface area due to acid treatment, which enhanced pore cleaning and removed heavy metal impurities [38], however, RFA and PEFA gave a higher BJH desorption average pore size. Hence, it can be deduced that acid treatment favors higher surface area and lower pore size distribution as shown in Fig. 3(b), while the addition of polymer coating on AFA gave PEFA with higher pore size distribution and higher surface area than the as received adsorbent.

3.2. Removal of Cd ions using $(PEFA)_5$ and $(PEFA)_{20}$

3.2.1. Effect of pH

One vital parameter regulating the sorption process is the initial pH of metal ion aqueous solutions, hence, its determination is of paramount importance [41]. The magnitude of ionization, adsorbent surface charge, and adsorbate description are likely to be affected by the solution pH [42]. Fig. 4 indicates pH effect on the removal capacity of Cd ions adsorbed by $(PEFA)_5$ and $(PEFA)_{20}$. The results obtained shows that the uptake of Cd ions from solution is intensely affected by pH. In acidic medium sorption was low but rises with an increase in solution pH. The percent Cd ions sorbed increases from 65.4% to 98.9% for $(PEFA)_5$ and 20.5% to 98.3% for $(PEFA)_{20}$ when there was an increase in pH from 4 to 9. In this study, pH 7 was used for all subsequent investigations

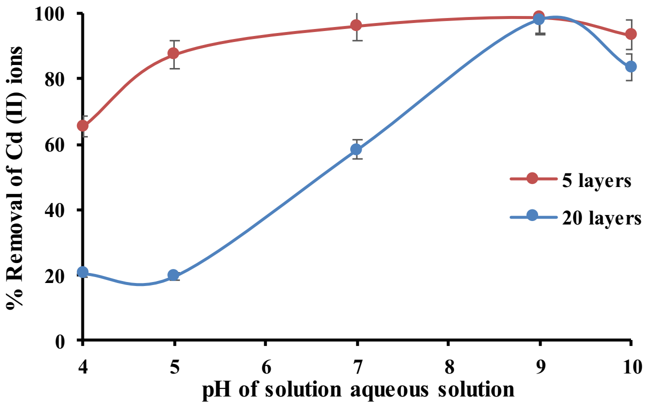

Fig. 4. pH effect on Cd ions adsorption onto $(PEFA)_{20}$ and $(PEFA)_5$ surfaces at 150 rpm speed, 15 min contact time, 200 mg quantity of adsorbent, 2 mg/L Cd ion concentration, 0.05 L volume of aqueous solution, and room temperature (RT).

due to the fact that at pH > 4, precipitation of metal ions may occur as OH⁻ species [43]. At low pH the sorption of Cd ions were rapid for $(PEFA)_5$ because physical adsorption phenomenon was more predominant and as well, there was ion trapping in the innermost spheres of the architecture network of $(PEFA)_5$ [44]. Though there was gradual uptake of Cd ions at low pH for $(PEFA)_{20}$ because there was competition for sorption sites between a significant number of hydrogen ions and Cd ions, this might have caused the relatively low percent removal at low pH [45].

3.2.2. *Effect of adsorbent dosage*

The influence of adsorbent quantity on Cd ions sorption from aqueous solutions on the external layers of both $(PEFA)_{20}$ and $(PEFA)_5$ were investigated. Fig. 5 shows adsorbent quantity effect on Cd ions uptake, the result indicates a direct relationship between the adsorbent weight and percent of Cd ions removed from aqueous solutions. There was an increase in the quantity from 1 to 6 g/L, which lead to a rise in the uptake of Cd ions. The adsorbed quantity increases from 44.5% to 97.8% and 25.1% to 95.3% for $(PEFA)_5$ and $(PEFA)_{20}$, respectively. This could be ascribed to surface area increase and accessibility of additional active sites on $(PEFA)_{20}$ and $(PEFA)_5$ surfaces for Cd ions sorption. Though the quantity of Cd ions adsorbed at equilibrium as presented in the secondary data of Fig. 5 indicates a contrasting trend [42], the sorption capacity declined from 0.918 to 0.336 mg/g and 0.518 to 0.328 mg/g for $(PEFA)_5$ and $(PEFA)_{20}$, respectively. These could be ascribed to a decline in the quantity of active vacant surface area for uptake of Cd ions that leads to the combination or intersecting of sorption sites, which escalate the path length of Cd ions diffusion [46]. This combination turns out to be gradually significant as the respective masses of both $(PEFA)_5$ and $(PEFA)_{20}$ increases. In addition, high quantity of adsorbents ($(PEFA)_5$ and $(PEFA)_{20}$) creates more active sites which makes the remaining sorption sites unsaturated after adsorption. Therefore, it could be inferred that as the mass of adsorbents increases, the amounts of adsorbed Cd ions onto a unit weight of $(PEFA)_5$ or $(PEFA)_{20}$ decreases, resulting into a drop in the sorption capacity (Q_e) values [42].

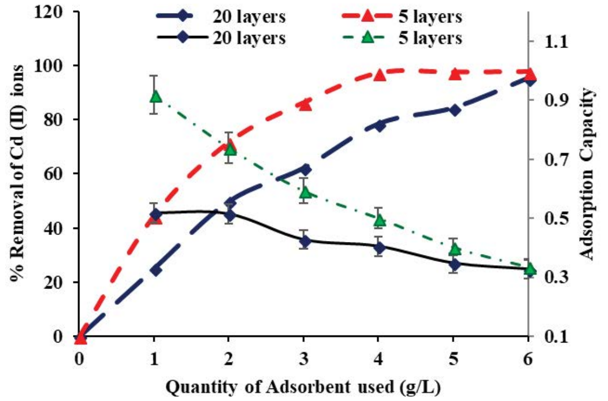

Fig. 5. Effects of adsorbent quantity on Cd ions adsorption onto $(PEFA)_{20}$ and $(PEFA)_5$ surfaces at 150 rpm speed, pH 7, 15 min contact time, 2 mg/L Cd ion concentration, 0.05 L volume of aqueous solution, and room temperature (RT).

3.2.3. *Time of contact effect*

Time of contact centers on the external architectural characteristics of the sorbent to be used [26]. The effects of contact time on Cd ions uptake onto the adsorbents surfaces is illustrated in Fig. 6. Initial sporadic adsorption of Cd ions was observed for both adsorbents $(PEFA)_{20}$ and $(PEFA)_5$ until it attains equilibrium time of around 15 min for $(PEFA)_5$ and 60 min for $(PEFA)_{20}$. Afterward there was no significant removal until 120 min. Contact time 15 min was used for subsequent parameter investigation as maximum sorption for $(PEFA)_5$ was achieved at this time even though it took $(PEFA)_{20}$ additional 45 min to attain equilibrium. The initially rapid sorption of Cd ions might be ascribed to the accessibility of abundant active sorption sites on the surface of the adsorbents which become filled up and get saturated as time increases [26,34,47].

3.2.4. *Effect of shaking speed*

The shaking speed certifies that Cd ions are moved to the active spots of the adsorbent by ensuring the contact between ions in solution and adsorbent accessible binding sites [48]. Fig. 7 indicates a rise in Cd(II) ion sorption as the shaking speed increased from 50 to 250 rpm. Approximately 97% removal was achieved for $(PEFA)_5$ and 84% for $(PEFA)_{20}$ at a speed of 150 rpm, aqueous solution volume of 50 mL, concentration of metal ion of 2 mg/L, adsorbents quantity of 4 g/L, pH 7, 15 min time of contact at room temperature. No significant removal was reached beyond this shaking speed with similar conditions in place, such observation could be as a result of enhanced interaction between the active spots of the sorption surface and metal ions in aqueous solution with an increase in shaking speed [8,23]. The value of 150 rpm was chosen as optimum shaking speed.

3.2.5. *Cadmium initial concentration effect*

In adsorption studies, knowing metal ion initial concentration is crucial because metal ion concentrations differ from one water and wastewater source to another, thus, knowing how its influence sorption investigation is important [16,49,50]. With adsorbent quantity of 4 g/L of $(PEFA)_5$ and

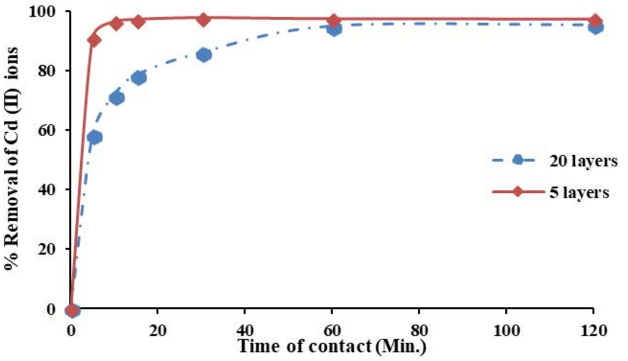

Fig. 6. Time of contact influence on Cd ions adsorption onto $(PEFA)_5$ and $(PEFA)_{20}$ surfaces at 150 rpm speed, 200 mg quantity of adsorbents, 2 mg/L Cd ion concentration, pH 7, 0.05 L volume of aqueous solution, and room temperature (RT).

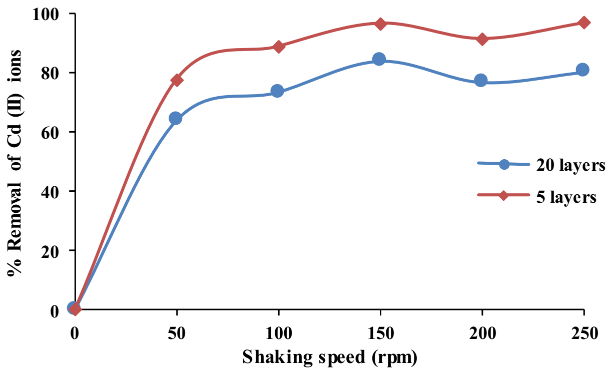

Fig. 7. Effects of shaking speed on Cd ions adsorption onto $(PEFA)_5$ and $(PEFA)_{20}$ surfaces at contact time 15 min, 200 mg quantity of adsorbents, 2 mg/L Cd ion concentration, pH 7, 0.05 L volume of aqueous solution, and room temperature (RT).

$(PEFA)_{20}$, 150 rpm shaking speed, pH 7, 15 min time of contact at room temperature as illustrated in Fig. 8, Cd ion concentration effect in aqueous media was conducted. Cd ions initial concentration examined were varied from 0.5 to 10 mg/L and its effect on the removal efficiency was ascertained. It was detected that increasing Cd ions initial concentration in aqueous solution could cause a decline in the removal efficiency of $(PEFA)_5$ and $(PEFA)_{20}$. This reduction can be ascribed to a fixed number of active sites for all adsorbents and this site becomes filled up as concentration increases. $(PEFA)_{20}$ performance was less inferior to $(PEFA)_5$ with 42.3% removal for 10 mg/L as compared with 68.7% in $(PEFA)_5$. This is due to large quantities of Cd ion with inadequate active spots on the adsorbents surface which bring about an increased Cd ions concentration in the greater part of the aqueous solution and as a result decreasing Cd ion removal [51].

3.2.6. *Effects of thickness of PEFA*

It is known from literature that one PE layer can have a thickness in the range of 0.5 nm to several nm (to around 8 nm), depending on the preparation conditions. In order to assess the effect of thickness of PEFA-coated layers on the removal efficiency of Cd from aqueous solution, batch adsorption runs were carried out using FA materials coated with 1, 2, 3, 4, 5, 10, 15, and 20 PE layers and the results are depicted in Fig. 9. Removal of Cd by uncoated AFA was also studied and results are presented in Fig. 9. About 96% removal efficiency of Cd was achieved using FA coated with 5 layers $(PEFA)_5$, followed by $(PEFA)_3$ and $(PEFA)_2$ with 92% and 89% removal, respectively. The highest Cd removal using the $(PEFA)_5$ material could be ascribed to the presence of greater number of sorption sites available for ion binding [37]. Moreover, results presented in Fig. 9 show that the rate of Cd ion sorption increases as the thickness of PE layers increased from 1 up to 5 layers but decreased as coated layers increased from 10 to 15 layers and then slightly increased when used 20 layers. More coated layers could mean more chemical sites become available for sorption, due to the increasing chemisorption mechanism being more predominant than physisorption mechanism compared with a non-coated FA, which adsorbs ions via physical mechanism by trapping ions in its inner pore spaces [46]. Therefore, it can be anticipated that increasing the coated layers (above 5 layers) may have caused the shift of Cd sorption mechanism to be governed by physical sorption and ion exchange attraction rather than chemical sorption which may have influenced the rate of uptake of Cd(II) ions.

3.3. *Desorption/regeneration study*

A potential adsorbent with good removal efficiency for metal ions must also have the capability to desorb the metal ions for recycling purposes [28,32,42]. Based on the aforementioned fact, it was pertinent to study the desorption of Cd(II) ions from AFA, $(PEFA)_5$, and $(PEFA)_{20}$ surfaces. 0.1 M HNO_3 was used in desorbing the metal ions from the loaded adsorbents as demonstrated in Fig. 10. As shown in Fig. 11, the desorption efficiency of AFA was 61% as compared with $(PEFA)_5$ and $(PEFA)_{20}$ with 55% and 35%, respectively. This also suggests that physisorption might have been involved in the adsorption process [12,44,45].

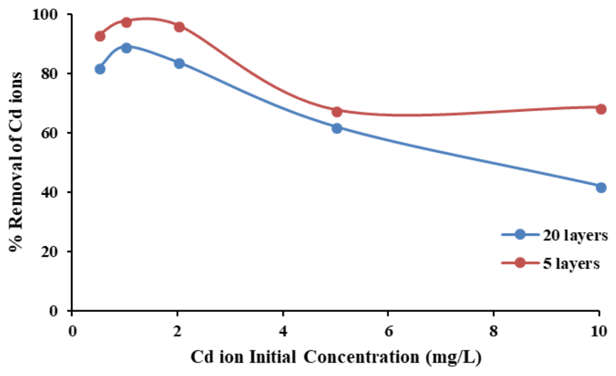

Fig. 8. Effects of initial concentration of Cd ions onto $(PEFA)_5$ and $(PEFA)_{20}$ surfaces at contact time 15 min, 200 mg quantity of adsorbents, 150 rpm, pH 7, 0.05 L volume of aqueous solution, and room temperature (RT).

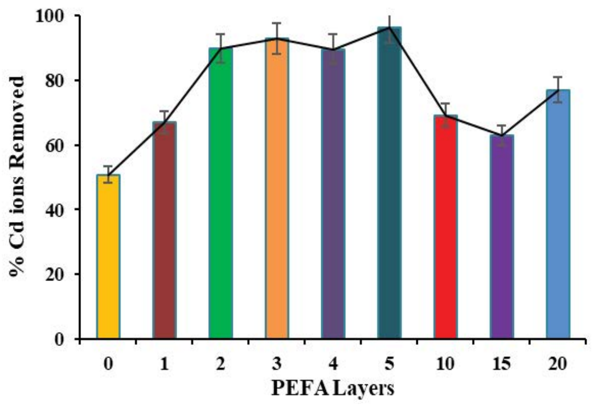

Fig. 9. Effects of layers on Cd(II) ions adsorption at contact time 15 min, 2 mg/L Cd(II) ion concentration, 200 mg quantity of adsorbents, 150 rpm, pH 7, 0.05 L volume of aqueous solution, and room temperature (RT).

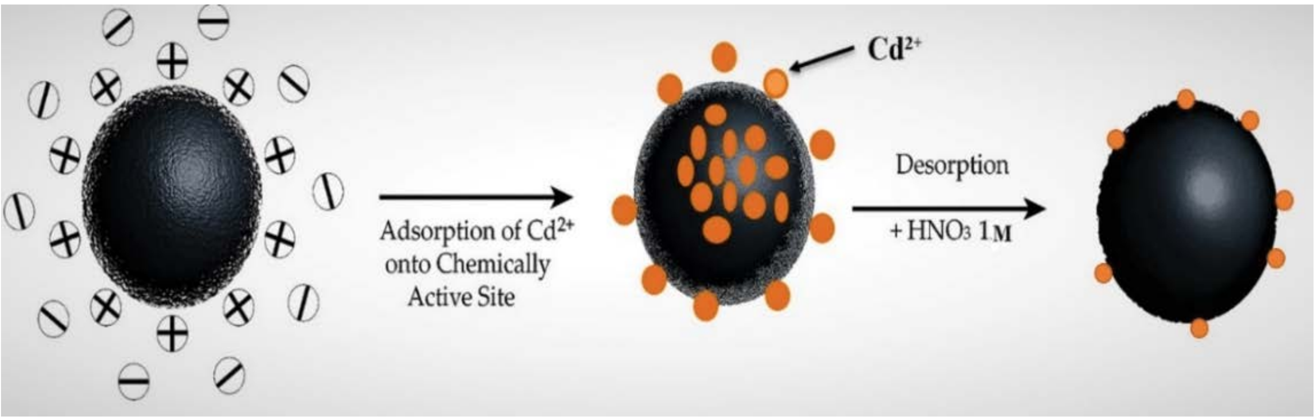

Fig. 10. Schematic illustrations of adsorption–desorption of Cd(II) ions onto the surface of PEFA.

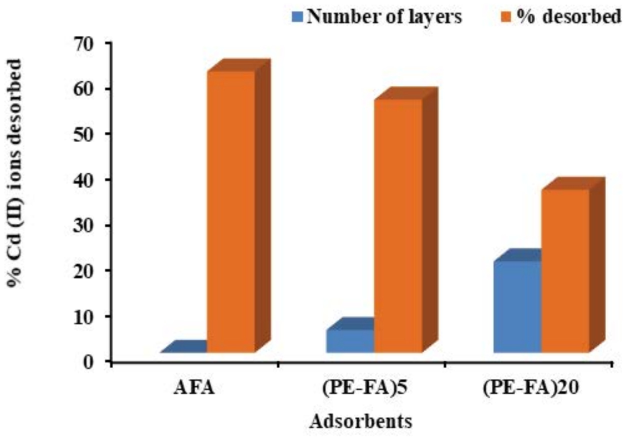

Fig. 11. Percent desorption of Cd(II) ions on FA-based adsorbents (AFA, $(PEFA)_5$ and $(PEFA)_{20}$) surfaces as a function of pH value of 7, 200 mg adsorbent quantity, 2 mg/L Cd ion concentration, contact time 24 h, mixing rate of 150 rpm, 0.05 L volume of aqueous solution, and room temperature.

3.4. Adsorption isotherms model

Table 3 illustrates Langmuir isotherm R^2 values for both adsorbents and this implies a good fit to the experimental data. Maximum sorption capacity (Q_m) was established to be 0.889 and 0.62 mg/g for $(PEFA)_5$ and $(PEFA)_{20}$, respectively. The value of dimensionless separation parameters (R_L) for this study as indicated in Table 3 favors the sorption process ($R_L < 1$) for 2 mg/L Cd(II) ion concentration [26,42,52]. This also implies that both adsorbents have high affinities for Cd(II) ions. Freundlich model on the other hand has a high R^2 values for $(PEFA)_{20}$ and $(PEFA)_5$ as shown in Table 3, this illustrates that the model fits well to the experimental data. Additionally, both adsorbents values of n indicate a favorable adsorption process [9,53]. The R^2 values for D-R isotherm provide a good fit to the data obtained during the experiment. The values of E, Q_m, and β are shown in Table 3. In addition, the E values obtained for this investigation are 5 and 3.16 kJ/mol for $(PEFA)_{20}$ and $(PEFA)_5$, respectively, this infers that physical mechanism has occurred between Cd ions and the adsorbents in aqueous medium. The Scatchard plot R^2 values for $(PEFA)_5$ and $(PEFA)_{20}$ are shown in Table 3 and this indicates a negative slope which is linearly conformed, this infers that the contact between the sorbent binding sites and

Table 3
Langmuir, Freundlich, D-R, and Scatchard plot isotherm constants for Cd(II) ion uptake

Langmuir isotherm	PEFA	R^2	K_L	Q_m	R_L
	20L	0.97	4.08	0.62	0.11
	5L	0.93	18.12	0.89	0.03
Freundlich isotherm		R^2	K_f	n	
	20L	0.94	2.06	3.87	
	5L	0.95	1.15	4.36	
		R^2	Q_m	β	E
D-R isotherm	20L	0.99	1.14	$-5\text{x}10^{-8}$	3.16
	5L	0.93	1.78	$-2\text{x}10^{-8}$	5.00
		R^2	b	Q_s	
Scatchard isotherm	20L	0.97	–4.07	0.62	
	5L	0.92	–16.48	0.92	

Table 4
Sorption kinetics parameters for Cd ion adsorption by PEFA

	Pseudo-first order			Pseudo-second order			Intraparticle diffusion		
	q_e	K_1	R^2	q_e	K_2	R^2	K_i	C	R^2
5 Layers	19.129	0.1195	0.9091	0.5076	4.442	0.9999	0.0104	0.447	0.8119
20 Layers	4.5064	0.0321	0.9713	0.516	0.4831	0.9999	0.0247	0.2977	0.9748

Cd ions obeys the Langmuir model. Also, a concave curve was found in the plot (figure not shown) of $(\text{PEFA})_{20}$, which implies that the contact between the sorbent surface and Cd ions is controlled by weak and strong positive co-operativity binding sites. Simultaneously, both negative and positive co-operativity with convex and concave shapes was observed for $(\text{PEFA})_5$, this indicates the existence of two classes of binding sites.

3.5. Kinetic modeling studies

Table 4 indicates values of K_i and q_e extracted from the ln q_e (intercept) and K_i (slope) of plot $\ln(q_e - q_t)$ versus t. The values of correlation coefficient (R^2 = 0.9091 and 0.9712 for $(\text{PEFA})_5$ and $(\text{PEFA})_{20}$, respectively) for pseudo-first order was lower than that of pseudo-second order as shown in Table 4. This could imply that sorption kinetics takes place chemically and comprises valency forces by electron exchange or ions sharing between adsorbed ions and the PEFA surfaces [43,54]. Values q_e and K_2 were calculated from $1/K_2q_e^2$ (intercept) and q_e and $1/q_e$ (slope) of the plot. The correlation values (*R^2 = 0.9999 and 0.9999 for $(\text{PEFA})_5$ and $(\text{PEFA})_{20}$, respectively*) for pseudo-second order were very strong and could be attributed to the fact that Cd ions materialized on a monolayer mode, which depend on the assumption that the rate-limiting factor could be chemical sorption [26]. A straight-line plot of q_t against $t^{1/2}$ from Weber intraparticle diffusion equation was elucidated [55]. Values of C and K_i were obtained from C (intercept) and K_i (slope) as shown in Table 4. The coefficient of correlation values R^2 = 0.8119 and 0.9748 for $(\text{PEFA})_5$ and $(\text{PEFA})_{20}$, respectively, and its intercept did not pass through the origin. This implies that the boundary layers are being controlled and also intraparticle pore diffusion (IPD) was not the solitary rate-limiting factor governing the reaction [26]. The plot for the IPD equation suggests multilinearity, confirming the occurrence of more than one step. The sharper region initially observed is related to Cd ions diffusion through the solution and PEFA outer surfaces or solid molecules boundary layer diffusion [5]. The second part gives description of ion phase where IPD is a rate-limiting factor. The third part is ascribed to the equilibrium in the final phase. Nonetheless, the plot intercept inability to pass via the origin may point to the variance in mass transfer rate in the final and initial phase of sorption [56].

4. Conclusion

The adsorption mechanisms and kinetics of multilayer PEFA were investigated. Sorption of Cd(II) ions using 5 and 20 layers PEFA surfaces were observed to be reliant on dose of adsorbent (PEFA), shaking speed, contact time, pH of aqueous solution, number of PEFA layers, and Cd ions initial concentration. Optimum Cd ions removal was attained at pH 7 in 15 min using 5-layer PEFA. The equilibrium adsorption isotherm models were evaluated and gave good fit to the experimental data for both 20 and 5 layers PEFA and followed the pseudo-second-order kinetics. The Scatchard plot analysis confirmed the heterogeneous surfaces of PEFA with multiple binding sites. The desorption experiment indicated that the more the layers, the difficult it would be to desorb metal ions from PE-coated FA as there was 35% and 55% desorption efficiencies for 20 and 5 layers PE-coated FA, respectively. Finally, this study provides an insight on the number of layers required to coat FA with polyelectrolyte solutions and its application in water treatment.

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