Research Article

Generation-3 Polyamidoamine Dendrimer-Silica Composite: Preparation and Cd(II) Removal Capacity

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Generation-3 polyamidoamine (PAMAM) dendrimer was implanted on silica to produce a very good adsorbent (G-3 PAMAM-SGA). The composite was characterized and used for the removal of Cd(II) ions from aqueous solution. Kinetic data fit the Lagergren pseudo-second-order model and also follow the intraparticle diffusion kinetic model to an extent, which is an indication that the sorption process is controlled by both mechanisms: intraparticle/film layer and adsorption inside the pores/crevices of the composite. Equilibrium sorption data of Cd(II) on G-3 PAMAM-SGA fit the Freundlich isotherm ($R^2 = 0.9993$) which is indicative of multilayered adsorption that occurred on heterogeneous surfaces. The $\Delta G^\circ$ values for all temperatures studied were negative, which indicated a spontaneous and feasible process. The result implies that G-3 PAMAM-SGA is a promising adsorbent for microscale scavenging of Cd(II) ions in aqueous solutions.

1. Introduction

The term “heavy metal” describes naturally occurring elements that have atomic weights between 63.5 and 200.6 g mol$^{-1}$ and specific gravity more than 5.0 g cm$^{-3}$, and they are found in groups III–V on the periodic table [1]. Some heavy metals usually found within industrial wastewater streams include nickel (Ni), lead (Pb), chromium (Cr), mercury (Hg), zinc (Zn), arsenic (Ar), cadmium (Cd), selenium (Se), uranium (U), silver (Ag), and gold (Au) [2].

Heavy metals are widely distributed in the environment due to their numerous uses in technological, industrial, domestic, agricultural, and medical fields as such their negative impact on environmental and human health is now a severe concern [3]. Investigations have shown that heavy metals are exceptionally toxic and can cause damaging effects on humans and other animals even at very low exposure levels because human beings and other animals do not have good elimination mechanisms for them [4]. Studies have shown that heavy metals could be emitted in their elemental or compound forms into the environment when triggered by natural or anthropogenic processes [5]. Humans ingest heavy metals through air, water, food, industrial products, and occupational exposure [6, 7]. When heavy metals go into the human body, they migrate into the stomach which is an acidic medium and are converted to their stable oxidation states such as Zn$^{2+}$, Pb$^{2+}$, Cd$^{2+}$, As$^{3+}$, As$^{5+}$, Hg$^{2+}$, and Ag$^+$, and these stable cations then interact with biomolecules such as enzymes and proteins to form strong and stable bonds which in turn inhibit the proper functioning of the biomolecules, thereby exhibiting poisoning effects to the human body [8]. Cd(II) ions are usually generated from a wide range of industrial processes such as metal smelting, alloy manufacturing, petroleum refining, solid mineral mining, and electroplating [9]. Cd(II) ions are easily dispersed into the environment through natural emissions/bioaccumulation processes which happen in some plants and animals [10]. Some other well-known means of exposure to Cd(II) ions include inhalation of cigarette smoke and intake of cadmium-contaminated food and water. Reports have it that cadmium is very poisonous even at very small concentrations because it causes damage to the human body cells [11, 12]. Some conventional procedures for decontaminating aqueous
systems polluted with heavy metal ions include chemical precipitation, ion exchange, coagulation/flocculation, ultrafiltration, electrochemical treatment, electrodialysis, and adsorption.

Adsorption is a renowned, straightforward, cost-effective, and proficient means of eliminating heavy metal ions from aqueous systems via a range of adsorbents such as fly ash, bentonite, metal-organic frameworks, layered double hydroxides, and many other carbon-based and agricultural waste materials [13]. In recent times, silica-based adsorbents have attracted attention in wastewater treatment because they possess special inherent properties such as chemical inertness, large pore sizes, large surface area, and susceptibility to functionalization to meet selectivity criteria for specific pollutants [14].

Studies have shown that when cross-linked polymeric resins are immobilized on silica by means of covalently attached functional groups, inorganic-organic hybrid adsorbents are formed [15]. One of such is the polyamidoamine (PAMAM) dendrimer-silica hybrid wherein the immobilization of PAMAM dendrimer on silica results in the versatility of PAMAM-functionalized silica materials as adsorbents. Owing to its elemental composition, PAMAM dendrimer contains very many forms of oxygen and nitrogen atoms that facilitate effective chelation and complexation reactions with metal ions, and they also enhance the chemical modification of the polymer for the purposes of improved adsorption capacity and selectivity [16, 17]. Thus, the presence of numerous amide and primary amine groups creates the special capability for PAMAM-silica composites to bind on various molecules in aqueous and nonaqueous media [18–20].

Thus, surface modification of adsorbent materials is enticing as a contemporary research component for the advance of low-cost procedures for the removal of heavy metal ions from aqueous systems [21].

In this study, functionalized generation-3 polyamidoamine dendrimer molecules were immobilized on silica using the graft to approach wherein the full dendritic character of the dendrimer is maintained. Consequently, a dendrimer-silica composite with unique physicochemical properties was fabricated (see Section 3.1). The prepared adsorbent was then tested for its sequestration of Cd(II) ions in aqueous solution under optimized reaction conditions of contact time, pH, initial concentration, and temperature.

2. Materials and Method

2.1. Synthesis of G-3 PAMAM-Functionalized Silica. All chemicals used during this study were of analytical grade; they include generation-3 polyamidoamine (PAMAM) dendrimers (with ethylenediamine core), succinic anhydride, 3-aminopropyltriethoxysilane (APTES), cadmium nitrate salt, and chromatographic-grade silica gel (particle size of 240–425 mesh, pore size of 15 nm, pH of 7, and pore volume of 1.15 cm³/g) acquired from Sigma-Aldrich, South Africa, and N-(3-dimethylaminopropyl)-N′-ethylcarbodiimide hydrochloride produced by Thermo Fisher Scientific, Belgium.

The linking agent 3-aminopropyltriethoxysilane (APTES) was grafted on silica gel using similar methods as described by Acres et al. [22]. Silica gel (30 g) was activated by oven-drying for 2 hours at a temperature of 130°C. The activated silica (20 g) was refluxed at 115°C for 6 hours in a mixture composed of 10% APTES and 100 mL anhydrous toluene. The ensuing product obtained is the amino-functionalized silica which was consequently separated from the solution by centrifugation at 4000 rpm for 10 min. The amino-functionalized silica was washed using water and ethanol alternatively in order to remove excess reagents, with the very last wash done with ethanol after which the product was oven-dried at 110°C for 1 hour. The product (amino-functionalized silica) was then stored in a preclean sample storage bottle for later use.

Another intermediate product (succinic acid-terminated generation-3 PAMAM dendrimer) was prepared using the method of Jiang et al [23]. The succinic acid-terminated generation-3 PAMAM dendrimers were prepared by dissolving approximately 3.7 mL of G-3 PAMAM dendrimer and 3.1 g of succinic anhydride in separate 50 mL volumes of dimethyl sulfoxide (DMSO). Both solutions were then transferred into a round-bottom flask and refluxed for 12 hours at a temperature of 80°C followed by dialysis with deionized water over 3 days (deionized water was replaced every 6 hours). The succinic acid-terminated generation-3 PAMAM was withdrawn from the dialysis setup by means of a micropipette and stored for further use.

The aim of this phase of synthesis was to synthesize a G-3 PAMAM dendrimer-functionalized silica (G-3 PAMAM-SGA) relying on the reaction between the succinic acid terminal of the succinic acid-terminated generation-3 PAMAM dendrimer and the amine terminal of the amino-functionalized silica. The method of Shi et al. [24] was adopted. Approximately 20 g of both intermediate products (i.e., silica grafted with APTES and succinic acid-terminated generation-3 PAMAM dendrimer) was added into a 250 mL round-bottom flask containing 75 mL methanol. The coupling agent N-(3-dimethylaminopropyl)-N′-ethylcarbodiimide hydrochloride (EDC) (=5 mg) [25] was added to the flask and the whole mixture was refluxed at 90°C for 12 hours. The product was separated from the solution by centrifugation at 4000 rpm for about 10 minutes, and thereafter, it was washed three times with ethanol and oven-dried at 110°C for 1 hour. The end product is the G-3 PAMAM-functionalized silica (G-3 PAMAM-SGA).

2.2. Characterization of the Adsorbent. The synthesized composite (G-3 PAMAM-SGA) and one of its precursor materials (unmodified silica) were characterized using Fourier transform infrared (FTIR) spectrometer (Spectrum Two, Perkin Elmer Instruments, USA) in order to determine the associated functional groups, Micromeritics TRISTAR II 3020 analyzer (Micromeritics Instrument Corporation, USA) was used to determine the surface area and porosity, thermogravimetric analyzer (PerkinElmer TGA 4000, Perkin Elmer Instruments, USA) was used for thermogravimetric analysis (TGA) in order to determine the material's
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thermal stability, and the scanning electron microscope (SEM) (Zeiss Auriga Field Emission) was used for the determination of the adsorbent’s surface morphology.

2.3. Adsorption Study. The stock of the adsorbate solution (1000 g/L) was prepared using cadmium nitrate salt (Cd(NO3)2), and working solutions were then prepared from the stock by serial dilution. Batch adsorption of Cd(II) ions was carried out in triplicate using G-3 PAMAM-SGA as an adsorbent with the aim of determining the effects of operation parameters such as contact time, concentration, pH, and temperature.

The adsorption procedure was performed as follows: 20 mg of adsorbent material was added to 20 mL adsorbate solution of specific concentration in plastic centrifuge bottles. The adsorbate/adsorbent mixture was then placed in an orbital shaker operated at 200 rpm until equilibrium was achieved. The solution’s pH was adjusted by either 0.1 M HCl or 0.1 M NaOH when necessary. At equilibrium, the centrifuge tubes were withdrawn, followed by centrifugation at 4000 rpm for 10 min. The amount of Cd(II) ions remaining in the solution was determined using a flame atomic absorption spectrophotometer (F-AAS, Shimadzu AA-7000, Japan).

2.4. Desorption Study. A desorption experiment was carried out on 20 mg of the previously used adsorbent. Adsorbate ions (Cd(II)) that were primarily adsorbed onto the adsorbent were desorbed by shaking in 20 mL 0.5 M nitric acid at 220 rpm for 10 minutes. The plastic centrifuge bottles were removed from the shaker and centrifuged at 3500 rpm for 10 minutes. The amount of Cd(II) ion left in the solution was determined using atomic adsorption spectrometry.

The adsorbent was washed twice with 0.5 M nitric acid and last of all with deionized water before the second round of reuse experiment (second cycle). The reuse investigation was carried out for three cycles.

2.5. Data Management. The adsorption capacity (qe) and removal capacity (R%) of Cd(II) ions by G-3 PAMAM-SGA were calculated using the following equations:

\[ q_e = \frac{(C_0 - C_e)V}{M}, \]

\[ R(\%) = \left(\frac{C_0 - C_e}{C_0}\right) \times 100, \]  

where \(C_0\) and \(C_e\) (mg/L) are the initial and equilibrium concentrations of Cd(II) ions in solution, V is the volume of adsorbate solution used (mL), and M is the mass of adsorbent used for the experiment.

Three kinetic isotherm models, pseudo-first-order (PFO) [26] (equation (2)), pseudo-second-order (PSO) [27] (equation (3)), and Weber–Morris intraparticle diffusion (IPD) [28] (equation (4)), were used in describing the effect of time data:

\[ q_t = q_e\left(1 - e^{-k_1t}\right) \times k_1, \]  

\[ q_t = \frac{q_e^2k_2t}{1 + q_ek_2t}, \]  

\[ q_e = k_{IPD}t^{1/2} + C, \]  

The symbols \(q_e\) and \(q_t\) are the amounts of Cd(II) adsorbed (mg/g) on the adsorbent (G-3 PAMAM-SGA) at equilibrium and time t, respectively, and \(k_1\) (min⁻¹), \(k_2\) (g/g/ min), and \(k_{IPD}\) (g/g min⁻¹/²) are the rate constants of the PFO, PSO, and IPD, respectively, while \(C\) (mg/g) is the amount of Cd(II) adsorbed on the adsorbent surfaces.

Equilibrium data at 294 K were calculated using Langmuir [29] (equation (5)), Freundlich [30] (equation (6)), and Flory–Huggins [31] (equation (7)):

\[ \frac{C_e}{q_e} = \frac{1}{K_mC_m} + \frac{C_e}{q_m}, \]  

where \(C_e\) is the concentration of adsorbate at equilibrium (mg g⁻¹) and \(K_m\) is the Langmuir constant related to adsorption capacity (mg g⁻¹).

\[ \log q_e = \log K_F + \frac{1}{n} \log C_e, \]  

where \(K_F\) is the adsorption capacity (L/mg) and \(1/n\) is the adsorption intensity and it also indicates the relative distribution of the energy and the heterogeneity of the adsorbate sites.

Flory–Huggins isotherm describes the degree of surface coverage characteristics of the adsorbate on the adsorbent [31].

The linear form of the Flory–Huggins equation is expressed as follows:

\[ \log \left(\frac{\theta}{C_e}\right) = \ln K_{FH} + n \ln (1 - \theta), \]  

where \(\theta\) is the degree of surface coverage, \(n\) is the number of adsorbates occupying adsorption sites, and \(K_{FH}\) is the Flory–Huggins equilibrium constant (Lmol⁻¹).

Thermodynamic parameters such as enthalpy change and entropy change were calculated using van’t Hoff equation [14] (equation (8)) and Gibbs free energy of adsorption was evaluated using equation (9):

\[ \ln K = \frac{\Delta S}{R} - \frac{\Delta H}{RT}, \]  

\[ \Delta G^* = \Delta H^* - TAS^*, \]  

where \(T\) is the temperature (K) and R is the ideal gas constant (8.314 J.mol⁻¹K⁻¹).

The linear form of the modified Arrhenius expression was applied to the experimental data to evaluate the activation energy \(E_a\) and sticking probability \(S^*\) as shown in the following equation [32]:
In \((1 - \theta) = \ln S^* + \frac{E_a}{RT}\)  \(\text{ (10)}\)

where \(\theta\) is the degree of surface coverage.

3. Results and Discussions

3.1. Characterization Results. A graphic representation for the synthesis of G-3 PAMAM-functionalized silica (G-3 PAMAM-SGA) adsorbent is shown in Figure 1. Pristine silica and G-3 PAMAM dendrimer were pretreated independently before both moieties were condensed to get the ultimate adsorbent. APTES was initially grafted on activated silica gel using surface hydroxyl groups ensuing in an amino(-NH\textsubscript{2}-) functionalized silica. Subsequently, generation-3 PAMAM dendrimers were functionalized with succinic anhydride to form the carboxylic acid-terminated dendrimer. Lastly, amino-functionalized silica moieties were combined with the acid-(-COOH-) terminated generation-3 PAMAM dendrimers using a linking agent N-(3-dimethylaminopropyl)-N'-ethylcarbodiimide hydrochloride (EDC) [26]. Literature has shown that surface coverage of silica with an organic compound leads to an increase in the pH at the point of zero charge \((\text{pH}_{\text{pzc}})\) from 2.1 to higher values [32]. The pH at point of zero charge \((\text{pH}_{\text{pzc}})\) of G-3 PAMAM-SGA is observed to be 3.1, which also corroborates the successful immobilization of the G-3 PAMAM dendrimer on silica. This means the surfaces of the dendrimer-functionalized silica composite become predominantly negatively charged with the pH value of above 3.1.

Other evidences of the successful synthesis of the G-3 PAMAM-SGA are shown in results of the physical and chemical properties (see Table 1 and Figure 2).

The \(\text{N}_2\) adsorption/desorption isotherm (not shown) implied a typical type IV isotherm, which points to the mesoporous nature of G-3 PAMAM-SGA. BET surface area was 16.9 m\textsuperscript{2}/g with a pore width of 17.4 nm which is larger than that for some previously reported silica-based adsorbents [34]. This large pore width would have facilitated the fast uptake of large adsorbate molecules from aqueous solutions by means of pore-filling mechanisms [33]. The FTIR spectra of the unmodified silica and G-3 PAMAM solutions by means of pore-filling mechanisms [33]. The first thermal transition was observed below 150 °C for both materials (Figures 2(b)–2(c)) and this was attributed to the loss of physisorbed water molecules within layers of the backbone silica material [35]. The second thermal transition was observed at 665 °C for pristine silica with a weight loss of 3.5 % (Figure 2(d)), while it was observed at a lower temperature (565°C) for the synthesized adsorbent (Figure 2(d)). The massive weight loss exhibited by G-3 PAMAM SGA at low temperature could be inferred as a confirmation of the presence of APTES and PAMAM groups which were more labile than the backbone silica material. Consequently, the weight losses at this second thermal transition were ascribed to the endothermic breakdown of surface hydroxyl groups on the unmodified silica and G-3 PAMAM SGA. The SEM images revealing pre- and postadsorption of Cd (II) ions onto G-3 PAMAM SGA are shown in Figures 2(e)–2(f). Figure 2(e) exhibits the clear surface image of the preadsorption SEM while the postadsorption surface SEM images (Figure 2(f)) show shiny agglomerated surfaces due to the presence of the adsorbed Cd(II) ions.

3.2. Effect of Time on Cd(II) Adsorption. The result of Cd(II) adsorption trend on the G-3 PAMAM SGA as time varied is shown in Figure 3(b). From this, it was observed that the uptake rate was quite fast at the beginning of the experiment to the initial 100 min when the adsorption-desorption rate became stable and equilibrium was achieved at approximately 180 min. The initial fast adsorption rate was attributed to adsorption on the several available surface adsorption sites and filling of the pore/cavities by adsorbate ions in solution. Subsequently, not much significant Cd(II) adsorption was feasible because vacant adsorption sites have been filled, and accordingly, equilibrium is said to have been attained. From this experiment, the time for equilibrium attainment by the adsorbate (G-3 PAMAM SGA) was observed to be 180 min (see Figure 3(a)). In order to establish the mechanism of Cd(II) adsorption by G-3 PAMAM SGA, the effect of time data was fitted to three adsorption kinetic models: the pseudo-first-order, pseudo-second-order, and the intraparticle kinetic models. The results are shown in Table 2.

The results represented in Table 2 showed a poor fitting correlation coefficient of \(r^2 < 0.6671\) in the pseudo-first-order kinetic model. In contrast to the experimental data, the fitting for the pseudo-second-order kinetic model was better correlated \((r^2 > 0.991)\) (figure not shown). Hence, the experimental data fitted the pseudo-second-order kinetic model better than the pseudo-first-order kinetic model and gave more insight into the mechanism of the adsorption process. This fitting connotes that Cd(II) removal mechanism was for the most part electrostatic interactions between the Cd(II) ions and the active functional groups on the G-3 PAMAM SGA composite because it has been shown that the pseudo-second-order kinetic model is similar to the universal rate law for chemical reactions [36–38]. The well-known intraparticle diffusion kinetic model by Weber–Morris [29] has been used to determine whether an adsorption process occurs at the surface of an adsorbent or within its pores/partitions. Reports have it that the IPD model parameter \(C\) (mg/g) is a means of estimating surface adsorption, this means when the numerical value of “\(C\)” is equal to the experimental value “\(q_e\)” then the adsorption process is mainly controlled by surface adsorption, and the remaining part of the adsorption process is attributed to pore filling/partitioning within the adsorbent [39]. Thus, the \(C\) value in Table 2 implied approximately 41.75 % was due to
surface adsorption and 58.25% was due to pore filling/partitioning.

3.3. Effect of pH on Cd(II) Adsorption. Establishing the performance of a novel adsorbent to pH variations within aqueous systems is imperative in predicting the worth of such an adsorbent. Investigations have shown that pH has a direct effect on the magnitude of charge density surrounding adsorbents and adsorbates, and this eventually directs the degree of adsorption [36]. Consequently, the effect of pH on Cd(II) adsorption onto G-3 PAMAM SGA was examined as pH varied from 3 to 7, and the results are shown in Figure 3(b). It was observed that the absorption increased with an increase in the pH of the adsorbate solution. The observed drift can be explained in terms of the pH at point of zero charge (pHpzc) of G-3 PAMAM SGA (pHpzc = 3.1). Below the observed pHpzc, the adsorbent’s surfaces which
bear anionic functional groups such as hydroxyl and carbonates are blocked by protonation making them uncharged, so the removal of Cd(II) ions is mostly feasible via pore filling due to marginal electrostatic attraction. Conversely, with increasing pH, the adsorbent’s surface adsorption sites become progressively deprotonated and negatively charged. This leads to additional electrostatic interactions between the Cd(II) ions in the solution and the charged surface functional groups on the adsorbent, and as a result, progressively more Cd(II) adsorption was recorded. From the experimental result, optimum adsorption was observed at pH = 5.

3.4. Effect of Concentration of Adsorbate Solution and Temperature on Adsorption Trend. The result of the effect of varying Cd(II) concentration on G-3 PAMAM SGA adsorption is represented as the adsorption trend plots in Figure 4. It was observed that an increase in Cd(II) ion concentration in solution resulted in higher uptake by G-3 PAMAM. This trend was also observed for the various temperatures investigated: 293 K, 303 K, and 313 K (Figure 4). Analogous trend has been reported in the literature [40]. This could be attributed to the fact that, at some point in adsorption, the transportation of adsorbate ions between the external surface film and internal cavities of the
adsorbent equilibrates, as such adsorbate ions may not be able to migrate across the boundary, but increasing the concentration of adsorbate solution reenacts this transboundary drift into the pores and cavities of the adsorbent and this may have facilitated multilayer adsorption. Similar findings have been reported in the literature [38].

Figure 3: Adsorption trend for Cd (II) on G-3 PAMAM SGA as time (a) and pH (b) increased.

Table 2: Kinetic model parameters for Cd(II) adsorption.

<table>
<thead>
<tr>
<th>Kinetic model</th>
<th>Parameter</th>
<th>Cd(II)</th>
</tr>
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<tbody>
<tr>
<td>PFO</td>
<td>$q_e$ (mg·g$^{-1}$)</td>
<td>37.21</td>
</tr>
<tr>
<td></td>
<td>$k_1$ (min$^{-1}$)</td>
<td>0.083</td>
</tr>
<tr>
<td></td>
<td>$r^2$</td>
<td>0.637</td>
</tr>
<tr>
<td>PSO</td>
<td>$q_e$ (mg·g$^{-1}$)</td>
<td>32.546</td>
</tr>
<tr>
<td></td>
<td>$k_2$ (g·mg$^{-1}$·min$^{-1}$)</td>
<td>0.8182</td>
</tr>
<tr>
<td></td>
<td>$r^2$</td>
<td>0.9912</td>
</tr>
<tr>
<td>IPD</td>
<td>$C$ (mg·g$^{-1}$)</td>
<td>19.64</td>
</tr>
<tr>
<td></td>
<td>$k_i$ (g·g$^{-1}$·min$^{-1/2}$)</td>
<td>1.524</td>
</tr>
<tr>
<td></td>
<td>$r^2$</td>
<td>0.7621</td>
</tr>
<tr>
<td>PPA from IPD</td>
<td>%</td>
<td>41.75</td>
</tr>
<tr>
<td>PSA from IPD</td>
<td>%</td>
<td>58.25</td>
</tr>
<tr>
<td>Experimental $q_e$</td>
<td>mg/g</td>
<td>75.0</td>
</tr>
</tbody>
</table>

PFO: pseudo-first-order model; PSO: pseudo-second-order model; IPD: intraparticle diffusion model; PPA: predicted pore adsorption from IPD; PSA: predicted surface adsorption from IPD.

Figure 4: Effect of initial concentration and operating temperature on the adsorption of Cd(II) ions onto G-3 PAMAM SGA.

3.5. Equilibrium/Thermodynamics Studies. To facilitate a better description of the adsorption mechanism, the equilibrium data at 293 K were fitted to three adsorption isotherm models: the Langmuir, Freundlich, and Flory–Huggins models. Comparison of model parameters in Table 3 showed that the experimental data fitted the Freundlich adsorption isotherm model better than the
Flory–Huggins and Langmuir models. The Langmuir model had a correlation coefficient ($r^2$) closer to unity (0.999) while the Flory–Huggins model ($r^2 = 0.983$) and Langmuir model had the least ($r^2 = 0.980$). The correlation of the experimental data to the Freundlich adsorption isotherm model implies that the adsorption of Cd(II) on G-3 PAMAM SGA might have occurred on sites of unequal affinity for the Cd(II) ions as such there were multilayers of Cd(II) ions formed on the adsorbent surface at equilibrium [30].

The value of the adsorption intensity ($n$) which describes the surface site energy distribution was less than unity, which means adsorption occurred on predominantly heterogeneous adsorption sites [42]. The probability of an adsorbate finding a vacant adsorption site on the surface of the adsorbent during adsorption has been determined by the number of hopping ($n$) done by adsorbate ions [43]. Accordingly, the hopping number ($n$) of Cd(II) ions on G-3 PAMAM SGA was correlated with an increase in adsorbate concentration and temperature (Figure 5). It was observed that the probability of adsorbate ions to find vacant adsorption sites on the adsorbent was highest when the initial concentration of adsorbate solution was 125 ppm at 303 K.

Increasing the ambient experimental temperature from 293 through 313 K (Figure 4) showed that temperature had a positive effect on the adsorption of Cd(II) ions on G-3 PAMAM SGA; thus, the adsorption process was also evaluated using the following thermodynamic parameters: enthalpy change ($\Delta H^\circ$), entropy change ($\Delta S^\circ$), Gibbs free energy ($\Delta G^\circ$), sticking probability ($S^*$), and activation energy ($E_a$). The aforementioned thermodynamic parameters were calculated from the experimental equilibrium data obtained at the various temperatures investigated using the modified Arrhenius equation and the parameters are shown in Table 4. The $\Delta G^\circ$ values for all temperatures studied were negative, which presupposes a spontaneous and feasible adsorption process. The value of $\Delta H^\circ$ obtained from the calculation was positive which is an affirmation that the adsorption process was endothermic because, for typical endothermic processes, an increase in external energy would favour the forward process; accordingly, there was an increase in the uptake of Cd(II) ions with an increase in solution temperature [38]. The positive value of the $\Delta S^\circ$ is an indication of increased randomness of adsorbate ions in the solution as the adsorption process tends towards equilibrium. Although the calculated value for activation energy ($E_a$) was low (2.49 × 10\(^{-3}\) kJ mol\(^{-1}\)) which is indicative of a diffusion-controlled adsorption process, its positive value is an additional evidence that the process was endothermic. Sticking probability, which is a function of adsorbate/adsorbent interactive system, was estimated to be approximately unity ($S^* = 1.0003$) which presupposes a linear sticking relationship between adsorbate ions and the adsorbent within a multilayered adsorption system. Thus, a possible combination of physisorption and chemisorption (cooperative adsorption) was presumed.

### Table 3: Adsorption isotherm model parameters for Cd(II).

<table>
<thead>
<tr>
<th>Adsorption isotherm model</th>
<th>Parameter</th>
<th>Cd(II)</th>
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<tbody>
<tr>
<td></td>
<td>$Q_e$ (mg/g)</td>
<td>28.49</td>
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<tr>
<td>Langmuir</td>
<td>$\beta$</td>
<td>0.02</td>
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<tr>
<td></td>
<td>$r^2$</td>
<td>0.980</td>
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<td></td>
<td>$1/n$</td>
<td>5.986</td>
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<tr>
<td>Freundlich</td>
<td>$k_f$</td>
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<tr>
<td></td>
<td>$R^2$</td>
<td>0.9993</td>
</tr>
<tr>
<td></td>
<td>$K_H$</td>
<td>0.539</td>
</tr>
<tr>
<td>Flory–Huggins</td>
<td>$n$</td>
<td>1.581</td>
</tr>
<tr>
<td></td>
<td>$R^2$</td>
<td>0.983</td>
</tr>
<tr>
<td>Experimental $Q_e$ (mg/g)</td>
<td></td>
<td>123.3</td>
</tr>
</tbody>
</table>

### Figure 5: Correlating the initial concentration of Cd(II) ions with hopping number ($n$) as operating temperature increased.

### Table 4: Thermodynamic parameters of G-3 PAMAM SGA for Cd(II) adsorption.

<table>
<thead>
<tr>
<th>Thermodynamic Parameter</th>
<th>Parameter</th>
<th>Cd(II)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta H^\circ$</td>
<td>kJ mol(^{-1})</td>
<td>3.293</td>
</tr>
<tr>
<td>$\Delta S^\circ$</td>
<td>J mol(^{-1})K(^{-1})</td>
<td>0.0786</td>
</tr>
<tr>
<td></td>
<td>293 K</td>
<td>-1.504</td>
</tr>
<tr>
<td></td>
<td>303 K</td>
<td>-1.55</td>
</tr>
<tr>
<td></td>
<td>313 K</td>
<td>-1.607</td>
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</tbody>
</table>

3.6. Regeneration and Reusability. Regeneration of previously used adsorbent and recovery of adsorbate ions are very crucial for improving sorption process economics since regeneration allows for repeated reuse of adsorbent material and in essence lowers cost. Results of three cycles of desorption tests were carried out on G-3 PAMAM SGA previously used for Cd(II) sequestration (see Table 5).

It can be inferred from Table 5 that the 3rd cycle was slightly lower than the 2nd by 12.95%, while the 2nd cycle was lower than the 1st cycle by 25.24%. The significant difference between the 1st and 2nd adsorption cycles could be attributed to insufficient vacant adsorption sites on the adsorbent after the 1st adsorption cycle. The desorbing solvent could not reach the inner pores/crevices of the adsorbent material but desorbed adsorbate ions at the surface and near-surface regions of the adsorbent after the 1st cycle. Thus, adsorbate...
ions that were initially adsorbed at the near-surface region of the adsorbent were not accessible at the 3rd cycle and this resulted in a reduction in adsorption capacity by 12.95%.

3.7. Comparison with Reported Adsorbents. The G-3 PAMAM SGA adsorption capacity for Cd(II) has been compared with some low-cost and silica-based adsorbents reported in the literature (Table 5). The comparison showed that the G-3 PAMAM SGA adsorbent performed better than a number of reported adsorbents for Cd(II) sequestration from aqueous solutions. The fact that the adsorption capacity of G-3 PAMAM SGA was comparable to some of the best performing adsorbents reported in the literature points to the prospective of this composite for the removal of Cd(II) from aqueous systems (Table 6).

### Table 5: Efficiency of desorption of Cd(II) using 0.5 M HNO₃.

<table>
<thead>
<tr>
<th>Adsorption cycle</th>
<th>Desorption efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>85.59</td>
</tr>
<tr>
<td>2</td>
<td>60.35</td>
</tr>
<tr>
<td>3</td>
<td>47.40</td>
</tr>
</tbody>
</table>

### Table 6: Comparison of G-3 PAMAM SGA Cd(II) adsorption capacity with some adsorbents reported in the literature.

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>qₑ (mg/g)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hematite</td>
<td>4.94</td>
<td>[37]</td>
</tr>
<tr>
<td>SBA-15</td>
<td>9.84</td>
<td>[44]</td>
</tr>
<tr>
<td>Bentonite-Carica papaya composite</td>
<td>10.9</td>
<td>[45]</td>
</tr>
<tr>
<td>Feldspar-pine cone composite</td>
<td>11.5</td>
<td>[46]</td>
</tr>
<tr>
<td>Wheat stem</td>
<td>11.6</td>
<td>[47]</td>
</tr>
<tr>
<td>Chitin</td>
<td>14.7</td>
<td>[48]</td>
</tr>
<tr>
<td>G-3 PAMAM-SGA</td>
<td>24.49</td>
<td>This study</td>
</tr>
<tr>
<td>STNTS-Ch beads</td>
<td>38.8</td>
<td>[49]</td>
</tr>
<tr>
<td>Orange waste</td>
<td>48.3</td>
<td>[50]</td>
</tr>
<tr>
<td>G-5-PAMAM SGA</td>
<td>123.4</td>
<td>[30]</td>
</tr>
<tr>
<td>Nanocomposite material</td>
<td>148.32</td>
<td>[51]</td>
</tr>
<tr>
<td>Silica-activated carbon (2:3)</td>
<td>178.5</td>
<td>[52]</td>
</tr>
<tr>
<td>Activated sludge</td>
<td>204.1</td>
<td>[53]</td>
</tr>
<tr>
<td>Biogenic Mn oxide</td>
<td>229.3</td>
<td>[54]</td>
</tr>
</tbody>
</table>

4. Conclusion

Generation-3 polyamidoamine dendrimer was functionalized with amide and amine groups and immobilized on activated silica using 3-aminopropyltriethoxysilane (APTES) linkage to produce a G-3 PAMAM SGA composite. Characterization results for the synthesized composite show successful synthesis due to the observation of FTIR peaks attributable to amide functional groups (1630 cm⁻¹) and moderately lower thermal stability when compared to pristine silica, which may be due to the presence of integrated moieties. SEM micrographs revealed irregular and heterogeneous surfaces of the composite before Cd(II) adsorption and the presence of agglomerated Cd(II) ions on the surface of the adsorbent after adsorption. Adsorption experiments showed an equilibration time of 180 minutes, an optimum pH of 5, and an experimental adsorption capacity of 24.9 mg·g⁻¹. Thermodynamic studies showed that the process was endothermic, spontaneous, and feasible. Equilibrium and kinetic data modeling suggests electrostatic interactions between surface active sites and Cd(II) ions in solution and adsorption via pore-filling mechanism. The mechanism of Cd(II) and G-3 PAMAM SGA interaction is believed to follow a chelation/complexation of Cd (II) ions via coordination reactions between amide (−NH(CO))- , amine (NH-R) groups, and Cd(II) ions. Pseudo-second-order kinetic model described the experimental data best, signifying a chemisorption controlled process. Freundlich isotherm had the best fit to equilibrium data which is indicative of multilayered adsorption that occurred on heterogeneous surfaces. However, the Langmuir model had a good correlation with equilibrium data too with the highest adsorption capacity (24.49 mg·g⁻¹) which suggests some occurrences of physisorption as well. This assumption was clarified by the calculated value for sticking probability of the adsorption process, which is an evidence of a possible combination of physisorption and chemisorption (cooperative adsorption). G-3 PAMAM SGA demonstrated good reusability after three cycles of adsorption.

Hence, the modification procedure was successful and the synthesized composite (G-3 PAMAM SGA) could be efficient for the removal of Cd(II) ions from aqueous systems.

Data Availability

All data were generated at Applied Chemistry and Nanoscience Laboratory, Department of Chemistry, Vaal University of Technology, Vanderbijlpark, South Africa, and Department of Chemical Sciences, Niger Delta University, Wilberforce Island, Nigeria.

Conflicts of Interest

The authors declare that there are no conflicts of interest.

References


