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SORPTION PROPERTIES OF HYDROLYZED STARCH GRAFT COPOLYMERS IN THE REMOVAL OF CADMIUM (II) AND COPPER (II) IONS FROM AQUEOUS MEDIA

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ABSTRACT

Sorption properties of hydrolyzed starch graft poly (acrylic acid) and starch graft poly(acrylonitrile) copolymers as sorbents for the removal of Cd (II) and Cu(II) ions from aqueous solution in batch process were assessed. The copolymers were prepared using methods as reported in literature and were characterized in terms of morphology using scanning electron microscopy, confirmation of sorbents produced using Fourier transform infrared spectroscopy and thermal stability using thermogravimetric analysis. The effect of contact time, initial concentration and temperature were assessed to optimize the conditions for the sorption of the metal ions. The experimental data were subjected to analysis using the models; Langmuir, Freundlich, Temkin, Dubinin Radushkevich and Sips isotherm models. The Freundlich and the Sips isotherms confirmed the applicability of the models. The sorption capacity of the copolymers was found to be 118.61mg/g for starch graft poly (acrylic acid) and 115.83mg/g for starch graft poly (acrylonitrile). The sorption kinetics was assessed by Lagergren pseudo first order, pseudo second order, Elovich equation, Intraparticle diffusion and the liquid film diffusion models. The experimental data fitted very well with the Elovich equation and the Intraparticle kinetic models. The thermodynamic analysis showed that the sorption was a spontaneous and endothermic process. The results indicated that starch graft copolymers can be used as effective sorbents for Cd (II) and Cu (II) removal from aqueous media.

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1. INTRODUCTION

Environmental studies revealed widespread contamination of water by chemicals used in the chemical industry during manufacturing process (Abd-Alla et al., 2007). These chemicals include organic compounds, heavy

metals and other pigments used in the textile industry. These chemicals find their way into ground water, which cause pollution disrupting plant growth and posed a great risk to human health and to the environment (Blais et al., 2000). A range of processes are available for the uptake of heavy metals and organics from aqueous media, such as electro-chemical precipitation, ultrafiltration, ion exchange, use of activated carbon and reverse osmosis (Rengaraj et al., 2001; Benito and Ruiz, 2002; Yurlova et al., 2002). A draw back with these processes is high operational and materials cost.

This has caused interest to be shifted to the use of low cost and renewable agricultural materials as precursor for the preparation of value added products. Incorporation of other monomers/polymers into polysaccharides will not only reduce our dependence on petrochemical derivatives, but also provides improved materials which will biodegrade rapidly in the environment.

Sorption isotherm is an invaluable curve describing the phenomenon governing the retention (or release) or mobility of a substance from the aqueous media or aquatic environments to a solid-phase at a constant temperature and pH (Allen et al. 2004; Liu et al. 2010). Sorption equilibrium (the ratio between the sorbed amount with the remaining in the solution) is established when a sorbate containing phase has been contacted with the sorbent for sufficient time, with its sorbate concentration in the bulk solution in a dynamic balance with the interface concentration (Kumar et al., 2008).

Its physico-chemical parameters together with the underlying thermodynamic assumptions provide an insight into the sorption mechanism, sorption properties as well as the degree of affinity of the sorbents (Borah and Senapati, 2006).

Over the years, a wide variety of equilibrium isotherm models (Langmuir, Freundlich, Brunauer–Emmett–Teller, Redlich–Peterson, Dubinin–Radushkevich, Temkin, Toth, Koble–Corrigan, Sips, Khan, Hill, Flory–Huggins and Radke–Prausnitz isotherm), have been formulated in terms of three fundamental approaches (Malek, and Farooq, 1996).

Development and geometrical increase of industrial activities has led to immense utilization of heavy metals, and other toxic chemicals, and inevitably resulted in an increased flux of these substances in to the environment. The contamination of water due to cadmium and copper ions is accountable for several diseases such as cancer, liver disorder, brain damage (Ahmed et al., 2000, Aisien et al., 2013). However, several hundred micrograms per litre of cadmium and copper ions can be in waste water which necessitates the need for effective removal sorbents before such waste water are disposed to the environment for public safety (Zulkali and Norulakal, 2003).

The present study evaluates the sorption properties of hydrolyzed starch graft copolymers in the removal of cadmium (II) and copper (II) ions from aqueous media.

2. MATERIALS AND METHODS

2.1. Materials

Sigma Aldrich, Germany supplied the reagent grade acrylic acid and acrylonitrile and were distilled under reduced pressure and stored in the dark at 5°C before use. Cassava starch was obtained from cassava roots sourced locally from Benin City, Nigeria. Cerium ammonium nitrate and other reagents used were of analytical grade and supplied by Sigma Aldrich, Germany. The sorbate Cadmium (II) and Copper (II) stock solutions were prepared by dissolving the required amount of Cadmium nitrate and Copper (II) sulphate in distilled water at room temperature from which the experimental solutions were obtained by dilution to the desired concentration.

2.2. Preparation and Characterization of the Graft Copolymers

The starch graft copolymers which are hydrolyzed cassava starch graft poly (acrylic acid) (HSPAA) and hydrolyzed starch graft poly(acrylonitrile) copolymer (HSPAN) were prepared according to the method described by Fanta (1973), reported by Okieimen et al. (1989). The thermal behaviour and morphological studies were obtained using thermogravimetric analyzer and scanning electron microscope respectively. Fourier transform infrared spectrometry was used to analyze the changes in the functional groups

2.3. Sorption Properties Study

The sorption properties were assessed as follows:

2.3.1. Isotherm studies

The sorption isotherm was obtained by shaking 0.5g of the graft copolymer with 100ml of cadmium (II) and copper (II) solutions of known initial concentration. The mixtures were then placed in a rotary shaker for 18.25h. The temperature was maintained at 27.5 °C in a water bath. After this time the mixture was filtered and analyzed with atomic absorption spectrometer (AAS). A range of cadmium (II) concentrations from 2 to 10 ppm and copper (II) concentrations from 2 to 50ppm were used and agitation were carried out (pH 7.85) in a rotary shaker agitated at 200rpm. The mixture of cadmium ions and copper ions and the sorbents were respectively separated by centrifugation at 5000 rpm for 10min, and the concentration of the remaining cadmium ions and copper ions were determined by AAS.

In this study, the Langmuir, Freundlich, Temkin, Dubinin–Radushkevich and the Sips sorption isotherms were used for the sorption of copper and Cadmium ions by the hydrolyzed graft copolymers.

The Langmuir Adsorption Isotherm is represented by Equation (1) (Langmuir, 1916):

$$q_e = \frac{Q_o K_L C_e}{1 + K_L C_e} \quad (1)$$

C_e is the equilibrium concentration of adsorbate (mg/L^{-1}), q_e is the amount of metal adsorbed per gram of the adsorbent at equilibrium (mg/g), Q_o is maximum monolayer coverage capacity (mg/g), K_L is Langmuir isotherm constant (L/mg). The values of q_{max} and K_L were computed from the slope and intercept of the Langmuir plot of $1/q_e$ versus $1/C_e$.

The Freundlich adsorption isotherm is commonly used to describe the adsorption characteristics for the heterogeneous surface (Equation 2).

$$Q_e = K_f C_e^{\frac{1}{n}} \quad (2)$$

K_f is Freundlich isotherm constant (mg/g), n is adsorption intensity; C_e is the equilibrium concentration of adsorbate (mg/L) Q_e is the amount of metal adsorbed per gram of the adsorbent at equilibrium (mg/g). Linearizing Equation (2) results in:

$$\log Q_e = \log K_f + \frac{1}{n} \log C_e \quad (3)$$

The constant K_f is an approximate indicator of adsorption capacity, while $1/n$ is a function of the strength of adsorption in the adsorption process. A plot of $\log q_e$ versus $\log C_e$ gives a linearity as shown in Figure 6, with the slope and intercept given as n and K_f respectively as shown in Table 2.

The Temkin Isotherm contains a factor that explicitly taking into the account of sorbent–sorbate interactions. By ignoring the extremely low and large value of concentrations, the model assumes that heat of sorption (function of temperature) of all molecules in the layer would decrease linearly rather than logarithmic with coverage. The model is given by the following Equations:

$$q_e = \frac{RT}{b} \ln(A_T C_e) \quad (4)$$

$$q_e = \frac{RT}{b} \ln A_T + \left(\frac{RT}{b}\right) \ln C_e \quad (5)$$

$$B = \frac{RT}{b_T} \quad (6)$$

$$q_e = B \ln A_T + B \ln C_e \quad (7)$$

A_T is the Temkin isotherm equilibrium binding constant (L/g), b_T is Temkin isotherm constant, R is universal gas constant (8.314J/mol/K), T is Temperature at 298K and B is Constant related to heat of sorption (J/mol).

The Dubinin–Radushkevich isotherm is generally applied to express the sorption mechanism with a Gaussian energy distribution onto a heterogeneous surface, (Dabrowski, 2001), The model has often successfully fitted high solute activities and the intermediate range of concentrations data well. Equation (8) is linearized to plot the DRK graph. The constant such as q_s , and K_{ad} are determined from the appropriate plot using Equation 9. The results are as presented in Table 2.

$$q_e = (q_s) e^{(-K_{ad} \mathcal{E}^2)} \quad (8)$$

$$\ln q_e = \ln(q_s) - K_{ad} \mathcal{E}^2 \quad (9)$$

Where: q_e is amount of adsorbate in the adsorbent at equilibrium (mg/g); q_s is theoretical isotherm saturation capacity (mg/g); K_{ad} is Dubinin–Radushkevich isotherm constant (mol^2/kJ^2) and \mathcal{E} is Dubinin–Radushkevich isotherm constant.

The Sips isotherm is derived from the limiting behavior of the Langmuir and Freundlich isotherms. The model is valid for localized adsorption without adsorbate-adsorbate interactions. When C_e approaches a low value, the Sips isotherm effectively reduces to Freundlich, while at high C_e , it predicts the Langmuir monolayer sorption characteristic. The Sips linear equation model is expressed as:

$$Q_e = \frac{Q_m b C_e^{\frac{1}{n}}}{1 + C_e^{\frac{1}{n}}} \quad (10)$$

where K_s (1/mg) and Q_{\max} (mg/g) are the Sips equilibrium constant and maximum adsorption capacity values obtained from the slope and the intercept of the plot. The Sips isotherm equation is characterized by the dimensionless heterogeneity factor, n , which can also be employed to describe the system's heterogeneity when n is between 0 and 1. When $n=1$, the Sips equation reduces to the Langmuir equation and it implies a homogeneous adsorption process. The the linear regression was used to determine the best-fitting isotherms as presented in Table 2.

2.3.2. Kinetic studies

In order to assess the rate of sorption of cadmium ions and copper ions, the experiments were carried out under the following conditions: amount of copolymer used was 0.5bg per 100ml solution; initial concentration was 20ppm for a varying shaking time of 6 to 36h. The temperature was maintained at 27.5°C (pH 7.85).

In this study, the pseudo first order, pseudo second order, Elovich equation, intra-particle diffusion model and the liquid film diffusion models were employed to analyze the data obtained from the sorption of the cadmium (II) ions and copper (II) ions by the hydrolyzed graft copolymers.

The Lagergren (1898) pseudo first-order rate equation is presented as follows:

$$\frac{dq_t}{dt} = k_{pl}(q_e - q_t) \quad (11)$$

where q_e and q_t (mg/g) are the adsorption capacities at equilibrium and time t (min), respectively. k_{p1} (min^{-1}) is the pseudo-first-order rate constant for the kinetic model. Integrating Equation (11) within limits and rearrangement, the equation becomes:

$$\log(q_e - q_t) = \log q_e - \frac{k_{pl}}{2.303} t \quad (12)$$

A plot of $\log(q_e - q_t)$ versus time (t) gives a straight line with slope and intercept as K_p and q_e respectively.

The pseudo second order rate expression given as (Ho and McKay, 2002):

$$\frac{dq_t}{dt} = k_{p2}(q_e - q_t)^2 \quad (13)$$

Integration and rearrangement yields:

$$\frac{t}{q_t} = \frac{1}{V_o} + \frac{1}{q_o} t \quad (14)$$

$$V_o = k_{p2} q_e^2 \quad (15)$$

where V_o ($\text{mg}/(\text{g}\cdot\text{min})$) means the initial adsorption rate, and the constants can be determined experimentally by plotting of t/q_t against t .

A kinetic equation of chemisorption was established and was used to describe the rate of adsorption of carbon monoxide on manganese dioxide that decreases exponentially with an increase in the amount of gas adsorbed, which is the so-called Elovich equation as follows:

$$\frac{dq}{dt} = a e^{-\alpha q} \quad (16)$$

Where q represents the amount of gas adsorbed at time t , a the desorption constant, and α the initial adsorption rate. Equation (16) can be rearranged to a linear form:

$$q = \left(\frac{2.3}{\alpha}\right) \log(t + t_o) - \left(\frac{2.3}{\alpha}\right) \log t_o \quad (17)$$

$$t_o = \frac{1}{\alpha a} \quad (18)$$

Weber-Morris found that in many adsorption cases, solute uptake varies almost proportionally with $t^{1/2}$ rather than with the contact time t (Alkan *et al.*, 2007):

$$q_t = k_m t^{\frac{1}{2}} \quad (19)$$

where k_{in} is the intraparticle diffusion rate constant. According to Equation (19), a plot of q_t vs $t^{1/2}$ yield a straight line with a slope k_{in} when the intraparticle diffusion is a rate-limiting step. For Weber-Morris model, it is essential for the $q_t \sim t^{1/2}$ plot to go through the origin if the intraparticle diffusion is the sole rate-limiting step, in the case of this study, the line did not pass through the origin. However, it is not always the case and adsorption kinetics may be controlled by film diffusion and Intraparticle diffusion simultaneously. Thus, the slope is not equal to zero. Dumwald-Wagner proposed another Intraparticle diffusion model simplified as:

$$\log(1 - F^2) = -\frac{K}{2.303} t \quad (20)$$

A plot of $\log(1-F^2)$ vs t yielded a linear graph from which the rate constant K was obtained from the slope.

2.3.3. Thermodynamic studies

The sorption equilibrium experiments were also carried out at 303, 313 and 323K, respectively. The initial concentration of the cadmium ions and copper ions was 20 ppm at a pH of 7.85 and shaking time 18.25h. To assess the effect of temperature on the sorption of the lead (II) ions onto the graft copolymers, changes in three thermodynamic parameters were evaluated: Gibbs free energy change ΔG was calculated from Equation (21):

$$\Delta G = \Delta H - T\Delta S \quad (21)$$

where ΔG is the Gibbs free energy change (kJmol^{-1}), R is the gas constant ($8.314\text{Jk}^{-1}\text{mol}^{-1}$), T is the absolute temperature (k), and K is an equilibrium constant obtained by multiplying the Langmuir constant K_L (Lmol^{-1}). The change of enthalpy (ΔH) and entropy (ΔS) can be obtained from the slope and intercept of the van't Hoff equation of $\Delta G = \Delta H - T\Delta S$ by plotting ΔG vs T (Blazquez et al., 2011). The sorption equilibrium constant, K_L was obtained from the Langmuir plot of the sorption data at different temperatures (303.3, 313 and 323K) to obtain the thermodynamic parameter ΔG .

3. RESULTS AND DISCUSSION

3.1. Characterization of the Graft Copolymers

The result of the characteristics of the starch graft copolymers are show in Table 1.

Table 1: Characteristics of the starch graft poly (acrylic acid) and starch graft poly(acrylonitrile) copolymers

Parameters	Starch-g-polyacrylonitrile (HSPAN)	Starch-g-polyacrylic acid (HSPAA)
Colour	White	White
Water Retention Value (g/g)	382	480
Water Soluble	No	No
Dimension (μm)	150-350	150-350
Density (g/cm^3)	1.5	1.54
Thermal Stability ($^{\circ}\text{C}$)	250-300	200-250
pH	8.0	8.0
Graft Yield (%)	92.2	86.96
Graft Efficiency (%)	88.55	70.82
Graft Frequency/AGU	46.95	83.98
Molecular weight	172,526.25	96,446.88

The appearance of the characteristics bands of starch and the starch grafted polymers in the Fourier transform infrared (FTIR) spectrum is taken as the prime evidence. The graft efficiency (70.82-88.55%) may be due to the greater polarity and solubility of the monomers used in this study.

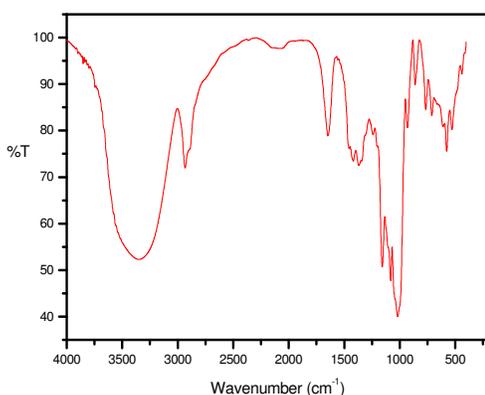


Figure 1: FTIR Spectrum of dried cassava starch

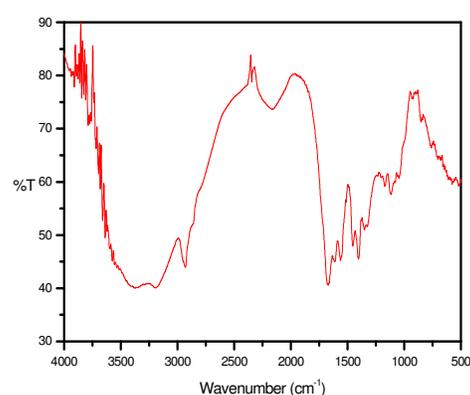


Figure 2: FTIR Spectrum of the starch-g-PAN graft copolymer

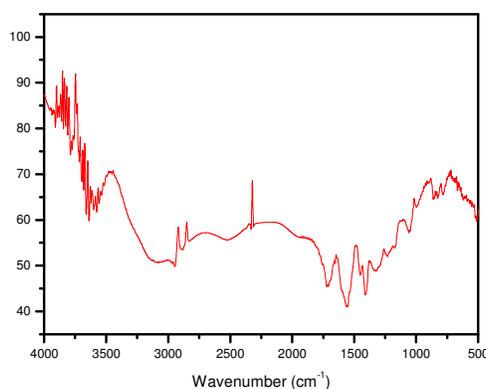


Figure 3: FTIR Spectrum of the starch-g-AA grafted copolymer

The FTIR spectrum of the starch in Figure 1, gives absorption bands at 3400 cm^{-1} , an -OH broad and single intermolecular polymeric band the C-H stretching at 2930 cm^{-1} , and C-O-C stretching in the $1,000\text{-}1100\text{ cm}^{-1}$ band (a triplet peak of starch), characteristic of amylase contained in the starch. The presence of the nitrile group at 2243 cm^{-1} and the strong asymmetrical stretching at 1570 cm^{-1} and a weak symmetrical stretching at $1430\text{-}1390\text{ cm}^{-1}$ coupled with characteristics bands at $3400, 1000\text{-}1100\text{ cm}^{-1}$ for amylase contained in the starch indicated the occurrence of grafting in Figure 2. However, the appearance of the nitrile group at 2243 cm^{-1} at grafting and disappearance at alkaline hydrolysis of the starch-PAN copolymer on the other hand resulted in the carboxylate and carboxamide bands. The carboxylate group (-COONa) gave rise to two bands: a strong asymmetrical stretching band at 1570 cm^{-1} and a weak symmetrical stretching band at 1400 cm^{-1} . These peaks are attributed to C=O stretching in the carboxamide functional groups, and symmetric and asymmetric stretching modes of the carboxylate groups, respectively (Silverstein and Webster, 1998). The absorption peaks at 2924 cm^{-1} and 1018 cm^{-1} , (Figure 3), are due to C-H stretching and bending vibrations respectively. The absorption peaks at 1647 cm^{-1} are due to O-H bending vibrations in original sample. The additional peaks were observed in FTIR spectra of grafted sample at 1427 cm^{-1} and 1155 cm^{-1} due to C-H and C-O stretching respectively. It has been observed that the absorption peaks shift towards low intensity. These additional peaks confirmed the grafting of poly(AA) sample onto cassava starch backbone.

The starch graft copolymers were characterized by scanning electron microscopy (SEM) and thermogravimetric analyzer (TGA). The granule sizes of the starch graft copolymers were large, the surfaces were rough, and the shape changed compared with the ungrafted starch. The SEM of hydrolyzed starch-g-polyacrylonitrile (HSPAN) and hydrolyzed starch-g-polyacrylic acid (HSPAA) showed that the

polyacrylonitrile and polyacrylic acid respectively were grafted both on the surface and in the interior of the granules (Plates 1-3).

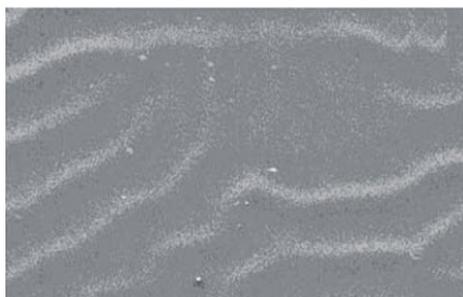


Plate 1: Scanning electron microscope (SEM) picture of the Cassava starch (1000X)

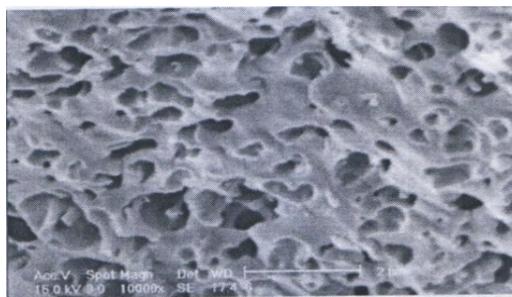


Plate 2: Scanning electron microscope (SEM) picture of the hydrolyzed starch-g-poly(acrylonitrile) (1000X)

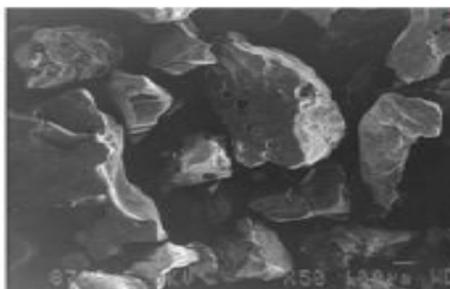


Plate 3: Scanning electron microscope (SEM) picture of the hydrolyzed starch-g-poly(acrylic acid) (1000X)

The starch graft copolymers showed thermal stability up to 200°C-300°C. The thermal stability of the starch graft copolymers was higher compared with the ungrafted starch.

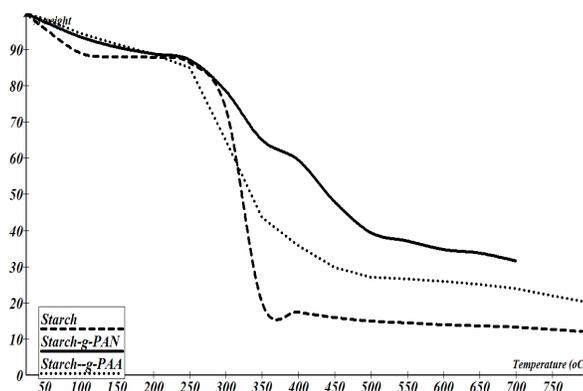


Figure 4: Thermogravimetric analyzer (TGA) results of the starch and the starch graft copolymers

The TGA of starch-g-poly (acrylonitrile) and starch-g-poly (acrylic acid) copolymers (Figure 4) indicated that grafting lowers the initial decomposition temperature of starch (Singh et al., 1993). An increase in percentage of graft add-on in the copolymers led to an overall improvement in the thermal stability.

3.2. Batch Sorption Isotherm of Cd²⁺ and Cu²⁺ unto Starch Graft Copolymers

In this study, the Langmuir, Freundlich, Temkin, and Dubinin–Radushkevich being two parameters isotherms and the Sips sorption isotherms being three parameter isotherms were used for the sorption of copper and Cadmium ions by the hydrolyzed graft copolymers.

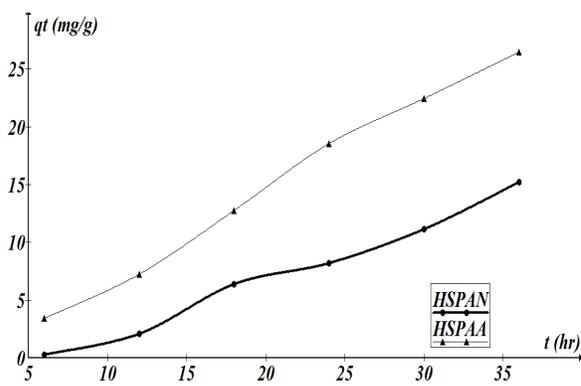


Figure 5: Sorption of Cu²⁺ by HSPAN and HSPAA in aqueous media

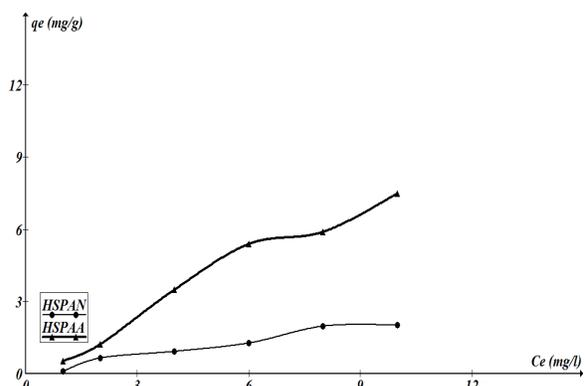


Figure 6: Sorption of Cd²⁺ by HSPAN and HSPAA in aqueous media

Figure 5, shows the Cu²⁺ sorption by the grafted copolymers. The amount of Cu(II) sorbed increased from 2-50mg/l. This is because in batch sorption the initial concentration of sorbate is attributed as a driving force to overcome the mass transfer resistance between the aqueous and solid phases. The increase in uptake of Cu²⁺ as the initial concentration increased upto 50mg/l also enhanced the interaction between the sorbate and the graft copolymer. The carboxyl groups in the polymers are primarily responsible for the sorption in the copolymer. Copper ions have stronger interactions with the carboxyl groups in macromolecular chains than the amide groups. When copper ions are associated with macromolecular ligands, both mononuclear and binuclear copper ion chelate complexes will be formed (Yokoi, 1986).

Figure 6 shows that the amount of Cd²⁺ sorbed increased with increasing initial Cd (II) concentration. This could be as a result of the structure of the material and the condition of the solution (pH). It is worthy to note that there are two factors which determine the status of metal ions in an aqueous solution. One is the pH of the solution and the other is the ratio of the residual functional groups in the polymeric material to the metal ions concentration. The presence of the –amide, carboxyl, carboxylate, and hydroxyl functional groups, as well as the ability of the sorbent to uptake the ions on the surface and in the body of the sorbent accounts for the observed trend in the figure.

A portion of the active sites in the copolymer are occupied by metal ions to form chelate complexes (Katono, 1991; Ogbefun and Okieimen, 1996; Okieimen and Idehen, 1996; Tsutsui et al., 2006; Akkaya, 2008) and the chain segments of the copolymers are confirmed. In addition, the amide groups in the copolymer do not form complexes with metal ions and thus do not contribute to metal uptake significantly. However, the amide groups are capable of adsorbing water. However, the extent of this biosorption capacity was not proportional to further increase of initial Cu²⁺ concentration beyond 30mg/l because of the limited sites available for the uptake of cationic Cu²⁺ ions in both the HSPAN and HSPAA. The maximum removal of Cu²⁺ by the graft copolymer was 14.15mg/g for HSPAN and 20.09mg/g for HSPAA respectively. It could be seen that cassava starch –g- polyacrylic acid yielded better sorption performance than cassava starch-g-polyacrylonitrile and this is mainly due to the presence of the carboxyl, carboxylate and the hydroxyl groups, which has strong affinity toward Cu²⁺, than the amide groups of the HSPAN.

3.2.1. Isotherm studies

Examination of the linear isotherm plots suggested that the Freundlich, Temkin and Dubinin models yielded a much better fitting than the Langmuir model. It's clear from Table 2, that the values of the Freundlich exponent, $1/n$ were approximately equal to 1 ($n < 1$), which represents a normal favorable sorption condition. Examination of the linear isotherm plots suggested that the Freundlich model and the Sips isotherm model yielded a much better fitting than the other models.

Freundlich, Temkin and Dubinin Radushkevich were able to give a good fit to the equilibrium data as the calculated q_{\max} agree with the experimental q_e values, with the R^2 values were fairly high (between 0.8997-0.9983 for Freundlich, between 0.7787-0.9517 for Temkin and between 0.7619-0.9645 for Dubinin Radushkevich). This means that the sorption process of the grafted copolymers encompassed the heterogeneity of the sorption sites on the copolymers. The fittings of the isotherms mentioned also suggested that the Cd^{2+} , and Cu^{2+} sorption onto the copolymers were not a physical process. The Temkin isotherm model, which assumes that the fall in the heat of sorption, is linear rather than as a logarithmic correlation as implied in the Freundlich equation model. The smaller values of the Temkin constant b_T for HSPAA (3.65kJ/mol) suggested that the sorption of Cu^{2+} was more favorable for Cd^{2+} for HSPAA than HSPAN (3.06kJ/mol). This is probably due to the presence of a strong affinity functional group on the HSPAA. Besides that, the high R^2 value with average >0.8747 shows some level of good linearity and indicates that the fall in the heat of sorption was probably linear.

The values of the Langmuir, Freundlich, Temkin and Dubinin Radushkevich and the correlation coefficients are listed in Table 2. Based on the coefficients of determination obtained, it can be concluded that the Freundlich isotherm gave better fit ($R^2 > 0.9$) to the experimental data than the other isotherms. The q_m values calculated from the Langmuir model differ from the experimental results mentioned earlier which further explains the non-fitting of the data to the Langmuir isotherm. The high coefficient of correlation (R^2) of Freundlich (0.9987) for HSPAA and (0.9975) for HSPAN of Cd^{2+} sorption and (0.9916) for HSPAA and (0.9911) for HSPAN of Cu^{2+} sorption, confirmed the applicability of the model, which assumes strong interaction for the sorption of Cd^{2+} , and Cu^{2+} onto the graft copolymers. Freundlich model was able to give a good fit to the equilibrium data as the calculated q_{\max} agreed with the experimental q_e values, with the high R^2 values were (between 0.997-0.998 for Freundlich and 0.95-0.999 for the Sips). This means that the sorption process of the grafted copolymers encompassed the heterogeneity of the sorption sites on the heterogeneous surface of the copolymers. The fittings of the isotherm also suggested that the Cd^{2+} and Cu^{2+} sorption onto the copolymers was more than a physical process.

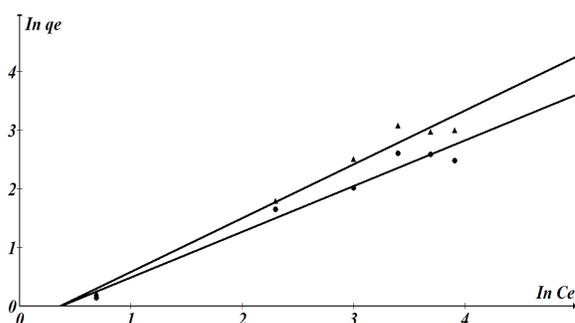


Figure 7: Freundlich Isotherm for the sorption of Cu(II) ions by the HSPAA and HSPAN

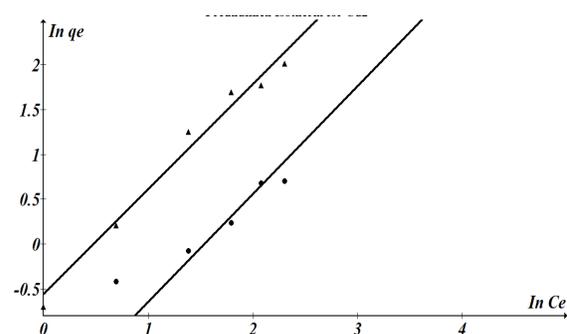


Figure 8: Freundlich Isotherm for the sorption of Cd(II) ions by the HSPAA and HSPAN

It is clear from Table 2 and Figures 5-16 that the metal ions uptake of Cd were higher than Cu in the case of both HSPAN and HSPAA. This can be attributed to the fact that the Cd ion has a lower atomic radius than other metal ions and consequently its sorption by copolymer is higher and the functional groups in HSPAA tend to attract Cd ions to itself more than that of HSPAN. In general, the amount of metal ions uptake by ion exchanger is affected by the electronegativity and hydrated values of metal ions. The sequence of metal ions sorption was as follows: Cd > Cu.

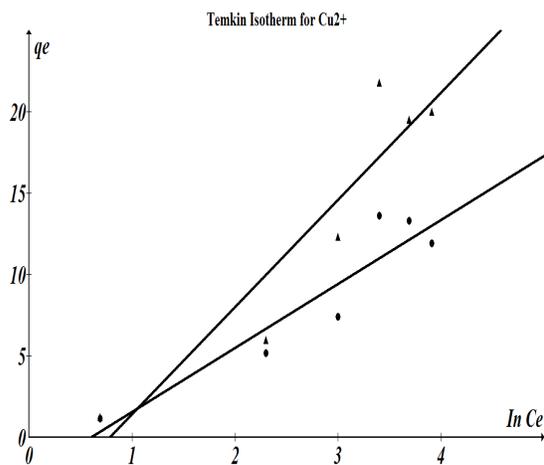


Figure 9: Temkin Isotherm for Cu(II)

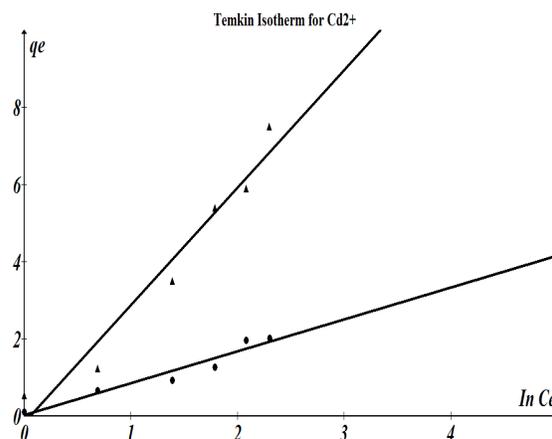


Figure 10: Temkin Isotherm for Cd(II)

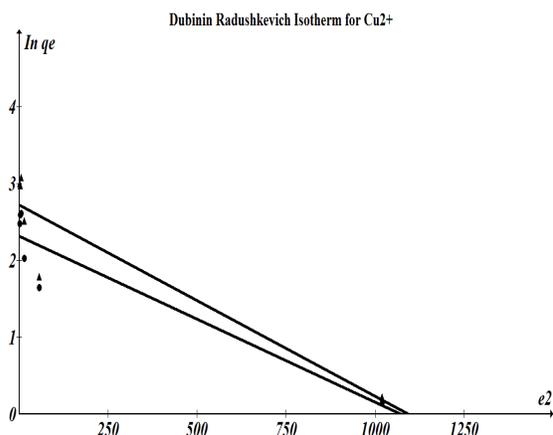


Figure 11: Dubinin Isotherm for Cu (II)

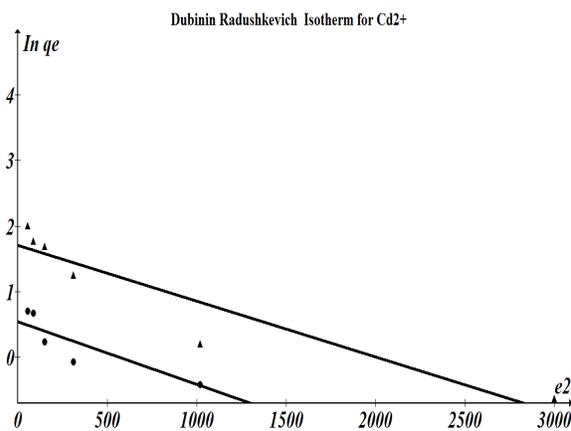


Figure 12: Dubinin Isotherm for Cd (II)

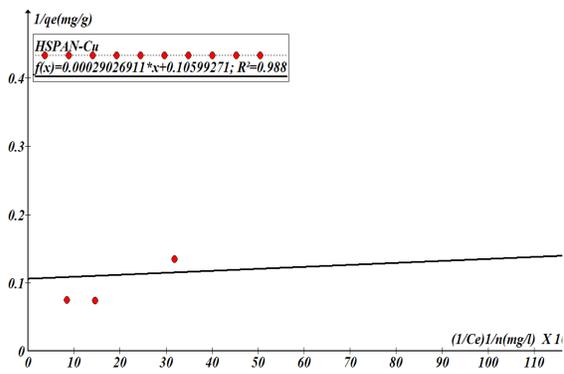


Figure 13: Sips isotherm of Cu for HSPAN at n = 0.52

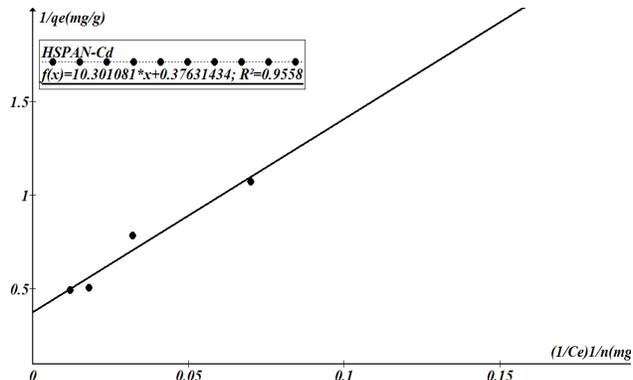


Figure 14: Sips isotherm of Cd for HSPAN at n = 0.52

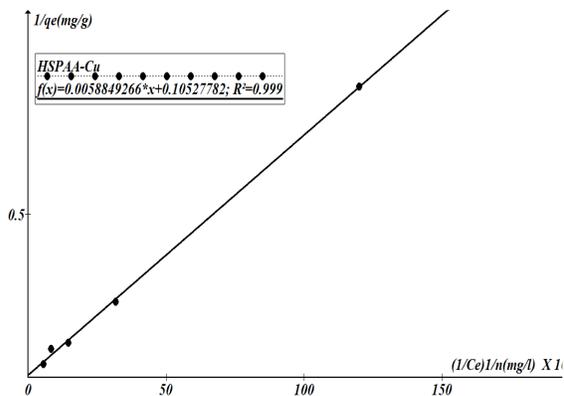


Figure 15: Sips isotherm of Cu for HSPAA at n = 0.52

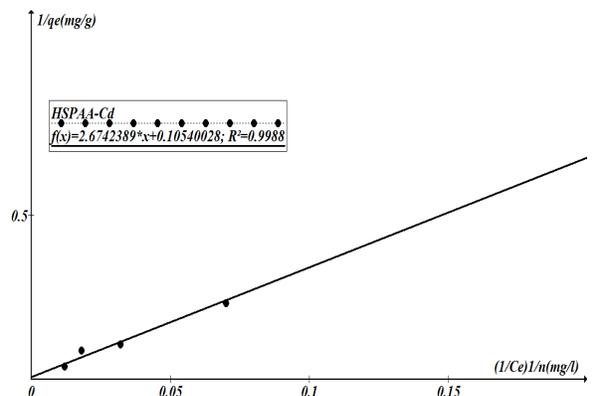


Figure 16: Sips isotherm of Cd for HSPAA at n = 0.52

Table 2: Isotherm Constants of Five Isotherm Models for the sorption of Cd^{2+} and Cu^{2+} ($C_0 = 2.0\text{-}50.0\text{mg/l}$ for Cu^{2+} and $1.0\text{-}10.0\text{mg/l}$ for Cd^{2+} , Dosage = 0.5g, $T = 27.3^\circ\text{C}$, $t = 18.25\text{hr}$)

Isotherm Model	Constants	Cu^{2+}	Cd^{2+}
Langmuir	q_{max} (mg/g)	27.64(42.00)	4.99(19.48)
	K_L (L/mg)	0.019(0.018)	0.071(0.030)
	R^2	0.7230(0.9488)	0.1368(0.9063)
Freundlich	K_F [$\text{mg/g(L/mg)}^{1/n}$]	0.90(0.76)	0.16(0.57)
	n	1.23(1.34)	0.85(0.88)
	R^2	0.9911(0.9916)	0.9975(0.9987)
Temkin	B_1	3.89(3.65)	3.06(1.25)
	b	642.65(683.84)	816.71(2000.55)
	K_t (L/mg)	0.76(1.13)	0.13(0.55)
	R^2	0.8465(0.9298)	0.8744(0.9224)
Dubinin	$K_{\text{ad}} \times 10^{-5}$	2.04(2.01)	1.59(1.74)
	q_s	12.07(18.16)	1.75(6.51)
	R^2	0.8260(0.9482)	0.8761(0.8896)
Sips	Q_{max}	9.43(9.50)	2.66(9.49)
	K_s	365.67(17.90)	0.037(0.039)
	R^2	0.988(0.999)	0.9558(0.9988)

KEY: Values in parenthesis for HSPAA and the other HSPA

3.2.2. Thermodynamics studies

The thermodynamic parameters, free energy change (ΔG°), enthalpy change (ΔH) and entropy change (ΔS) were calculated to evaluate the thermodynamic feasibility of the sorption process and to confirm the nature of the process. All the thermodynamic parameters, as calculated are presented in Table 3. With the increase in temperature from 300.3K to 323K, the ΔG° values varies (decreased negatively) significantly indicating that the favourable sorption of metal ions took place on the graft copolymers (HSPAN/HSPAA).

It was observed that the biosorption of metal ions increased as the solution temperature increased from 283K to 323K, indicating the sorption was an endothermic process. The increase in sorption with the increase of temperature might be attributed to the increase in the frequency of interaction between the sorbent-sorbate leading to sorption on the graft copolymers or due to the decrease of the mass transfer resistance of sorbate as the boundary layer thickness decreased (Meena *et al.*, 2005).

As can be seen from Table 3, ΔH values were found to be positive due to endothermic nature of the sorption. Even though there were no certain criteria related to the ΔH values that could define the sorption type, normally the heat of sorption values is between 20 and 420KJ/mol, which are heats of chemical reactions, are often assumed as the comparable values for the chemical sorption process, (Unlu *et al.*, 2006).

As seen in Table 3, the Gibb's free energy change (ΔG°) values were found to be negative which indicates the feasibility and spontaneity of the adsorption process at temperatures below 323K. As a rule of thumb, a decrease in the negative value of ΔG° with an increase in temperature indicates that the adsorption process is more favourable at higher temperatures. This could be possible because the mobility of adsorbate ions/molecules in the solution increase with increase in temperature and that the affinity of adsorbate on the adsorbent is higher at high temperatures. On the contrary, an increase in the negative value of ΔG° with an increase in temperature implies that lower temperature makes the adsorption easier, (Gupta and Rastogi, 2009).

Table 3: Thermodynamics Parameters for the Sorption of Cu^{2+} , and Cd^{2+} at Different Temperatures ($T = 300.3, 313, 323\text{K}$, Initial $\text{pH}=7.85$, Dosage = $0.5\text{g}/100\text{ml}$, $C_e = 20\text{mg}/\text{l}$)

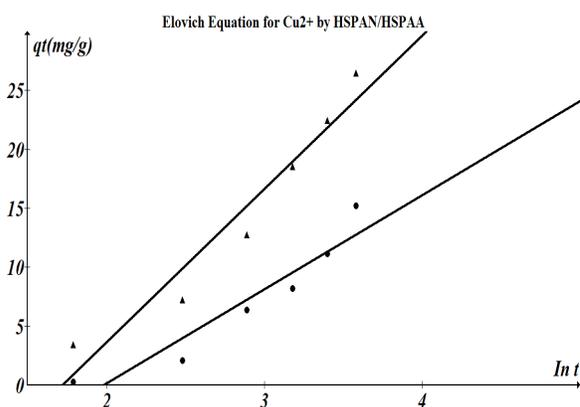
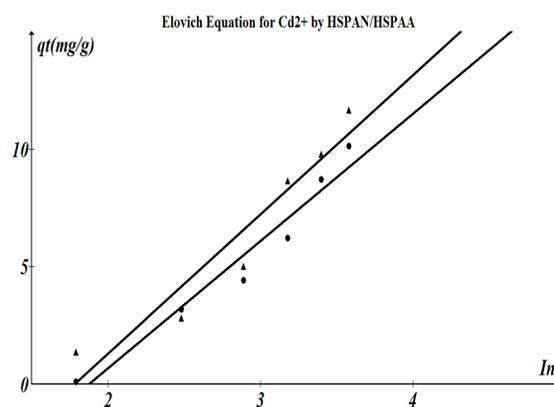
Temperature	Parameter	Cu^{2+}	Cd^{2+}	
300.3K	q_{max} (mg/g)	27.64(42.00)	4.99(19.48)	
	R^2	0.7230(0.9488)	0.1368(0.9063)	
	K_L (L/mg)	0.019(0.018)	0.071(0.030)	
	ΔG (KJ/mol)	-9.90(-10.03)	-6.62(-0.86)	
	ΔH (KJ/mol)	48.22(49.47)	15.80(72.75)	
	ΔS (J/mol.K)	126.21(131.67)	29.74(212.12)	
	E_a (KJ/mol)	2.54(2.54)	2.51(2.57)	
313K	q_{max} (mg/g)	15.85(25.38)	2.60(4.05)	
	R^2	0.9620(0.9808)	0.9800(0.9624)	
	K_L (L/mg)	0.035(0.063)	0.075(0.112)	
	ΔG	-3.53(-4.58)	-4.15(-3.09)	
	323K	q_{max} (mg/g)	20.24(31.70)	7.95(7.30)
		R^2	0.9195(0.9818)	0.9943(0.9828)
		K_L (L/mg)	0.061(0.059)	0.103(0.172)
ΔG		-7.51(-7.59)	-6.09(-4.73)	

Key: Values in parenthesis is for HSPAA, the other for HSPAN. ΔH : Enthalpy, ΔS : Entropy, ΔG : Gibb's free energy, E_a : Activation Energy, A = Frequency factor.

Therefore, as seen from Tables 3, it seems that adsorption of the heavy metal ions by the graft copolymers can be attributed to a physico-chemical sorption process rather than a pure physical or chemical adsorption process (Ho *et al.*, 2002). A positive value of ΔS° reflects the affinity of the adsorbent towards the adsorbate species. In addition, positive value of ΔS° suggests increased randomness at the solid/solution interface with some structural changes in the adsorbate and the adsorbent.

3.2.3. Kinetic studies

Except for adsorption capacity, kinetic performance of a given adsorbent is also of great significance for the pilot application. From the kinetic analysis, the solute uptake rate, which determines the residence time required for completion of adsorption reaction, may be established. Also, one can know the scale of an adsorption apparatus based on the kinetic information. Generally speaking, adsorption kinetics is the base to determine the performance of fixed-bed or any other flow-through systems.

Figure 17: Elovich Equation of Cu^{2+} by the graft copolymers (HSPAN/HSPAA)Figure 18: Elovich Equation of Cd^{2+} by the graft copolymers (HSPAN/HSPAA)

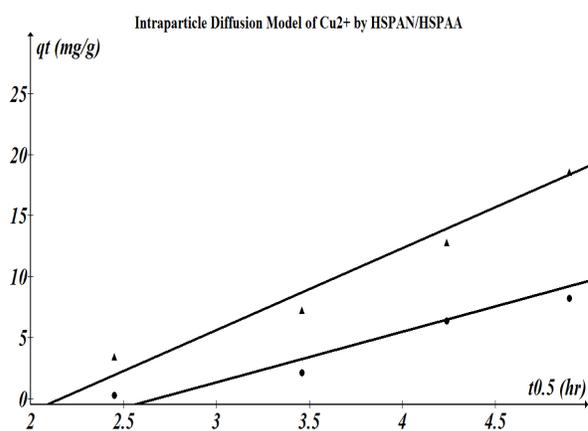


Figure 19: Intraparticle diffusion model of Cu^{2+} by the graft copolymers (HSPAN/HSPAA)

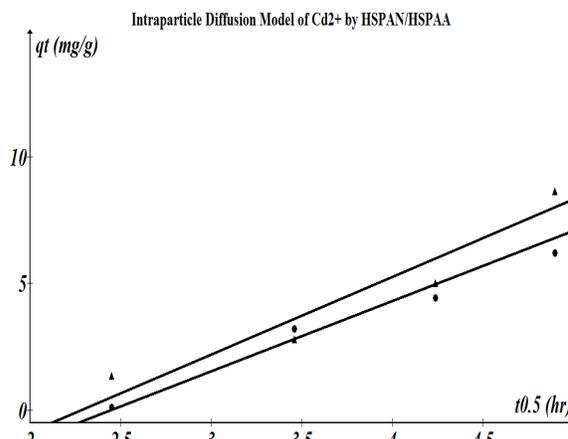


Figure 20: Intraparticle diffusion model of Cd^{2+} by the graft copolymers (HSPAN/HSPAA)

Figures 17 and 18, show plots of the Elovich equation for the heavy metals (Cd^{2+} , and Cu^{2+}). In this case, linear relationships were obtained between q_t and $\ln t$, over the whole sorption period, with high correlation coefficient ($R^2 > 0.9$) for all lines (Table 4). This demonstrate a high degree of correlation between the experimental and the theoretical data predicted by the elovich model. It is clear that a simple Elovich equation may be used to describe the kinetics of sorption of Cd^{2+} and Cu^{2+} on to graft copolymers (HSPAN and HSPAA).

As shown in Figures 19 and 20, none of the lines passed through the origin. This indicates that the intraparticle diffusion was not the only rate controlling step (Liu *et al.*, 2010). Other mechanisms such as the boundry layer may dominate the sorption process to some extent. The values of k_d obtained from the linear regression analysis are listed in Table 4.

Kinetic models can be helpful to comprehend the mechanism of metal sorption and estimate performance of the sorbents for metal removal. In order to further determine the mechanism of Cd^{2+} and Cu^{2+} sorbed onto the graft copolymers (HSPAN and HSPAA), several kinetic models were exploited to discern the controlling mechanism. They included the pseudo first order, pseudo second order, the Elovich equation, the intra particle diffusion model and the Liquid film diffusion models (Figures 17-24). The conformity between the experimental data and the model predicted values were expressed by coefficient of determination (R^2) and standard deviation (SD) values (Table 4).

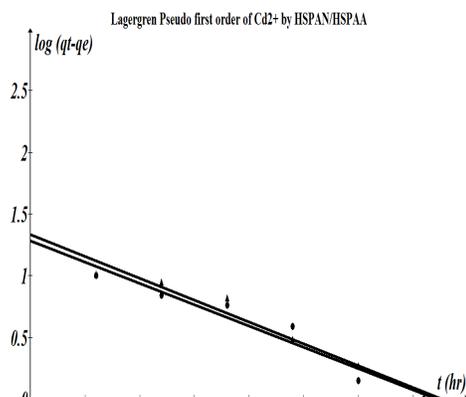


Figure 21: Pseudo first order for Cd(II)

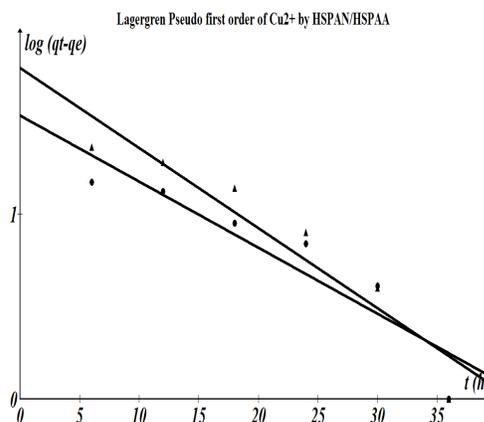
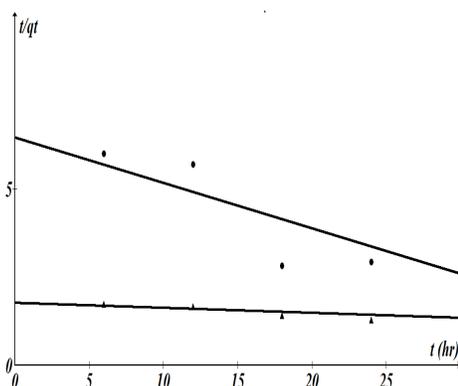
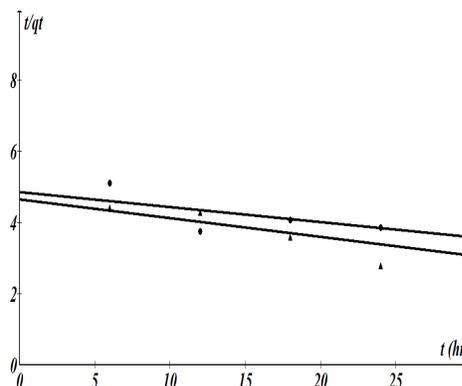


Figure 22: Pseudo first order for Cu(II)

Figure 23: Pseudo second order for
Cu(II)Figure 24: Pseudo second order for
Cd(II)

Different kinetic parameters calculated by linear regression of the adsorption data are summarized in Table 4. As shown in Table 4, the coefficients of determination (R^2) obtained from the plots of elovich equation kinetics and intraparticle diffusion models were higher ($R^2 > 0.9$) for both HSPAN and HSPAA, than those of the pseudo first order, pseudo second order and the liquid film model.

It can also be seen in Table 4 that, the initial sorption rate (h_0) for pseudo second order was higher for HSPAA (Cd^{2+}) compared to Cu^{2+} . HSPAN had the highest value above all others in the case of Cu^{2+} . This may be attributed to the increase of driving force between the liquid and the graft copolymers with the increasing metal concentration. On the other hand, the rate constant (k_2) of HSPAA is higher for both Cu^{2+} and Cd^{2+} . A similar observation has also been reported by earlier researchers (Allen *et al.*, 2004, Liu *et al.*, 2010). Table 4, lists the kinetic constants obtained from the Elovich equation. It will be seen from the data that the values of α and β varied as a function of the set conditions for the metal ions. α is higher for HSPAA for Cu^{2+} and Pb^{2+} , and slightly lower for Cd^{2+} . HSPAN is higher for β for all the metal ions. The quantity α in the Elovich equation is equivalent to the initial gradient which varied with the set conditions (Ho and McKay, 2002). Although the Elovich equation does not provide any mechanistic evidence, it has proved suitable for highly heterogeneous systems of which the sorption Cu^{2+} and Cd^{2+} onto the graft copolymers (HSPAN and HSPAA) fall under.

A linear relationship between $\ln(q_e - q_t)$ and t for pseudo first order was established with high correlation coefficients ($R^2 = 0.9$) for Cd^{2+} with both HSPAN and HSPAA and ($R^2 = 0.85$) for Cu^{2+} for both HSPAN and HSPAA. However, the Elovich equation provides an excellent description of the sorption with high correlation coefficients. If the sorption process is chemisorption, the experimental results may be described by the Elovich model.

The applicability of the pseudo second order kinetic model to experimental data is presented in Table 4. The deviation between the calculated q_e values and the experimental q_e values were relatively high and a regression coefficient of 0.62-0.75 shows that the model can not be applied fairly or moderately for the sorption. Because of the high correlation coefficients obtained using the Elovich equation and the pseudo first order kinetic models it was impossible to conclude which sorption mechanism actually occurred and reasons responsible for the ability of the graft copolymers to sorb the metal ions completely. It was therefore necessary to review the literature in an attempt to identify the specific sorption mechanism. Because of the presence of the carboxylic, amine,

hydroxyl and other functional groups present in the graft copolymers, metal sorption may readily take place via exchange sorption, chelation, polar organic bonding and polar inorganic bonding (Ho and McKay, 2002).

The Elovich equation has been found useful in describing predominantly chemical sorption on highly heterogeneous sorbents, but no definite mechanism for the sorbate-sorbent interactions (Ho and McKay, 2002). Although the mechanism is uncertain, it is predicted that metal ions are held strongly to the graft copolymers by chemisorptive bonds.

In order to obtain the rate determining step in the sorption process, intraparticle diffusion model was used to analyze the results obtained from this study. The plots gave a linear plot though not through the origin which indicate that intraparticle pore diffusion is the main rate determining step in the sorption process (Oladoja *et al.*, 2010). The liquid film diffusion model was also employed in the interpretation of the results obtained. A linear plot with zero intercept would suggest that the kinetics of the sorption process is controlled by diffusion through the liquid film surrounding the graft copolymers. This was tested and the results presented in Table 4. The results confirm the significance of liquid film diffusion in rate determination of the sorption process because the intercept of the plots was closer to the origin as shown in Figures 11 and 12.

Table 4: Kinetic Parameters of the Kinetic Models for the Sorption of Cd^{2+} , and Cu^{2+} ($T = 300.3\text{K}$, Initial $\text{pH}=7.85$, Dosage = $0.5\text{g}/100\text{ml}$, $C_e = 20\text{mg/l}$)

Kinetic Model	Parameter	Cu^{2+}	Cd^{2+}
Lagergren Pseudo first order	q_e , exp(mg/g)	14.15(20.09)	2.41(8.17)
	q_e , calc(mg/g)	26.28(54.71)	19.07(18.92)
	$K_1 \times 10^{-2}$ (hr ⁻¹)	9.4(10.3)	8.3(7.2)
	R^2	0.9871(0.9589)	0.9396(0.9252)
	SD	0.321	0.118
Pseudo Second Order	q_e , calc(mg/g)	13.91(139.53)	136.47(58.82)
	ho(mg/ghr)	0.291(0.343)	0.300(0.368)
	$K_2 \times 10^{-3}$ (hr ⁻¹)	1.50(0.02)	0.02(0.11)
	R^2	0.3256(0.0540)	0.0904(0.3343)
	SD	0.11	0.95
Elovich Equation	α (mmol/ghr)	1.10(2.38)	8.11(0.838)
	β (g/mmol)	0.128(0.076)	1.709(0.169)
	R^2	0.9971(0.9977)	0.9711(0.9808)
	SD	0.671	0.484
Intraparticle Diffusion Model	K_{id} (mg/ghr ^{-1/2})	3.89(6.58)	2.96(2.99)
	Intercept	-10.02(-13.65)	-6.73(-7.61)
	R^2	0.9806(0.9881)	0.9713(0.9740)
	SD	4.12	1.11
Liquid Film Diffusion Model	K_{fd}	0.211(0.178)	0.173(0.110)
	Intercept	1.93(1.09)	1.36(0.52)
	R^2	0.9909(0.9759)	0.9043(0.9811)
	SD X 10 ⁻²	1.11	2.38

Key: Values in parenthesis is for HSPAA, the other for HSPAN. SD: Standard Deviation

4. CONCLUSION

Starch graft copolymers were successfully used to remove Cd (II) and Cu(II) ions from aqueous media. The sorption affinity for the metal ions shows the effectiveness of the amide and the carboxylate ions in the binding of the metal ions. The high coefficient of correlation (R^2) of Freundlich and Sips confirmed the applicability of the models, which assumes strong interaction for the sorption of metal ions onto the graft copolymers. Elovich

equation in this study for sorption has proved suitable for highly heterogeneous systems of the sorption of Cd^{2+} and Cu^{2+} ions onto the graft copolymers (HSPAN and HSPAA). The Gibb's free energy change (ΔG°) values for the sorption were found to be negative. Considering the results, it can be concluded that starch graft copolymers are convenient sorbents for the removal of Cd (II) and Cu(II) ions from aqueous environments due to its significant sorption capacity, low cost and from renewable materials.

5. CONFLICT OF INTEREST

There is no conflict of interest associated with this work.

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