

**COMPETITIVE SORPTION OF Cd (II), Pb (II) AND Cu (II) IONS ON
HYDROLYZED STARCH GRAFT COPOLYMERS**

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ABSTRACT

Hydrolyzed starch graft copolymers of acrylic acid and acrylonitrile were used as a sorbents for the competitive removal of Pb (II), Cd (II) and Cu (II) ions from aqueous solution in batch process. The sorbents were characterized by scanning electron microscopy, Fourier transform infrared spectroscopy, wide-angle x-ray diffractometer and thermogravimetric analysis. The equilibrium sorption properties were assessed to optimize the conditions for maximum competitive sorption of the metal ions. The experimental data were subjected to sorption models: Langmuir, Freundlich, Temkin, Dubinin Radushkevich and Sips isotherm. 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 Cd^{2+} , Pb^{2+} and Cu^{2+} onto the graft copolymers. Pseudo second order rate have proved suitable for highly heterogeneous systems of the sorption of Cu^{2+} , Pb^{2+} and Cd^{2+} onto the graft copolymers. The Gibb's free energy change (ΔG^0) values were found to be negative. Sorption affinity for the metals followed the order of $Pb > Cu > Cd$. No correlation was observed between metal affinity and its ionic or hydrated radii suggesting that size is not a significant factor for sorption of these heavy metals to the graft copolymers. This order suggested that electronegativity may be the most important factor as metal sorption increased with increasing electronegativity

Keywords: Competitive sorption, Heavy metal ions, Kinetics studies, thermodynamics studies, Starch graft copolymer

INTRODUCTION

Many environmental management assessments have revealed widespread contamination of water by different chemicals used in the chemical industry during manufacturing processes [1]. These chemicals include organic compounds, heavy metals and other pigments like dyes in the textile industry. Studies have shown that at least 20 metals are classified as toxic and

half of these are emitted into the environment in quantities that pose risks to human health [2]. Some of these metals constitute the major source of contaminants in portable water supply to humans and livestock. These chemicals find their way into ground water, which cause pollution and could impair plant growth and result to a great risk to human health and the environment [2, 3]. The Efficient removal of these pollutants from the environment is still a problem.

Pollution of the environment with toxic metals is essentially as a result of many industrial and human activities such as mining and metallurgy. It means that these effluents would carry admixtures of heavy metal ions in solution. The sorption of aqueous metal ions is strongly influenced by the competition of those metal ions to occupy the limited number of sorption sites. This will influence the removal efficiency of the sorbents for the metals of interest.

A wide range of physical and chemical processes are available for the uptake of heavy metals and organics from aqueous media, such as electro-chemical precipitation, ultrafiltration, ion exchange and reverse osmosis [4-6]. A draw back with these methods are high operational cost, which has caused interest to be shifted to the use of other low cost and readily available agricultural products as precursor for the preparation of value added products.

Graft copolymerization is a unique method among the techniques for modifying natural polymers mostly polysaccharides. Polysaccharides graft co-polymers have been prepared in order to add new properties to the natural polymer with a minimum loss of native properties and are relatively cheap [7].

In view of the growing interest and research activities in the use of renewable agriculturally derived products as extenders and replacement for synthetic petroleum-based polymers, 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.

This study therefore is meant to evaluate the competitive sorption of heavy metals in aqueous media and assess the equilibrium sorption properties of the hydrolyzed grafted copolymers.

METHODOLOGY

Materials

Reagent grade acrylic acid and acrylonitrile were supplied by Sigma Aldrich, Germany and was 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 were supplied by Sigma Aldrich, Germany.

Preparation and characterization of the graft copolymers

Preparation and characterization of the hydrolyzed cassava starch graft poly (acrylic acid) and hydrolyzed cassava starch graft poly (acrylonitrile) copolymers were prepared according to the method described by Okieimen et. al., 1986, 1996 and reported in Ekebafé et., al. [8-10].

Competitive Sorption Studies of Cd²⁺, Cu²⁺, and Pb²⁺

Aqueous solutions containing a mixture of Cd²⁺, Cu²⁺, and Pb²⁺ with concentrations of each metal ion ranging from 10 to 50 ppm were prepared in the same solution. The initial concentrations after preparation were confirmed using Atomic Absorption Spectrophotometer (AAS).

Effect of heavy metal ions concentration on sorption

The conditions used to generate data are as follows: sorbent dosage, 0.5 g copolymer in 100 mL of metal ion mixture solution; metal ions of same concentration ranges 2 to 50 ppm for Cd²⁺, Cu²⁺, and Pb²⁺; the pH: 7.85 for all the sorption experiments; the shaking time was 18.25 h. In order to get the concentration of Cd²⁺ in the samples within the calibration range of 2 to 10 ppm, the samples were diluted in 10-fold. The sorption experiments were carried out at 27.5 °C

Effect of contact time on sorption

In order to assess the rate of the sorption for Cd²⁺, Cu²⁺, and Pb²⁺, experiments were carried out under the following conditions: amount of copolymer: 0.5 g per 100 mL of solution; the initial metal concentration for Cd²⁺, Cu²⁺, and Pb²⁺: 20 ppm; the pH :7.85; and the shaking time: 6, 12, 18, 24h. The temperature of the mixtures was maintained at 27.5°C.

Effect of temperature on sorption

The conditions used to generate sorption thermodynamic data are as follows: sorbent dosage, 0.5 g copolymer in 100 mL of solution; metal ion concentration was 2 ppm for Cd²⁺, and 20 ppm for Cu²⁺, and Pb²⁺; the pH: 7.85 for all the adsorption experiments; the shaking time:

18.25 h. The adsorption experiments carried out with the temperature varied: 10, 20, 30, 40, 50°C.

RESULTS AND DISCUSSION

Characterization of the grafted copolymer

The results of the proximate analysis of the cassava starch, grafting characteristics, spectral and scanning characterization have been previously reported [10-12].

Table 1: Characteristics of the starch graft 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 (°C)	250-300	200-250
pH	8.0	8.0
Graft Yield (%)	92.2	86.96
Graft Efficiency (%)	88.55	70.82

Results of Competitive Sorption Studies of Cu²⁺, Pb²⁺ and Cd²⁺ From Aqueous Media

For isotherm and competition studies, pH 7.85 was chosen as it is a common pH in natural waters [13]. Furthermore, this pH allows metal concentrations up to 10⁻⁶ M without precipitation. Dilute or trace concentrations of heavy metals are relevant with respect to contaminants existing and of concern [14]. Sorption affinity for the metals follows the order of Pb>Cu> Cd. No correlation is observed between metal affinity and its ionic or hydrated radii suggesting that size is not a significant factor for sorption of these heavy metals to HSPAA and HSPAN. This order suggests that electronegativity may be the most important factor as metal sorption increased with increasing electronegativity. Schwertman and Taylor [15] reported the affinity of heavy metals for sorbents followed Cu>Pb>Zn>Cd>Co>Ni>Mn order which is in agreement with electronegativity being the most important factor. Copper, which has a greater electronegativity than cadmium, displaced cadmium in all studies. The total sites occupied per gram of the graft copolymers are equal to that observed in the copper isotherm studies, suggesting that copper and cadmium bind on the same type of sites.

The results in Table 2 show that the Freundlich and the Sips models apparently fit the isotherms for all the metals in both HSPAA and HSPAN investigated with regression coefficients $R^2 > 0.931$ for Freundlich and 0.95 for Sips (Table 2). The isotherm constants values are given in Table 2. The results of Figure 1-2 and Table 2 showed that the sorption affinity and sorption maximum for the Pb (II) in competitive sorption systems were higher than Cu^{2+} and Cd^{2+} ions. The sorption maxima (mgg^{-1}) for the Cd, Pb and Cu ions followed the order $\text{Cu}^{2+} > \text{Pb}^{2+} > \text{Cd}^{2+}$, for HSPAA with a sorption maximum of 1651.4, 286.4, 273.3 (mgg^{-1}) while for HSPAN: 422.4, 116.6, and 42.4 (mg/g) for Pb^{2+} , Cd^{2+} and Cu^{2+} respectively. The sorption maxima seems to follow the same order of the hydrated ionic radii of the metals, being Pb^{2+} (4.01\AA) $>$ Cu^{2+} (4.19\AA) $>$ Cd^{2+} (4.26\AA) [16] (Lide, 1998). This is in agreement with results [17, 18].

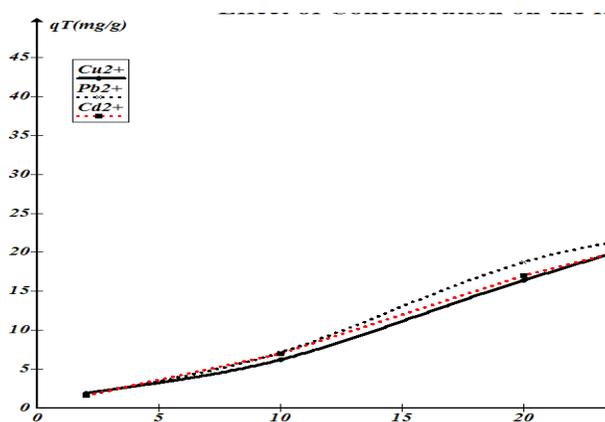


Figure 1: Effect of concentration on the level of metal ions sorption by HSPAN

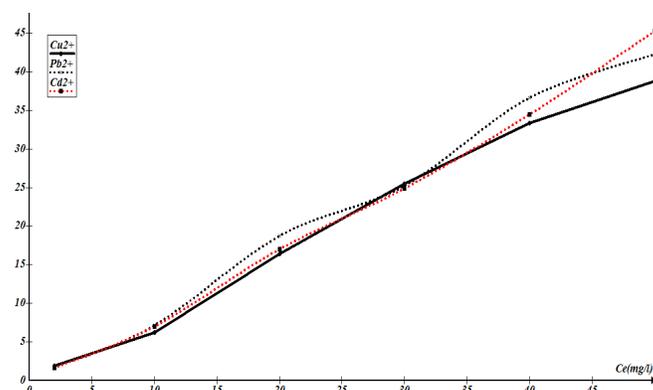


Figure 2: Effect of concentration on the level of metal ions sorption by HSPAA

Figure 1-7, show the adsorption isotherms of $\text{Cd}^{2+}(\text{aq})$, $\text{Pb}^{2+}(\text{aq})$ and $\text{Cu}^{2+}(\text{aq})$ on HSPAN/HSPAA against the final metal concentration in solution in a competitive reaction system. The isotherms were characterized by increasing slopes as equilibrium metals concentration increases, indicating high affinity of the sorbent for high concentrations of metals in solution [19, 20].

The plot of sorption Vs the final concentration of metals in equilibrium solution shows that the sorption increases as the concentration increases (Figure 8-9).

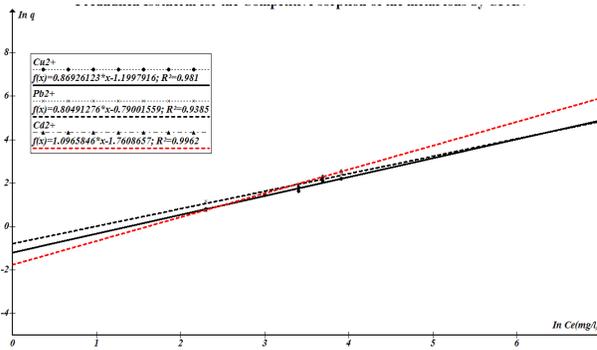


Figure 3: Freundlich Isotherm for the competitive sorption of the metal ions by HSPAN

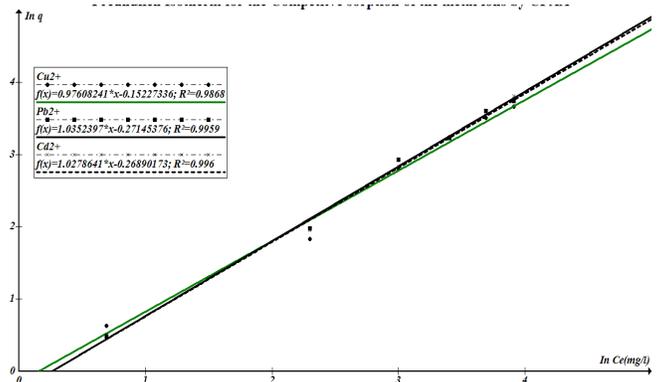


Figure 4: Freundlich Isotherm for the competitive sorption of the metal ions by HSPAA

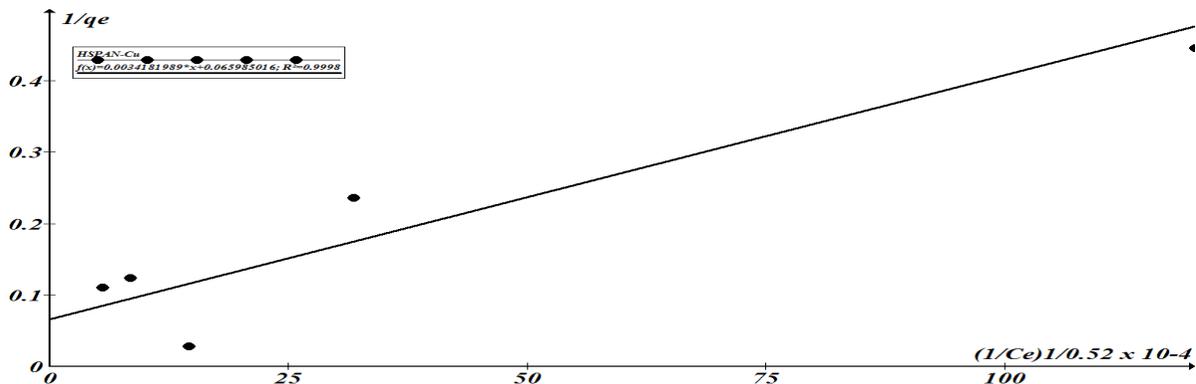


Figure 5: Sips Isotherm for the competitive sorption of the Cu metal ions by HSPAN (n=0.52)

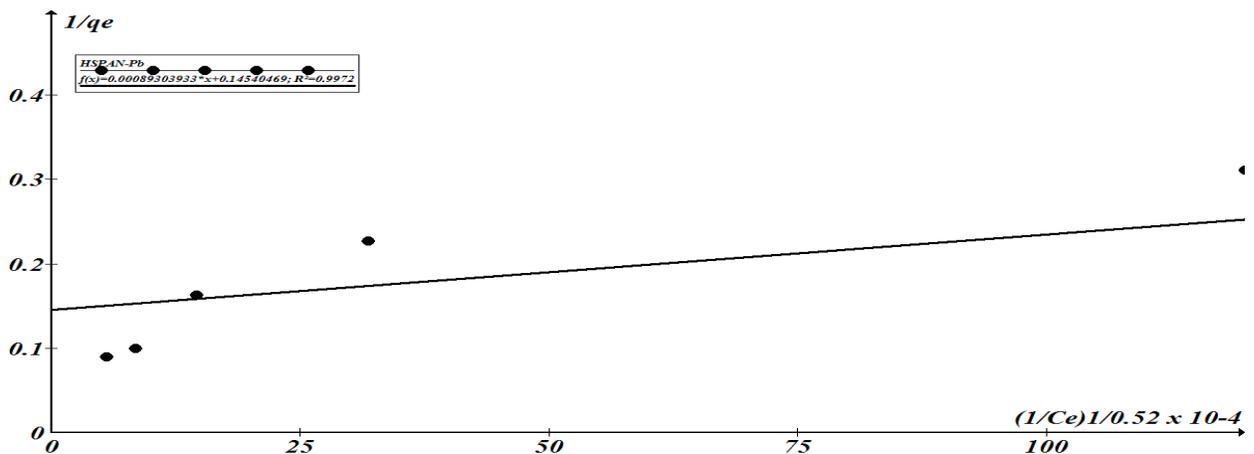


Figure 6: Sips Isotherm for the competitive sorption of the Pb metal ions by HSPAN (n=0.52)

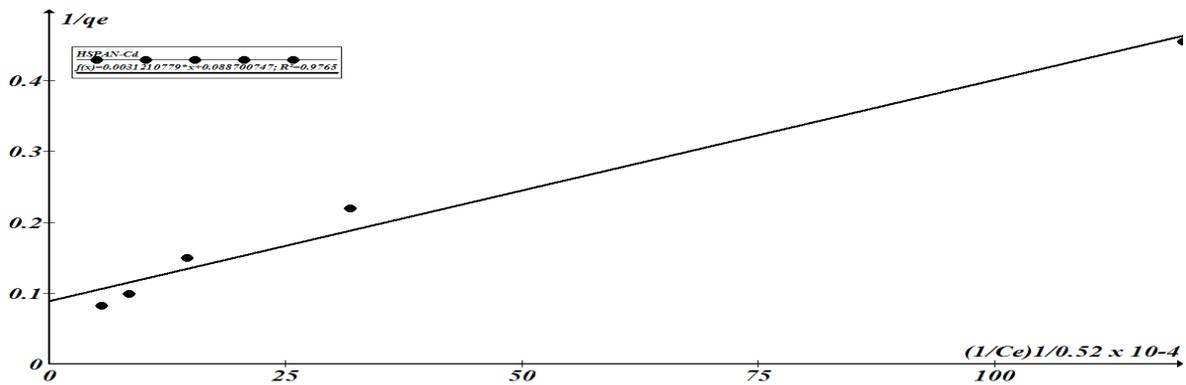


Figure 7: Sips Isotherm for the competitive sorption of the Cd metal ions by HSPAN (n=0.52)

In competitive sorption systems, the number of surface sites available for Cd^{2+} , Pb^{2+} and Cu^{2+} sorption on HSPAN/HSPAA is constant. Consequently, the concentration of Cd^{2+} (Pb^{2+} or Cu^{2+}) in equilibration solution increases with competitive metal ions. In competitive sorption reaction systems, the competitive sorption data of the metal ions cannot be fitted to the Langmuir isotherm with acceptable square errors. However, the Freundlich equation and the Sips fit the sorption data for all the ions with an acceptable linear coefficient ($R^2 = 0.93$ and 0.97) respectively. On the other hand, the sorption maximum (q) derived from the equation is generally less than that in single Pb sorption system, which implied that only high affinity sorption sites can sorb Pb^{2+} when some sorption sites are occupied by Cd^{2+} and Cu^{2+} in solution.

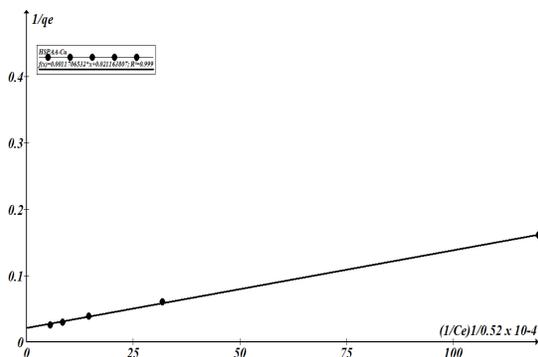


Figure 8: Sips Isotherm for the competitive sorption of the Cu metal ions by HSPAA (n=0.52)

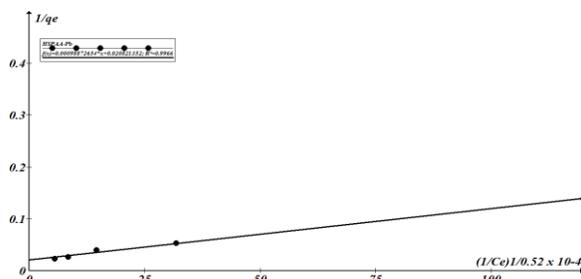


Figure 9: Sips Isotherm for the competitive sorption of the Pb metal ions by HSPAA (n=0.52)

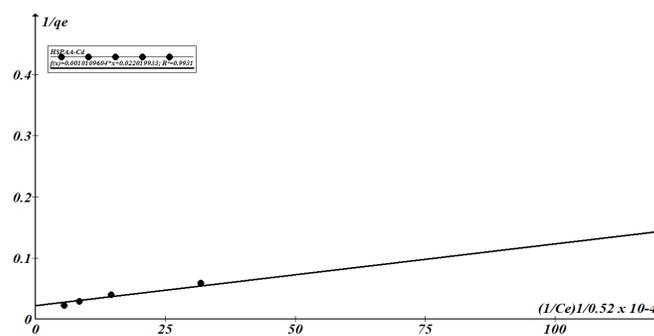


Figure 10: Sips Isotherm for the competitive sorption of the Cd metal ions by HSPAA (n=0.52)

Cd was set as the target metal for displacement, with Cu, and Pb as the competing metals. Simple linear regression using least squares was the basic approach in the analysis of results from the displacement experiments. This was done considering the hypothesis that a metal that is displaced from the graft surface will show increasing aqueous concentration corresponding to increased additions of its competitor ion. The more suitable ion is preferentially sorbed by grafts. The less preferred ion will tend to stay in or be released to aqueous solution.

Table 2: Isotherm Constants of four Isotherm Models for the competitive sorption of Cd²⁺, Cu²⁺ and Pb²⁺ by HSPAN/HSPAA (C₀ = 2.0-50.0mg/l for Pb²⁺, Cu²⁺ and Cd²⁺, Dosage = 0.5g, T = 27.3^oC, t = 18.25hr)

Isotherm Model	Constants	Cu ²⁺	Pb ²⁺	Cd ²⁺
Langmuir Isotherm	q _{max} (mg/g)	42.37(1651.40)	422.48(286.40)	116.55(274.30)
	K _L x 10 ⁻³ (L/mg)	5.37(0.47)	0.55(2.73)	2.21(2.79)
	R ²	0.4057(0.0035)	0.0038(0.3186)	0.0849(0.3811)
Freundlich Isotherm	K _f	3.32(1.16)	2.21(1.31)	5.82(1.31)
	n	1.15(1.02)	1.24(0.97)	0.91(0.97)
	R ²	0.9810(0.9868)	0.9385(0.9959)	0.9962(0.9960)
Temkin Isotherm	B ₁	2.65(11.28)	3.30(12.24)	3.35(12.36)
	b	941.8(221.3)	757.3(204.0)	745.9(202.0)
	K _t	2.77(2.80)	2.69(2.83)	2.78(2.94)
	R ²	0.8666(0.8310)	0.7989(0.8347)	0.7901(0.7974)
Dubinin Radushkevich	K _{ad} x 10 ⁻⁵	2.23(2.99)	1.90(2.94)	2.75(3.11)
	q _s	7.47(35.55)	8.64(13.37)	9.65(34.23)
	R ²	0.8367(0.8897)	0.6859(0.8347)	0.8518(0.9368)
Sips	K _s	18.74(391.90)	21.10(2.11)	28.42(3.14)
	Q _{max}	15.65(1.22)	6.88(48.08)	11.27(45.45)
	R ²	0.9998(0.9990)	0.9972(0.9966)	0.9765(0.9931)

Cassava starch-g-polyacrylonitrile (cassava starch-g-polyacrylic acid, in parenthesis)

Temperature has a pronounced effect on the removal capacity of hydrolyzed graft copolymers (HGCs) Figure 11-12. The result follow the pattern Cd(II) >Pb(II) >Cu(II) for HSPAN and for HSPAA the sorption of Cd(II) increases at high temperature as shown in Figure 11. A decrease in the removal for ions with the rise in temperature may be explained by being more active sorbent sites at low temperature. Also an increase in temperature result in an increased mobility of the ions and a decrease in the retarding forces acting on the removal ions.

Competitive Sorption Thermodynamics of The Metal Ions by The Graft Copolymers

This result may also confirm the endothermic nature of Cd(II), Cu(II) and Pb(II) ions removal onto HSPAN and exothermic nature of Cd (II), Cu (II), Pb (II) ions removal onto HSPAA. So 300.3, 313 and 323K were selected as the solution temperatures. Similar trends have been observed for the removal of other heavy metal ions. The effect of different temperature on the adsorption of Cd(II), Pb(II) and Cu(II) ions onto HSPAN/HSPAA based on Langmuir isotherm were shown in Table 3. It was found that the adsorption capacity (Q) values decreased as the temperature increased, The Pb(II) had the highest for HSPAN and Cu(II) for HSPAA; which was similar to the work by Prasad and Saxena [21].

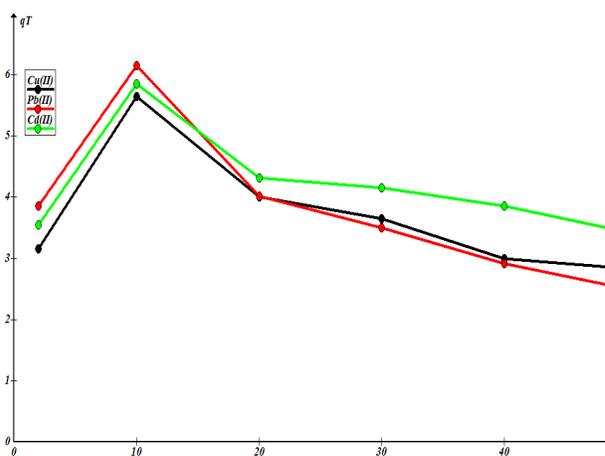


Figure 11: Effect of temperature on the competitive sorption of the metal ions by HSPAN

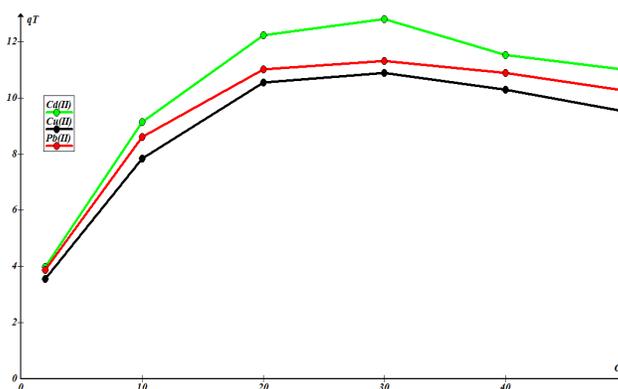


Figure 12: Effect of temperature on the competitive sorption of the metal ions by HSPAA

Due to the dependence on temperature, K_L values were used to evaluate the Gibbs free energy change (ΔG), enthalpy change (ΔH) and entropy change (ΔS). These thermodynamic parameters were determined by using the following equation [22, 23](Ho, 2006; Ozcan et al., 2005):

$$\Delta G = RT \ln K_L$$

$$\ln K_L = \Delta S/R - \Delta H/RT$$

where R is the gas constant (8.314 J/K mol), T is the temperature in Kelvin and K_L is the Langmuir constant related to the affinity of binding sites (mol/L). The Van't Hoff plot yields a straight line (Figure 13 and 14) from which ΔH and ΔS was calculated from the slope and intercept, respectively. The correlation coefficient, r obtained for Cd(II), Pb(II) and Cu(II) ions increases with temperature for each of the metals respectively.

A negative value of ΔG indicates the spontaneous nature of the reaction, while the positive value for ΔS reflects an increase in the randomness at the solid/solution interface during the sorption process [24]. According to Crini and Badot [25], a more negative value of ΔG at higher temperatures, as was observed in this study, implies greater driving force for sorption at high temperature for both the HSPAN/HSPAA for the metals with Cu(II) having the most negative ΔG more than Pb(II) and Cd(II) for both HSPAN/HSPAA. Meanwhile, the sign of ΔS indicated the direction of adsorption system [25]. The ΔS obtained for Cu(II) and Pb(II) ions were positive indicating favourable competitive sorption than the Cd(II). The thermodynamic parameters are actually helpful in the practical application of the process.

Thermodynamics parameters are employed to describe macroscopically the average properties of adsorbents and provide in-depth information on energy changes during the sorption of heavy metal ions. ΔG^0 (standard free energy change, kJ/mol), ΔH^0 (standard enthalpy change, kJ/mol), and ΔS^0 (standard entropy change, [kJ/(mol K)] [26] were calculated at 300.3, 313, and 323 K.

The Gibbs free energy change indicates the degree of spontaneously of removal process and higher negative value reflects a more energetically favorable removal [27]. The negative values of the standard enthalpy change obtained in this study indicates that the removal of both ions by HSPAA is exothermic, which is evidenced by the decrease in the removal of both

ions with temperature increase, the reverse is the case for HSPAN. A negative change in ΔG^0 reveals that the removal reaction is spontaneous [28]. The standard entropy change was found to be positive values for the processes. This means a increase in the randomness at solid-solution interface during the removal of Cd(II), Cu(II) and Pb(II) ions onto HSPAN/HSPAA. The results are similar in trend to results indicated in previous literatures [29, 30]. With the attention at this point, HSPAN and HSPAA can be used as products or sorbent for purification of water. Also the products (HSPAN and HSPAA) are not toxic for human and have the potential to biodegrade.

A positive value of ΔS^0 reflects the affinity of the adsorbent towards the adsorbate species. In addition, positive value of ΔS^0 suggests increased randomness at the solid/solution interface with some structural changes in the adsorbate and the adsorbent. The adsorbed solvent molecules, which are displaced by the adsorbate species, gain more translational entropy than is lost by the adsorbate ions/molecules, thus allowing for the prevalence of randomness in the system. The positive ΔS^0 value also corresponds to an increase in the degree of freedom of the adsorbed species.

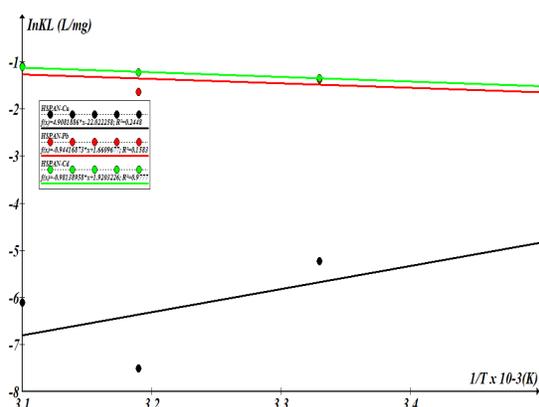


Figure 13: Van't Hoff Plot for the sorption of Cu, Pb and Cd ions by HSPAN

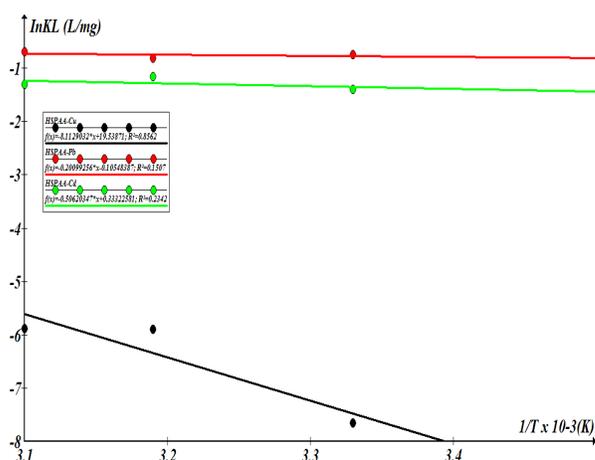


Figure 14: Van't Hoff Plot for the sorption of Cu, Pb and Cd ions by HSPAA

Table 3: Thermodynamics Parameters for the Competitive Sorption of Cd²⁺, Pb²⁺ and Cu²⁺ at Different Temperatures (T = 300.3, 313, 323K, Initial pH=7.85, Dosage = 0.5g/100ml, Ce = 20mg/l)

Temperatur e/K	Constants	Cu ²⁺	Pb ²⁺	Cd ²⁺
300.3	q _{max} (mg/g)	42.4(1653.4)	422.5(286.4)	116.6(274.3)
	R ²	0.4057(0.0035)	0.0038(0.3186)	0.0849(0.3818)
	K _L ×10 ⁻³	5.37(0.47)	0.55(2.73)	2.21(2.79)
	ΔG	-13.05(-1.91)	-18.74(-14.68)	-15.27(-14.68)
	ΔH(KJ/mol)	40.81(-67.45)	7.85(-1.67)	8.16(-4.21)
	ΔS(J/mol.K)	-183.09(162.44)	13.81(0.88)	15.97(2.77)
	Ea (KJ/mol)	2.537(2.429)	2.504(2.495)	2.504(2.492)
	A (Sec ⁻¹)	2.73×10 ⁻¹⁰ (3.06×10 ⁸)	5.26(0.90)	6.82(1.40)
313	q _{max}	2.76(10.59)	2.46(11.26)	3.43(12.08)
	R ²	0.9974(0.9813)	0.9626(0.9879)	0.984(0.9801)
	K _L	0.254(0.471)	0.194(0.447)	0.337(0.503)
	ΔG	-3.57(-19.59)	-4.27(-20.95)	-2.83(-17.88)
323	q _{max}	3.18(11.88)	3.36(12.11)	3.81(13.46)
	R ²	0.9666(0.9857)	0.9698(0.9912)	0.979(0.9902)
	K _L	0.263(0.247)	0.292(0.313)	0.336(0.270)
	ΔG	-3.59(-37.55)	-3.31(-31.19)	-2.93(-35.16)

Hydrolyzed starch-g-polyacrylonitrile, HSPAN (Hydrolyzed starch-g-polyacrylic acid, HSPAA, in parenthesis) ΔH: Enthalpy, ΔS: Entropy, ΔG: Gibb's free energy, Ea: Activation Energy, A = Frequency factor

Competitive sorption kinetics of the metal ions by the graft copolymers

In order to examine the possible mechanism of the competitive sorption, the kinetic test data were further analyzed with three kinetic models and two diffusion models- the pseudo first order, the pseudo second order and elovich equation, and the intraparticle diffusion and liquid film diffusion models. In Table 4, the parameters of sorption kinetics for the metal ions, the calculated rate constants, sorbed amount of metals and the correlation coefficient of linear regression (R²) were showed. The sorption kinetics of the metals were not express properly (R²<0.5) for the Elovich equation for HSPAN/HSPAA and the first order equation for Cu²⁺ and Cd²⁺ for both HSPAN/HSPAA. It was properly expressed for the pseudo second order equation (R²>0.9).

From Table 4, shows the fraction of amount of metal ions sorbed per unit time and it shows that the Cd had higher sorption followed by Pb and then Cu both for the HSPAN/HSPAA. This has been attributed to the ionic radius of the metal ions. This means that the smaller the ionic radius of a metal ions, the higher the sorption rate. It has been noted that the smaller the ionic diameter, the higher the sorption rate. The ionic radii of the metal ions are Cd^{2+} (0.97Å), Pb^{2+} (1.20Å) and Cu^{2+} (0.73Å). Therefore the trend of ionic radii is in opposite direction to the trend of the sorption rate.

This trend of the kinetics of the competitive sorption can also be explained based on the trend of the hydration energies of the metal ions (ΔH_{hyd}), which is given as -2099 KJmol^{-1} for Cu^{2+} , -1806 KJmol^{-1} for Cd^{2+} and -1480 KJmol^{-1} for Pb^{2+} [31]. It could be seen that the trend of the sorption process also follow in opposite direction the trend of the hydration enthalpies of the metal ions.

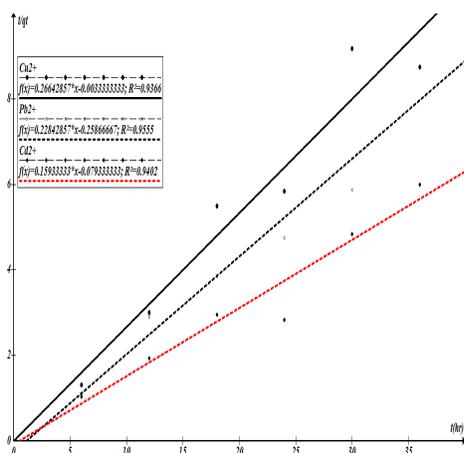


Figure 15: Pseudo second order for the competitive sorption of metal ions by HSPAN

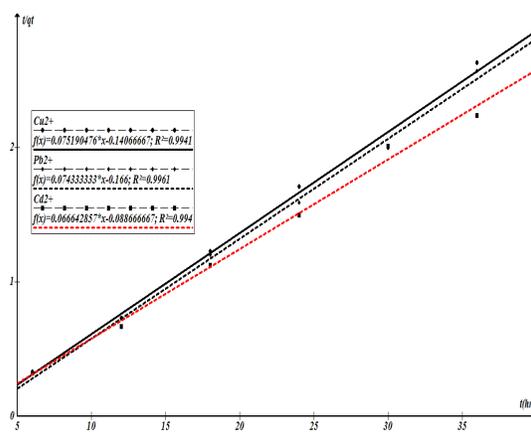


Figure 16: Pseudo second order for the competitive sorption of metal ions by HSPAA

Table 4: Kinetic Parameters of the Kinetic Models for the Competitive Sorption of Cd²⁺, Pb²⁺ and Cu²⁺ (T = 300.3K, Initial pH=7.85, Dosage = 0.5g/100ml, Ce = 20mg/l)

Kinetics Model	Constants	Cu ²⁺	Pb ²⁺	Cd ²⁺
Pseudo first order	q _e exp.(mg/g)	9.04(38.80)	11.12(42.21)	12.2(45.21)
	q _e calc.(mg/g)	1.175(1396.400)	1.058(1.774)	2.464(1.372)
	K ₁	0.0257(0.0914)	0.0379(0.1124)	0.0041(0.0675)
	R ²	0.0371(0.7486)	0.0934(0.8026)	0.1018(0.5349)
Pseudo Second order	q _e calc	3.75(13.30)	4.38(13.46)	6.28(15.02)
	h ₀	303.03(7.11)	3.87(6.02)	12.61(11.27)
	K ₂	21.550(0.040)	0.20(0.033)	0.32(0.050)
	R ²	0.9356(0.9341)	0.9555(0.9961)	0.9402(0.994)
Elovich Equation	α(mmol/g) x 10 ⁵	1.42((0.30)	361.00(0.26)	0.76(9.87)
	β(g/mmol)	2.55(0.43)	3.31(0.42)	2.32(0.61)
	R ²	0.2580(0.8758)	0.1342(0.8401)	0.0846(0.7333)
Intraparticle Diffusion model	K _{id} (mg/gin ^{-1/2})	0.1701.135)	0.139(1.200)	0.178(0.780)
	Intercept	4.64(20.33)	5.37(21.15)	5.67(20.46)
	R ²	0.1924(0.8221)	0.1122(0.8495)	0.057(0.6591)
Liquid Film Diffusion model	K _{fd}	0.035(0.011)	0.042(0.039)	0.002(0.008)
	Intercept	0.327(0.729)	0.312(0.065)	0.638(1.151)
	R ²	0.3242(0.0496)	0.3406(0.5482)	0.0034(0.0107)

Cassava starch-g-polyacrylonitrile (cassava starch-g-polyacrylic acid, in parenthesis)

CONCLUSION

This study has provided a set of data and scientific information on the potentials of Nigeria grown native cassava starch–g-polyacrylonitrile and cassava starch –g- polyacrylic acid hydrolyzed copolymers in the competitive removal of metal ions from aqueous media. The use of the graft copolymers for metal ions removal was technically feasible, eco-friendly and with high efficiency. The results from the studies have provided baseline information on the use of the graft copolymers in treatment of cadmium, lead and copper contaminated water.

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