

# Synthesis of a Hydrogel Composite of K-carrageenan and Tetraethylortho-Silicate for Improved Removal of Lead and Nickel from Aqueous Solution

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## Abstract

This study investigated the adsorption potential of a hydrogel composite (Kc-PAA-Si) synthesized through incorporation tetraethylortho-silicate (TEOS) into a K-carrageenan-based hydrogel (Kc-PAA). The synthesized Kc-PAA-Si was characterized using Fourier transform infrared spectroscopy (FT-IR) and scanning electron microscopy (SEM). Kc-PAA-Si exhibited different morphology and binding groups to the original hydrogel. The adsorption of Pb(II) and Ni(II) from aqueous solutions by Kc-PAA and Kc-PAA-Si was found to follow the pseudo-second order kinetic model and Freundlich isotherm model. The hydrogel composite achieved higher adsorption capacity than the hydrogel (23 mg/g and 26.24 mg/g for Ni(II), then 28.31 mg/g and 29.5 mg/g for Pb(II), respectively). Both adsorbents exhibited higher binding affinity for Pb(II).

The newly synthesized adsorbent has shown improved adsorption capability and could therefore be considered for further investigation towards the development of effective strategy for wastewater treatment.

**Keywords:** Hydrogel, hydrogel composite, adsorption, Pb(II), Ni(II), thermodynamic

## 1. INTRODUCTION

Polymeric substances have been often considered as adsorbents for metals removal from solution because of their intrinsic properties among which the multitude of anionic groups and porosity are of significant importance (Dumat et al., 2000; Fosso-Kankeu et al., 2017). For example, carboxylic acid, hydroxyl, and amine groups have been reported as dominant binding groups in natural biopolymers such as chitosan and alginate (Hassan et al., 1991; Lasko et al., 1993). A host of biopolymers-based adsorbents which are abundant in nature or by-products of industrial processes have been reported in the literature and include among others chitosan, lignin, bark/tannin-rich materials, seaweed/algae/alginate, cellulose, dead biomass and cyclodextrin. The properties of biopolymers can be altered to improve their potential as adsorbents; such modifications may consist of the copolymerization of polymers with monomers having different functional groups or by post-modification of polymerized products. Hydrogels with high hydrophilic

capacity have been produced from crosslinking of monomers to polymers. Hydrophilic groups such as -COOH, SO<sub>3</sub>H, -OH, -NH<sub>2</sub> and -CONH<sub>2</sub> which are present in the backbone of hydrogels are responsible for the adsorption of significant amount of water and solute molecules (Peppas and Peppas, 1991; Taleb et al., 2007; Ozay et al., 2009; Guilherme et al., 2010; Fu and Soboyejo, 2010; Shirsath et al., 2011). Hydrogels are useful for a wide range of commercial applications including drug delivery, recovery of secondary oil, separation of biomolecules, stabilization of minerals and sedimentation, purification of wastewater and metal extraction (Wu et al., 1991; Christopher et al., 2002; Liu et al., 2008). The potential of hydrogel as adsorbent has been investigated for the removal of organic and inorganic pollutants from wastewater. Cationic hydrogels were used by Barakat and Sahiner (2008) for the removal of toxic arsenate from aqueous solution; while in another investigation, Li and colleagues (2010) hydrophobically modified poly(acrylic acid-acrylamide) hydrogel to adsorb cationic dye from water. Hybrid materials with improved capacity as adsorbents can be prepared by combining hydrogel with inorganic compounds; the resulting composite generally exhibits better mechanical strength, corrosion protection, increased surface area and biofunctionality (Bunsow et al., 2009; Fosso-Kankeu et al., 2016a). In our previous work (Fosso-Kankeu et al., 2017) it was observed that the adsorption capacity of hydrogel derived from gelatine for the removal of Cd from industrial wastewater was increased by incorporating clinoptilolite within the hydrogel matrix. Mahdavinia et al. (2013) synthesized hydrogels composed of kappa-carrageenan and sodium alginate biopolymers by incorporating sodium montmorillonite nanoclay; the synthesized nanocomposite hydrogels were successfully used for the cationic crystal violet. K-carrageenan is a non-toxic sulphated polysaccharide with a structure made up of  $\alpha(1\rightarrow4)$  D-galactose-4-sulphate and  $\beta(1\rightarrow3)$  3,6-anhydro-D-galactose which is extracted from specific species of red seaweed (Harding et al., 1997; Thanh et al., 2002; Mishra et al., 2008).

In this study k-carrageenan serves as backbone for the synthesis of a hydrogel composite with incorporation of the tetraethylortho-silicate likely to improve the capacity of the newly developed adsorbents which was used to remove lead and nickel from solution. The adsorption potential of the hybrid hydrogel was further investigated by thermodynamic, isotherm and kinetic studies.

## 2. METHODOLOGY

### 2.1 Chemicals and reagents

All the chemicals and reagents used were analytical grade. K-carrageenan, potassium persulphate, acrylamide, methyl-bisacrylamide and tetraethylortho-silicate (TEOS) were purchased from Sigma Aldrich (South Africa); nitric acid (HNO<sub>3</sub>), sodium hydroxide (NaOH), lead nitrate (Pb(NO<sub>3</sub>)<sub>2</sub>) and nickel(II) nitrate hexahydrate (Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O) were purchased from Associated Chemical Enterprises (PTY) LTD (ACE South Africa).

### 2.2 Synthesis of adsorbents

#### 2.2.1 Hydrogel

The free radical graft co-polymerization technique was considered for the synthesis of the adsorbents (Fosso-Kankeu et al., 2015). Stock solutions of 1 mg/L of the initiator and 1.5 mg/L the crosslinker were prepared using deionised water. Then K-carrageenan was now dissolved in 20 mL deionized water to form a solution of 20 mg/L which was vigorously stirred by using a magnetic stirrer, then 5 mL of the initiator solution was added to the mixture followed by 5 mL of the cross-linker solution under continuous stirring until 1 g Acrylonitrile was finally added. The obtained gel was then incubated in the oven for 2 hours at 60 °C to stimulate the reaction leading to copolymerization. The obtained gel was then allowed to cool down at room temperature, then the unreacted homopolymer, monomers, cross-linkers and initiators were washed off with deionised water at 85°C. Lastly the hydrogel was left to dry for 24 hours in the oven at 40 °C and crushed.

#### 2.2.2 Hydrogel-silica composite

For the synthesis of the hydrogel-silica composite, the process of the hydrogel synthesis repeated with the only difference that 600 µL TEOS was added to the 20 mL deionised water at the beginning and stirred for 2 min prior to the addition of the other reactants as mentioned above.

The characterization of the synthesized adsorbents was carried through Fourier Transform infrared spectroscopy (FTIR) and Scanning Electron Microscopy (SEM), Energy-dispersive X-ray spectroscopy (EDS) analyses.

The surface morphology of each adsorbent was determined using scanning electron microscopy (SEM) photography (TESCAN, VEGA SEM) under a 20-kV electron acceleration voltage coupled with energy-dispersive x-ray spectroscopy (EDS) for elemental analysis (Fosso-Kankeu et al., 2015). For the identification of the functional groups present in the hydrogel and the hydrogel-silica composite as well as to evaluate the surface activation, the IRAffinity-1S Fourier transform infrared spectrophotometer from Shimadzu, with a spectral range from 4000-400 cm<sup>-1</sup> was used (Fosso-Kankeu et al., 2016b).

### 2.3 Adsorption experiments

#### 2.3.1 Optimization experiments

The adsorption process was carried out using a batch system; for the determination of the optimum dosage of adsorbent, 0.1, 0.2, 0.3 and 0.4 g of adsorbent were used to remove the metal ion from a solution of 30 ppm concentration, keeping

constant parameters. The optimum dosage was determined for both adsorbents, namely hydrogel and the composite during the removal of lead and nickel. The pH was then varied using nitric acid (HNO<sub>3</sub>) and sodium hydroxide (NaOH) to obtain pH in the range 5, 7 and 9, and under conditions similar to the above, optimum pH for the removal of lead and nickel from solution was investigated. The optimum pH for each adsorbent was considered for the determination of the effect of time on the adsorption as well as the development of adsorption isotherm, kinetics and thermodynamic parameters.

#### 2.3.2 Metal adsorption overtime

To determine the adsorption rate, time intervals of 10, 20, 30, 40, 60, 80, 100 and 120 min were considered for the adsorption of lead and nickel onto both adsorbents; the other parameters were kept constants, this included a solution volume of 100 mL containing 30 ppm of metal, a stirring speed of 160 rpm and the optimum adsorbent dosage determined in the previous experiments.

#### 2.3.3 Metal adsorption at various initial concentrations

The initial concentrations of lead and nickel were varied between 10, 20, 30, 40, 60, 70, 80 and 100 mg/L, while keeping the other parameters at the optimum during adsorption in a batch system.

#### 2.3.4 Metal adsorption at various temperatures

The adsorption of lead and nickel was conducted at various temperatures, 25, 35, 45 and 55°C while keeping the other parameters constants; stirring speed 160 rpm, metal concentration at 30 mg/L and one hour incubation time.

Following exposure of metals to adsorbents, the mixture was centrifuged at 4000 rpm for 10 mins and the supernatant was collected for analysis. The residual metal in the supernatant was measured using the Inductively coupled plasma (ICP) atomic emission spectroscopy (Agilent Technologies, USA) analysis.

### 2.4 Data processing

After ICP-OES analysis, data were recorded on excel to obtain the equilibrium concentrations which were used to determine the adsorption capacity according to the following equation:

$$q_i = \frac{(C_0 - C_i)V}{m}; \quad i = e, t \quad (1)$$

Where  $q_i$  is the amount of metal adsorbed per unit mass of adsorbent (mg/g);  $C_0$  is the initial metal ions concentration in the solution (mg/L);  $C_i$  is the metal ion concentration (mg/L);  $m$  is the amount of adsorbent (g) and  $V$  is the solution volume (L). The subscript "i" denotes the state of the system either at equilibrium (e) or at a time interval (t).

## 3. RESULTS AND DISCUSSION

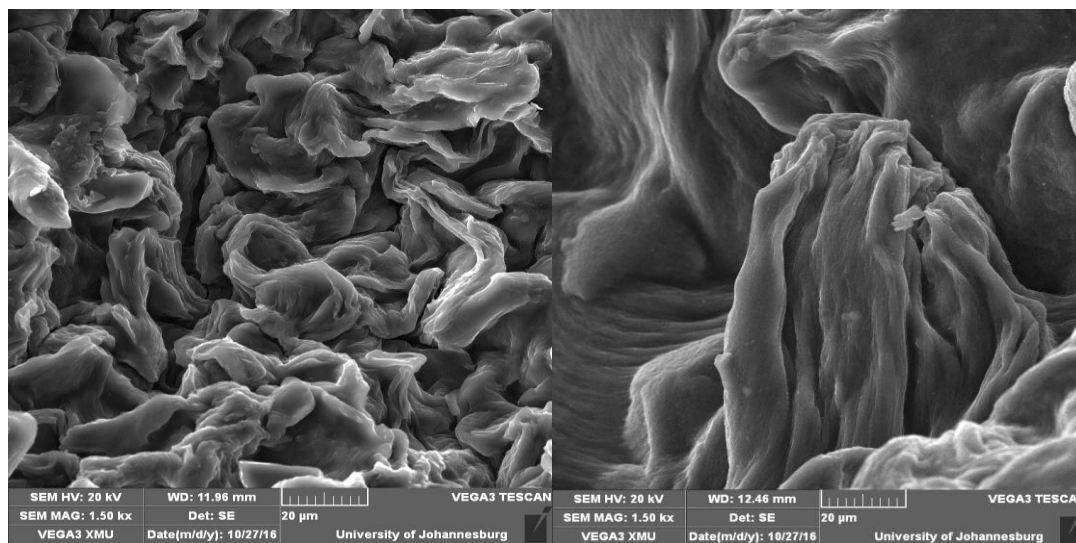
### 3.1 Characterization of the adsorbents

#### 3.1.1 Determination of the morphology

The SEM analysis showed (Fig. 1) some discrepancies between the hydrogel and the hydrogel composite morphologies. It can be clearly observed on Figure 1(a) that

the surface texture of hydrogel is more flakier, irregular and heterogeneous, while the surface texture of the polymer changes after incorporation of the tetraethylortho-silicate into

the hydrogel polymer matrix; as shown in Fig. 1(b) the surface texture of hydrogel composite is comparatively more smoother and homogeneous.



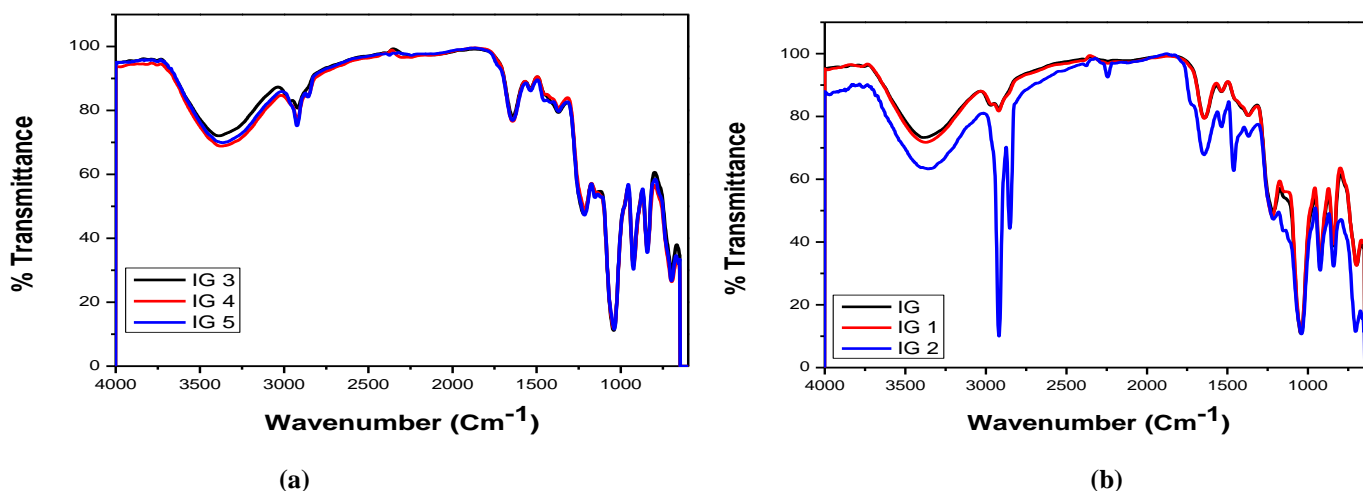
**Figure 1:** Scanning electron microscope of (a) hydrogel and (b) hydrogel composite

### 3.1.2 Identification of binding groups

The FTIR spectra of the hydrogel (Kc-PAA) and the hydrogel composite (Kc-PAA-Si) are shown in Fig. 2(a) and (b). A broad band is observed between 3300 and 3400  $\text{cm}^{-1}$  in all the spectra, and this can be ascribed to the hydrogen-bonded O-H stretching vibration, which is an important binding group (Ge et al., 2012). In the region 2918 – 2851  $\text{cm}^{-1}$ , there are two strong peaks which indicate the symmetric and asymmetric stretching vibration of the C-H groups

(Fosso-Kankeu et al., 2016b). A strong adsorption band is also observed at 1650  $\text{cm}^{-1}$ , which is a characteristic band for C = O stretching vibration. In the region 1500 – 1400  $\text{cm}^{-1}$ , there are two strong peaks which indicate N-H bend.

A decrease in peaks intensities of the above bands was generally observed after exposure of adsorbents to the metal ions in solutions, indicating that these groups were indeed involved in the binding of metal ions at the surface of adsorbents.



**Figure 2:** FT-IR spectra of (a) Kc-PAA (IG5 before adsorption; IG4 after adsorption of Ni(II); IG3 after adsorption of Pb(II)), (b) Kc-PAA-Si (IG2 before adsorption; IG1 after adsorption of Ni(II); IG after adsorption of Pb(II))

### 3.2 Effect of initial pH on the adsorption

The pH of the solution determines the speciation of ions in solution as well as the ionisation state of the binding groups at the surface of the adsorbent. It therefore controls the electrostatic interaction between the sorbate and the sorbent, making it an important parameter to consider for the optimization of adsorption experiment. In this study, a range of pH between the acidic, neutral and alkaline pHs were considered to determine the impact of pH on the adsorption of Pb(II) and Ni(II) by Kc-PAA and Kc-PAA-Si. It can be observed on Fig. 3(a) and 3(b) that the absorption of Pb(II) and Ni(II) varied depending of the value of pH. The effect of pH on the adsorption was more pronounced for the removal of Pb(II) (Fig. 3(a)) than for the removal of Ni(II) (Fig. 3(b)).

The removal of Pb(II) was favorable at a pH of 5 for both adsorbents, while maximum Ni(II) removal was achieved at a pH of 7 for both adsorbents. This can be explained by the fact that at very low pH the large amount of protons available in solution competes with the metal ions for the binding sites at the surface of the adsorbents, while at very high pH the hydroxyl groups in solution complex with metal ions, leading to their precipitation therefore reducing the affinity for binding sites on the adsorbents (Jeon et al., 2008; Sand et al., 2010; Abdel-Halim and Al-Deyab, 2011; Fosso-Kankeu et al., 2015). The optimum pHs obtained were close to neutrality, therefore suitable for implementation at large scale as minimal adjustment of pH will be needed; these pHs were then considered for the rest of the experiments.

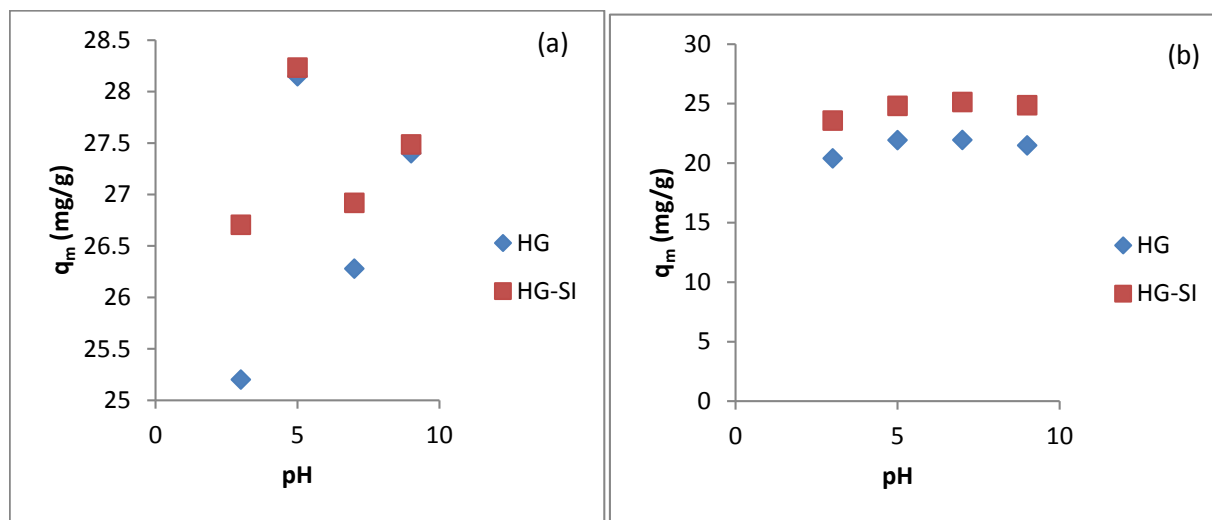


Figure 3. Adsorption of Pb(II) (a) and Ni(II) (b) at various pHs

### 3.3 Adsorption isotherms

The prediction of the adsorption process as well as the interactive behavior of metal ions with the adsorbents was done using the isotherms models such as Langmuir, Freundlich and Dubinin-Kaganer-Radushkevich (Fig. 4).

The Langmuir isotherm model assumes monolayer adsorption in single solute systems; the model's linear form is represented as follows:

$$\frac{c_e}{q_e} = \frac{1}{bq_m} + \frac{c_e}{q_m} \quad (2)$$

The Freundlich model can be applied in heterogeneous systems and is not limited to monolayer adsorption. The model's linear form is represented as follows:

$$\log q_e = \log k_F + \frac{1}{n} \log C_e \quad (3)$$

Dubinin-Kaganer-Radushkevich (DKR) isotherm expresses the adsorption mechanism with a Gaussian energy distribution onto a heterogeneous surface (Mittal et al., 2013). The mathematical expression of the DKR model is as follows:

$$\ln q_e = \ln q_D + \beta \varepsilon^2 \quad (4)$$

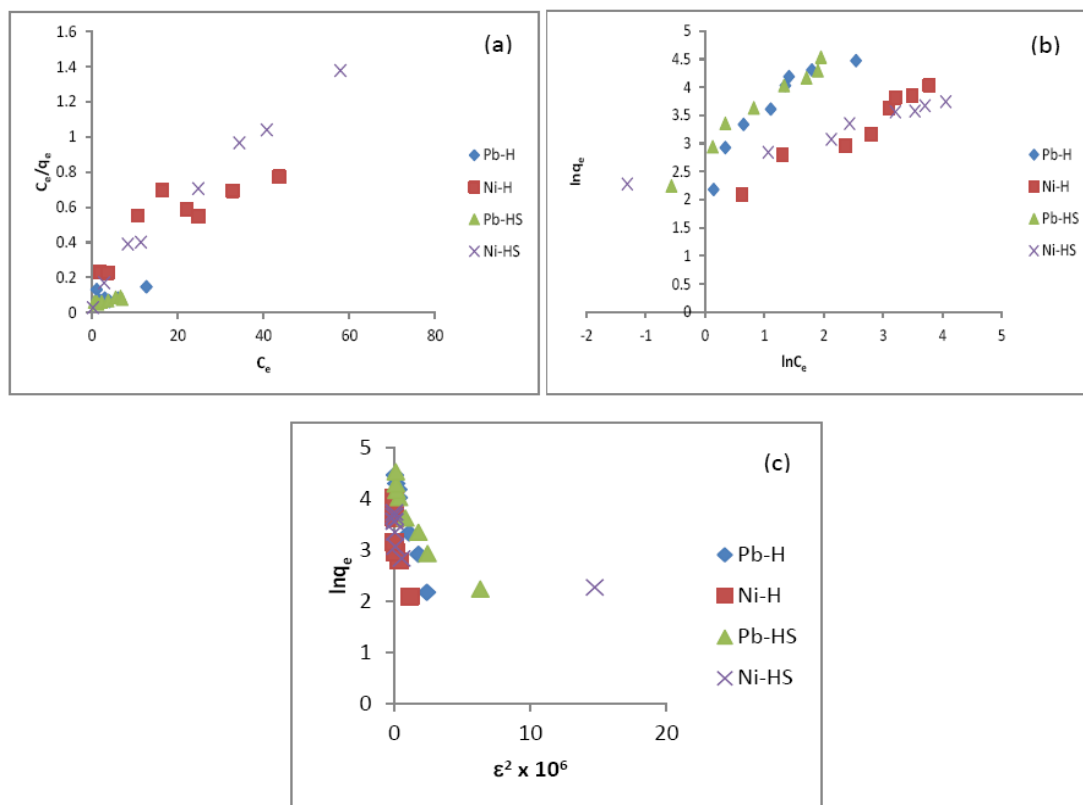
Where  $q_e$  is the amount of metal adsorbed at equilibrium (mg/g),  $q_m$  is the maximum adsorption capacity (mg/g) of adsorbent,  $b$  is Langmuir constant related to adsorption energy,  $R_L$  is the separation factor, a dimensionless constant which represents essential features of Langmuir isotherm and is expressed below, while  $k_F$  is the Freundlich isotherm constant and  $n$  is a dimensionless constant known as heterogeneity factor;  $q_D$  is the DKR isotherm constant related to the degree of metal ion adsorption,  $\beta$  is the activity coefficient and  $\varepsilon$  is known as Polanyi Potential..

$$R_L = 1/(1 + bC_0) \quad (5)$$

Where  $C_0$  is the initial concentration of metal in solution, while  $b$  is the Langmuir constant.

$$\varepsilon = RT \ln(1 + \frac{1}{C_e}) \quad (6)$$

Where  $R$  is the universal gas constant in J/mol/K, is the temperature in K and  $C_e$  is the concentration of residual metal at equilibrium (mg/L).



**Figure 4** (a) Langmuir, (b) Freundlich and Dubinin-Kaganer-Radushkevich adsorption isotherm model plots for the removal of Pb(II) and Ni(II) by Kc-PAA and Kc-PAA-Si

The adsorption equilibrium results obtained from the experimentation of the effect of initial metal concentrations have been fitted in the plot of  $C_e/q_e$  vs  $C_e$  (Fig. 4a) for the Langmuir study while the same results were fitted in the plot

of  $\log q_e$  vs  $\log C_e$  for the Freundlich model (Fig. 4b) and in the plot  $\ln q_e$  vs  $\varepsilon^2$  for the DKR model (Fig. 4c); the isotherms constants derived from the intercept and slope of these plots are reported in Table 1.

**Table 1:** Isotherms parameters for the adsorption of Pb(II) and Ni(II) onto Kc-PAA and Kc-PAA-Si

Isotherms	Parameters	Hydrogel		Hydrogel silica	
		Pb(II)	Ni(II)	Pb(II)	Ni(II)
Langmuir	$q_m$ (mg/g)	222.2	81.3	208.33	44.248
	$b$	0.64	0.041	0.0928	0.1846
	$R^2$	0.2958	0.7258	0.7603	0.9839
	$R_L$	0.05	0.45	0.264	0.153
Freundlich	$1/n$	0.9138	0.5815	0.8236	0.2815
	$K_f$	12.935	6	17.51	13.42
	$R^2$	0.8599	0.9357	0.9729	0.9829
Dubinin-Kaganer-Radushkevich	$q_D$ (mg/g)	78.67	35.53	64.168	30.3
	$E$ (Kj/mol)	0.784	0.5037	2.079	8.9963
	$R^2$	0.9649	0.7045	0.876	0.6517

The fitness of a model to the equilibrium adsorption data is expressed by the coefficient of determination ( $R^2$ ) which should be ideally closer to unity; based on the values of  $R^2$  it was found that the Freundlich isotherm model was the more suitable model to describe the mechanism of adsorption of all the metal ions for both adsorbents; while the Langmuir

isotherm was only suitable ( $R^2 = 0.9839$ ) to describe the adsorption behavior of Ni(II) onto Kc-PAA-Si and DKR was suitable ( $R^2 = 0.9649$ ) to describe the adsorption behavior of Pb(II) onto Kc-PAA. This implies that the adsorption of Pb(II) and Ni(II) occurred through heterogeneous binding to the surface of adsorbents as more than one layer were involved

(Abdel-Halim et al., 2011).

The affinity of the adsorbents for metal ions could be determined by considering isotherms constants such  $R_L$ ,  $n$  and  $E$  for the Langmuir, Freundlich and DKR models respectively. The  $R_L$  value allows to predict whether the adsorption process is favorable; the adsorption will be unfavorable if  $R_L > 1$ , favorable if  $0 < R_L < 1$ , linear if  $R_L = 1$  and irreversible if  $R_L = 0$  (Pandey and Mishra, 2012; Fosso-Kankeu et al. 2015).

As the Langmuir model was only suitable for Ni(II) adsorption, the  $R_L$  value in this case (0.153) is less than 1, implying that the adsorption of Ni(II) onto Kc-PAA-Si is favorable. The  $n$  value indicates applicability of adsorbent and feasibility of the adsorption process (Fosso-Kankeu et al., 2015).

If  $n > 1$  the adsorbent is good over the entire range of concentrations studied and if  $n < 1$ , then the adsorbent is good only for higher concentrations studied. The values of  $n$  obtained in this study were all greater than 1, therefore implying that the Freundlich isotherm model predicts favorable adsorption of Pb(II) and Ni(II) onto both adsorbents over the entire range of metal ions concentrations.

$E$  is the free energy per molecule of adsorbate required to remove a molecule from its location in the sorption space of infinity; it was found to be  $< 8$  KJ/mol for the adsorption of Pb(II) onto Kc-PAA, therefore implying that the physisorption process was dominant; however, the estimated adsorption capacity  $q_D$ , is far beyond range making the model less suitable.

### 3.4 Adsorption kinetics

The determination of the adsorption rate is very important when effective escalation of the process is to be considered for the implementation of a wastewater treatment plant; the pseudo-first order, pseudo-second order and intraparticle diffusion models are used to predict metal adsorption overtime (Fig. 5).

The pseudo-first order kinetic model is represented by the following equation:

$$\log(q_e - q_t) = \log q_e - k_1 \frac{t}{2.303} \quad (7)$$

The pseudo-second order kinetic model is represented by the following equation:

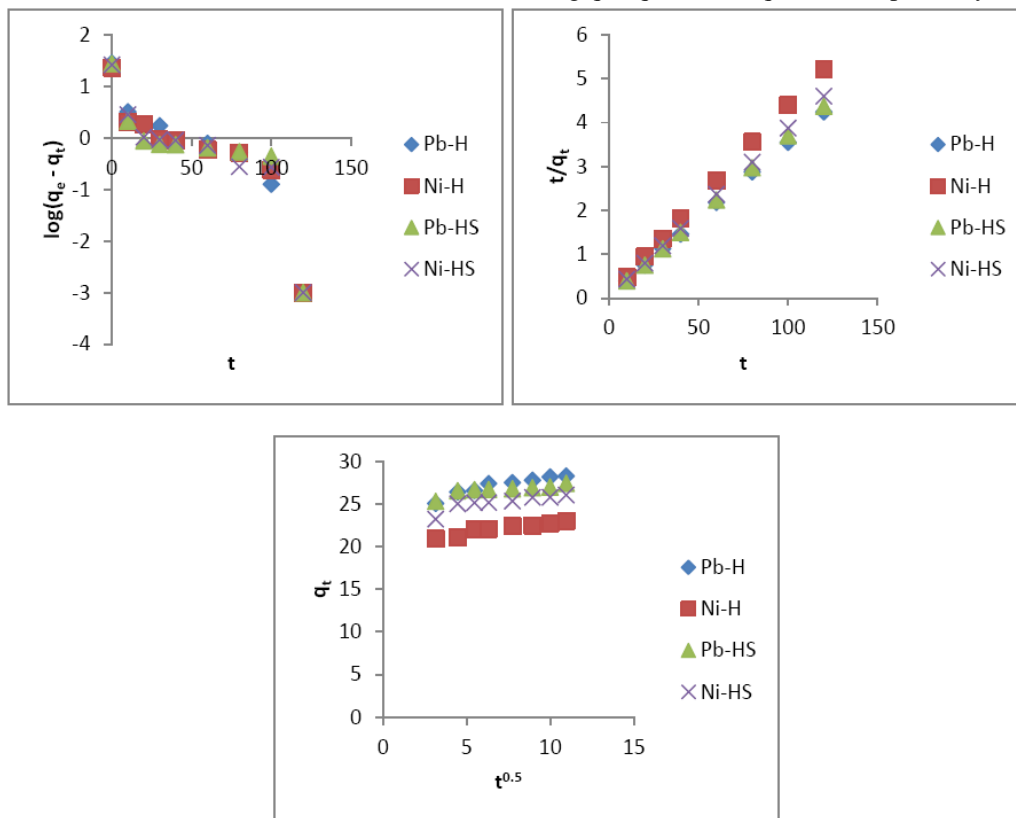
$$\frac{t}{q_t} = \frac{1}{(k_2 q_e^2)} + \frac{1}{q_e} t \quad (8)$$

The intraparticle kinetic model is represented by the following equation:

$$q_t = k_1 t^{0.5} + C \quad (9)$$

Where  $q_e$  is the concentration of metal at equilibrium (mg/g),  $q_t$  is the amount of metal adsorbed at time  $t$  (mg/g),  $k_1$  is the pseudo-first order rate constant ( $\text{min}^{-1}$ ),  $k_2$  is the pseudo-second order rate constant ( $\text{g/mg/min}$ ),  $k_i$  is the intraparticle diffusion rate constant ( $\text{mg/gmin}^{0.5}$ ).

The values of  $k_2$  and  $C$  can be obtained from the intercepts of the plots of  $t/q_t$  vs  $t$  and  $q_t$  vs  $t^{0.5}$ , respectively; while the value of  $k_1$  and  $k_i$  can be obtained from the slopes of the plots of  $\log(q_e - q_t)$  vs  $t$  and  $q_t$  vs  $t^{0.5}$ , respectively.



**Figure 5(a)** Pseudo-first order, **(b)** Pseudo-second order and Intraparticle diffusion adsorption kinetic model plots for the removal of Pb(II) and Ni(II) by Kc-PAA and Kc-PAA-Si

Adsorption equilibrium data obtained from the experimentation of the effect of time were fitted using the above mentioned kinetic models and the corresponding parameters are reported in Table 2.

It can be observed in Table 2 that the values of the coefficient of determination were higher (closer to unity) for the pseudo-second order model compared to other kinetic models; implying that the pseudo-second order kinetic model was more suitable to describe the adsorption process for the removal of Pb(II) and Ni(II) by Kc-PAA and Kc-PAA-Si. This was further confirmed by the calculated values of  $q_e$  which were closer to the experimental values. The adsorption process is therefore more likely to occur through the chemisorption mechanism. It is also observed that the intraparticle diffusion model was suitable to describe the adsorption of Pb(II) and Ni(II) only onto the hydrogel and not the composite, which could confirm the compactness of the

composite after incorporation of TEOS (silicon) into the hydrogel, reducing the porosity. The values of the adsorption capacity ( $q_e$ ) also demonstrate that better adsorption of metal ions was achieved when using Kc-PAA-Si, which implies that the hybridization of the hydrogel with TEOS has not only stabilized the adsorbent, but has also increased its adsorption capacity. It was also found that Pb(II) was easily adsorbed compared to Ni(II) implying that the adsorbents had higher affinity for Pb(II). According to the electronegativity order established by Pauling (1932), Pb(II) with higher electronegativity is most likely to be adsorbed compared to Ni(II) of lower electronegativity; furthermore, it has been reported that metal ions with higher atomic weight can generate a higher momentum energy, which may promote the adsorption of the metal ion by increasing the probability of effective cohesion between the metal ion and the sorbent surface (Fosso-Kankeu and Waanders, 2014; Fosso-Kankeu et al., 2016c).

**Table 2:** Kinetics parameters for the adsorption of Pb(II) and Ni(II) onto Kc-PAA and Kc-PAA-Si

Kinetics	Parameters	Hydrogel		Hydrogel silica	
		Pb(II)	Ni(II)	Pb(II)	Ni(II)
Pseudo first order	$k_1$	0.0265	0.0242	0.0226	0.0246
	$q_e$ (cal.)	13.98	9.69	7.82	9.625
	$q_e$ (exp.)	28.309	23.002	29.451	26.076
	$R^2$	0.8116	0.7442	0.6573	0.7523
Pseudo second order	$k_2$	0.0182	0.0249	0.0364	0.0267
	$q_e$ (cal.)	28.65	23.26	29.47	26.24
	$q_e$ (exp.)	28.309	23.002	29.451	26.076
	$R^2$	0.9999	0.9998	0.9998	0.9999
Intraparticle diffusion	$k_i$	0.3717	0.2532	0.1886	0.2757
	C	24.515	20.312	25.344	23.241
	$R^2$	0.8973	0.9103	0.7201	0.7461

### 3.5 Thermodynamics study

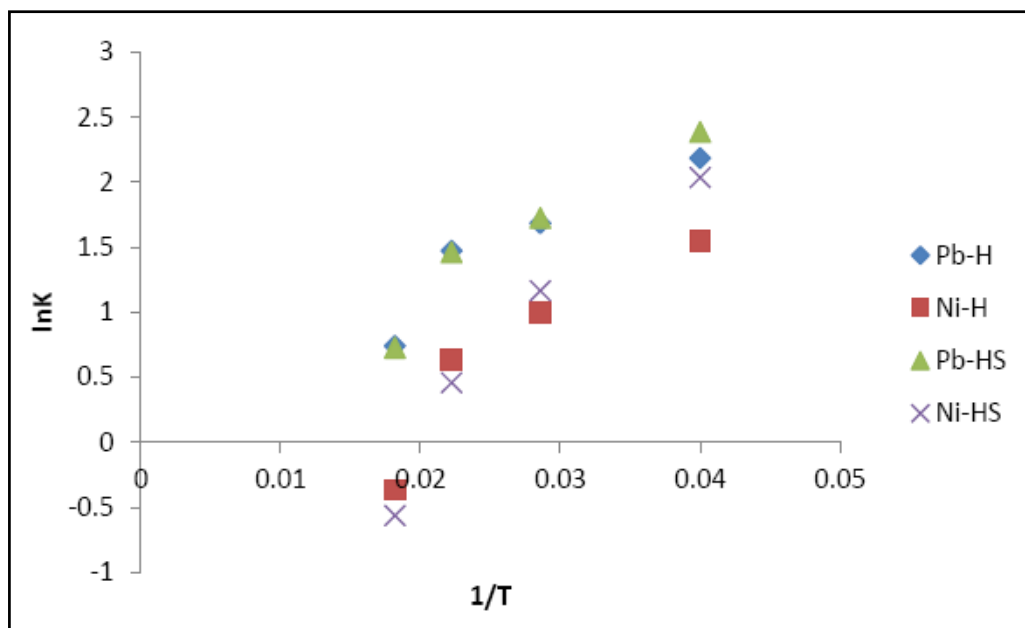
The effect of temperature on the adsorption of Pb(II) and Ni(II) was investigated at 25, 35, 45 and 55°C; it was observed that the adsorption of metal ions decreased with an increase in temperature which implies that the adsorption was predominantly exothermic. Using equilibrium contact change as well as the temperatures, the thermodynamic parameters such Gibbs free energy change ( $\Delta G^\circ$ ), enthalpy ( $\Delta H^\circ$ ) and entropy ( $\Delta S^\circ$ ) were determined.

The Gibbs free energy ( $\Delta G^\circ$ ) for the adsorption of Pb(II) and Ni(II) ions onto Kc-PAA and Kc-PAA-Si was calculated using the van't Hoff equation below:

$$\ln K = -\frac{\Delta G^\circ}{RT} = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \quad [7]$$

where,  $K$  ( $q_e/C_e$ ) is the equilibrium constant or the linear adsorption distribution coefficient,  $T$  is the solution temperature (K), and  $R$  is the gas constant ( $8.314 \times 10^{-3}$  KJ/mol/K).

The values of  $\Delta S^\circ$  and  $\Delta H^\circ$  were obtained from the intercept and slope of the plot  $\ln K$  vs  $1/T$  (Fig. 4), these values are shown in Table 3. The negative value of  $\Delta G^\circ$  for the adsorption of Pb(II) onto Kc-PAA shows that the process is spontaneous in this case while a positive value in other cases indicates a non-spontaneous adsorption process. The value of  $\Delta H^\circ$  was negative in all the cases, confirming that the adsorption process is exothermic (Kula et al., 2008). The negative value of  $\Delta S^\circ$  indicates that the Pb(II) and Ni(II) were orderly adsorbed onto the adsorbent-adsorbate interface.



**Figure 6:** Van't Hoff plot for the adsorption of Pb(II) and Ni(II)

**Table 3:** Thermodynamic parameters for the adsorption of Pb(II) and Ni(II) onto Kc-PAA and Kc-PAA-Si

Polymer	Metals	$\Delta G^\circ$ (KJ/mol)				$\Delta H$ (KJ/mol)	$\Delta S$ (KJ/mol/K)
		298 K	308 K	318 K	328 K		
Hydrogel	Pb(II)	-281.61	-274.63	-267.75	-260.67	-489.61	-0.698
	Ni(II)	2857.98	2329.08	3093.18	3210.78	-646.5	-11.76
Hydrogel silica	Pb(II)	196.22	222.12	248.02	273.92	-575.6	-2.59
	Ni(II)	4686.72	4875.12	5063.5	5251.92	-927.68	-18.84

#### 4. CONCLUSION

The development of better adsorbent for the removal of Pb(II) and Ni(II) was achieved in this study through incorporation of tetraethylortho-silicate (TEOS) into the hydrogel. The successful synthesis of the composite Kc-PAA-Si was confirmed through observation of morphological characteristics using SEM. Both Kc-PAA and Kc-PAA-Si exhibited good performance as adsorbents with optimum performance at relatively neutral pH. The adsorption process was found to occur at a multilayer surface of the adsorbents, and dominated by a chemisorption mechanism. The incorporation of TEOS into the hydrogel resulted into an increase of the adsorption capacity by 23% for Pb(II) removal and 14% for Ni(II) removal. All the adsorbents had higher affinity for Pb(II) than Ni(II) which was explained by the higher electronegativity and atomic weight of Pb(II) compared to Ni(II). The adsorption was not favoured by an increase in temperature and the binding of metal ions onto the adsorbents was found to occur through an orderly manner.

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