# Sorption Studies on the Remediation of Cadmium (II) Ions Contaminated Water Using Succinic Acid Modified Red Onion Skin Extract

**Dr. Orji Ikodiya**
Lecturer, Africa Centre of Excellence for Oil Field Chemicals Research, Institute of Petroleum Studies,
University of Port Harcourt, Choba, Rivers State, Port Harcourt, Nigeria
**Millicent Uzoamaka Ibezim-Ezeani**
Senior Lecturer, Department of Pure and Industrial Chemistry of the Faculty of Sciences,
University of Port Harcourt, Rivers State, Nigeria

*Abstract:*
*Batch experiments were conducted for the removal of cadmium (II) ions from synthetic wastewater using succinic acid modified red onion skin extract (SROSE). Effects of pH, initial metal ion concentration and contact time were investigated. Maximum metal removal for cadmium was observed at pH 6.2, initial metal ion concentration of 20 mg/L, 28°C temperature and 50 min. contact time. The experimental data were analyzed based on Freundlich, Langmuir, Temkin and Flory-Huggins adsorption isotherms; and the results obtained from the correlation coefficients of the plots indicated that Freundlich adsorption isotherm gives the best fit for the experimental data. The thermodynamic parameters were calculated and the results obtained indicated that the sorption process was spontaneous and exothermic. The likely mechanism responsible for the Cd (II) ions removal was analyzed using the Dubinin-Radushkevich (DR) isotherm at different temperatures, and the results obtained showed that the major sorption mechanism was particle diffusion. Kinetic studies revealed that the adsorption of metal ions followed a pseudo-second order reaction.*

*Keywords: Cadmium (II) metal ions, Dubinin-Raduskevich model, freundlich isotherm, pseudo-second order, red onion skin, succinic acid.*

## 1. Introduction

Heavy metal pollution has become an environmental and public health concern worldwide. This is because they are stable and persistent environmental contaminants, since they cannot be degraded and destroyed (Ayhan Demirbas, 2008). They are discharged by industries such as agrochemical, petrochemical, fertilizer, mining operations and tanneries. Anthropogenic cadmium contamination often results from mining or smelting of metal ores, but cadmium is also released into the environment by power stations, heating systems, waste incinerators, urban traffic, cement factories and as a by-product of phosphate fertilizers (Sanità di Toppi and Gabbrielli, 1999). Cadmium waste streams from the industries mainly end up in soils where it can be very dangerous because of increased uptake through food. However, in aquatic ecosystems cadmium has the capacity to accumulate in aquatic organisms like shrimps, oysters and fish (Ali and Ahmad, 2013). As one of the most eco-toxic metals (Adriano, 2001; Kabata-Pendias and Pendias, 2001), the most apparent visible symptoms of Cd toxicity in plants are retardation of plant growth, chlorosis and stunting (Das *et al.*, 1997; Sanità di Toppi and Gabbrielli, 1999). In animals and humans, Cd may produce disorders in the metabolism of calcium and vitamin D, including bone degeneration and kidney damages (Wagner, 1993; Burgat-Sacaze *et al.*, 1996).

Utilization of agricultural by-products as adsorbent material to purify heavy metal contaminated water has become increasingly popular through decades of research because they are less expensive, biodegradable, abundant and efficient. The major advantages are its effectiveness in reducing the concentration of heavy metal ions to very low levels and the inexpensive nature of the raw materials employed. Onion skin in its modified and unmodified state has been investigated as a possible candidate for the removal of heavy metals. Chowdhury *et al.* (2012) , investigated the Cu (II) ions removal properties of unmodified onion and garlic skin. They found out that the pseudo-second order kinetic model fitted the experimental data adequately, and the maximum adsorption capacity of onion skin was slightly higher than that of garlic skin at pH of 5.3 and temperature of 303K. Waweru *et al.* (2016), in their study of the feasibility of removing Pb, Cd and Cu (II) ions from synthetic waste water using both modified and unmodified onion skin, reported that the metal removal efficiency of the ethylene-1,2-diamine modified onion skin was less than that of the unmodified one. However they discovered that modification solved the problem of leached soluble organic substances and smell from the unmodified onion skin into the water.

Other modifying agents investigated include a combination of toluene diisocyanate and sulphonic acid (Obi and Onwucha, 2014); and epichlorohydrin and 4-hydroxybenzoic acid (Ibezim-Ezeani and Okon, 2016).

This study was carried out to investigate the metal removal capacity of succinic acid modified red onion skin extract (SROSE) in the remediation of Cd (II) ions contaminated water, and thus contribute in the search for less expensive agricultural waste raw materials capable of remediating cadmium metal contaminated effluent from industries.

## 2. Materials and Methods
The collection and extraction of the red onion skin, the preparation of the succinic acid modified red onion skin resin (SROSE), and the spectroscopic analyses were described by Orji *et al.* (2016)

### 2.1. Sorption Studies
A series of batch experiments were carried out to determine the adsorption isotherms of Cd (II) ions on the SROSE. Each heavy metal solution of Cd (II) ions was placed in 100ml conical flasks at pH 7± 0.2 and 0.3g of SROSE sample were added to 20ml of 20mg/L metal in the sample container.

The sample containers were shaken at a constant rate of 250 rpm for one hour to ensure that equilibrium was reached. It was assumed that the applied shaking speed allowed the surface area to come in contact with heavy metals ions over the course of the experiments. The study was performed at a constant temperature of 28°C to be representative of environmentally relevant condition. All experiments were carried out in duplicates and the average values were used for further calculation. At the end of the agitation period, the solution was filtered and the concentration of metal ion in the filtrate analyzed using a Buck Scientific Atomic Absorption Spectrophotometer (model 205A). The procedure was repeated at different pH values (~2 to 10), initial ion concentrations (5 to 50mg/l), contact time (10 to 70 mins) and temperature (28 to 70 $^o$C). The percentage metal ion exchange was deduced using equation (2) and plotted as a function of pH, initial ion concentrations, and contact time in each case.

## 3. Results and Discussion

### 3.1. Sorption Studies
The sorption capacity ($q_e$) of SROSE was evaluated by the mass balance from initial to equilibrium compositions of Cd (II) ions in the liquid phase using the relationship in equation (1) and the values plotted against those of initial metal ion concentration (Ibezim-Ezeani and Akaranta, 2016).

$$q_e = \frac{V}{m} (C_o - C_e) \tag{1}$$

The percentage metal ion removed was calculated using equation (2):

$$\% \text{ Metal Ion exchange} = \frac{C_o - C_e}{C_0} \ x \ 100 \tag{2}$$

Where V is volume of initial Cd ion solution used (l), and m is mass of SROSE (g), $C_o$ is the initial concentration of metal ion in solution (mol/L) and $C_e$ is the concentration of metal ion present at equilibrium (mol/L).

### 3.1.1. Effect of Contact Time
The metal removing capacity of SROSE as a function of contact time was investigated in order to determine the optimum contact time. A more complete metal ion removal is achieved after a longer contact time. The minimum time required for considerable adsorption to take place provides an insight into the metal removal process involved in the system, as well as the possible diffusion controlled mechanism between the metal ion as it moves from the bulk solution towards the active site of the SROSE. The plot of the percentage Cd (II) ions as a function of the contact time is represented in Figure 1. The plot showed a steady increase in the percentage removal of Cd (II) ions at 10mins (85.32 %) to 50 mins (94.45%). Thereafter, the percentage of Cd (II) ions removed reduced to 94.43% at 60 mins and 94.42% at 70 mins. Thus, the maximum uptake of the ions took place within the first 50 mins of agitation.
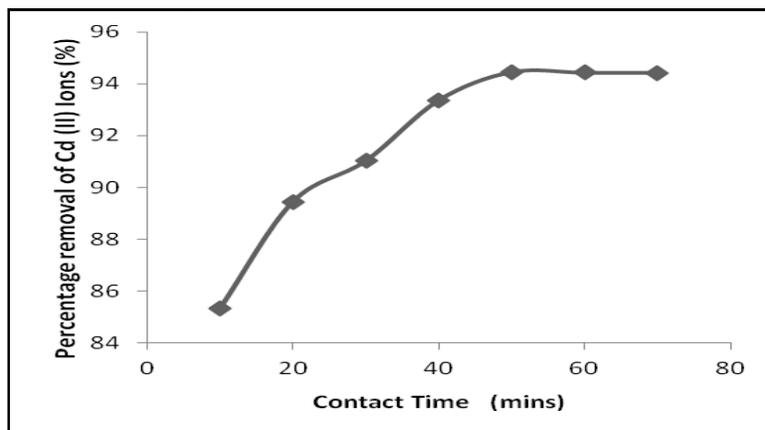
*Figure1: Plot of Percentage Metal Ion Sorption at Different Contact Times*

This could be explained based on the availability of the active sites of the SROSE for interaction with the Cd (II) ions at the beginning of the process. However, as more metal ions are adsorbed, increased metal – metal repulsion and the reduced availability of the active sites for attachment of the metal ions do not lead to a remarkable increase in the percentage of Cd (II) ions removed (Ibezim-Ezeani and Okon, 2016). Therefore, it could be rightly inferred that the time for most of the active sites of the SROSE to be saturated with Cd (II) ions and thereby attain equilibrium is 50 mins.

### 3.1.2. Effect of Initial Ion Concentration
The movement of removable metal ions from the bulk of the solution to the active sites is dependent upon the chemical potential gradient of the system. Therefore, these metal ions will move from a region of higher metal ion concentration (metal ion solution) to a region of lower metal ion concentration (active site of modified extract), where they replace equal amount of positively charged ions. The relationship between the initial Cd (II) ions concentration in the synthetic waste water and the percentage removal of the ions is represented in Figure 2. The plot shows that the highest percentage removal of 94.45% removal occurred at the initial concentration of 20 mg/L.
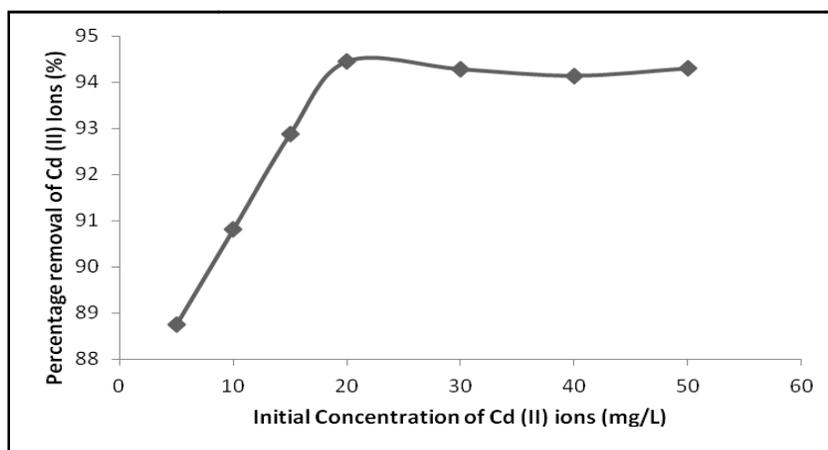


*Figure 2: Plot of Percentage Removal of Cadmium Ions at Different Initial Ion Concentrations*

At low concentrations, the active sites available for interaction with the metal ions in solution are more numerous relative to those available at high concentrations. Therefore at higher concentrations, there will be an increase in the competition of the metal ions for the limited number of active binding sites in the modified extract and once the binding site is exhausted, the remaining metal ions will remain in solution without being removed. This brought about a 94.45 percentage removal of the Cd (II) ions at the initial concentration of the ions of 20 mg/ml and a reduction to 94.14% ions removed as the initial concentration increased to 40 mg/ml. Thus the optimal concentration of Cadmium (II) Ions that could be effectively handled by SROSE at the experimental conditions under investigation is 20 mg/L.

### 3.1.3. Effect of pH
The pH of any solution affects the ionization of the chemical species in the solution. It also affects the solubility of the metal ions in solution and the degree of ionization of the active binding sites of the adsorbate during the sorption process (Zvinowanda *et al.,* 2009). The effect of the pH of the aqueous solution on the percentage of Cd (II) ions removed is represented in Figure 3. From the plot, it can be seen that the percentage of Cd (II) ions removed from the aqueous solution increased from 85.27% at pH 2.1 to 90.42% at pH 4.1.

The percentage of Cd (II) ions removed attained the maximum value of 94.7 % when the pH of the solution was ~ 6. Beyond this pH, the percentage Cd (II) ions removal decreased to 89.17% at pH 8.3 and 83.36% at pH of 10.2.
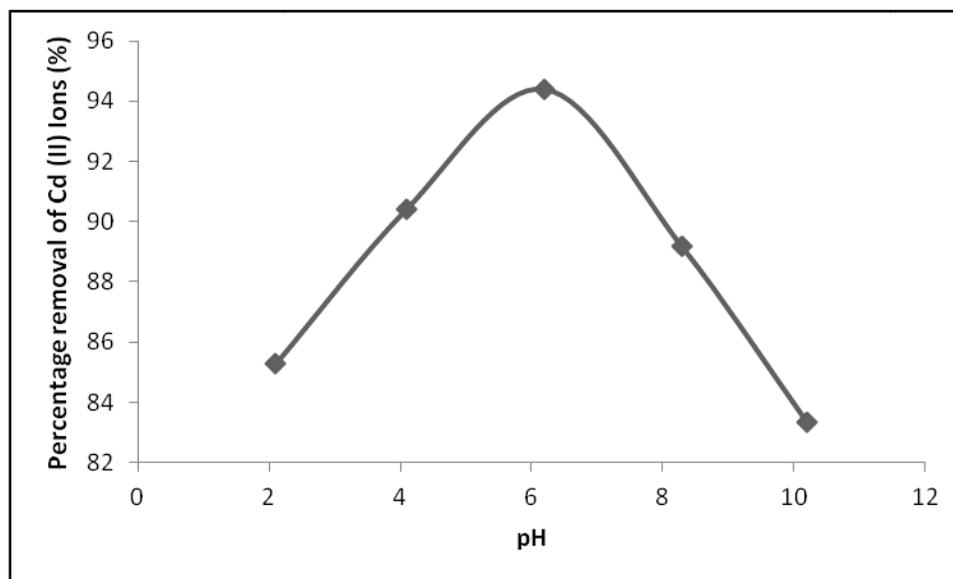


*Figure 3: Plot of Percentage Removal of Cadmium Ions at Different pH Values*

At low pH, there is high concentration of $H^+$ in solution. Thus, there will be a competition between the Cd (II) ions and the numerous $H^+$ for the active binding sites of the SROSE. As the pH is increased, the concentration of $H^+$ in solution is decreased and the competition between the ions is reduced, thereby allowing more of the positively charged Cd (II) ions to diffuse faster towards the active binding site bringing about an increase in the percentage metal ion removed. Beyond pH of 6, the concentration of $OH^-$ ions increases, while that of the $H^+$ reduces. The presence of excess $OH^-$ ions may lead to the formation of $Cd(OH)_2$ and complexation between the Cd(II) ions and the hydroxyl ions to form $Cd(OH)_4$. This reduces the availability of the Cd (II) ions in solution and results in reduction of the quantity of the ions removed (Zvinowanda et al., 2009; Vinod *et al*., 2003).

*3.2. Thermodynamic Studies*
The basic requirements for the design of any adsorption system for the removal of heavy metals are the equilibrium data obtained from studies on the adsorption process. Equilibrium is established at the maximum adsorption capacity of the adsorbent (SROSE) and adsorption isotherms enable the adsorption capacity of the adsorbent to be determined from experimental analysis. The experimental data obtained from this research were fitted into the linearized form of four adsorption isotherms: Langmiur, Freundlich, Temkin, and Flory-Huggins (Langmiur, 1918; Freundlich, 1926; Ibezim-Ezeani and Anusiem, 2011; Chowdhury *et al*., 2012). These models are presented in equations (3) to (6).

$$q_e = \frac{1}{x_m b} + \frac{C_e}{X_m} \qquad\qquad (3)$$

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \qquad\qquad (4)$$

$$q_e = \frac{RT}{b_T} \ln K_T + \frac{RT}{b_T} \ln C_e \qquad\qquad (5)$$

$$\ln \frac{\theta}{C_o} = \ln K_{FH} + n \ln (1 - \theta) \qquad\qquad (6)$$

The constants b, $K_F$, $K_T$, $K_{FH}$ and are the Langmuir, Freundlich, Temkin and Flory-Huggins isotherm constants, respectively. $X_m$ is the maximum adsorption capacity upon complete coverage of the adsorption sites of the modified extract; $1/n$ is a measure of the surface heterogeneity, with values between 0 and 1, R is the gas constant and T is temperature in Kelvin, $b_T$ is related to the adsorption intensity, and $\theta$ is given by:

$$\theta = \left(1 - \frac{C_e}{C_o}\right) \qquad\qquad (7)$$

The plots of the adsorption isotherms are presented in Figures 4 to 7.
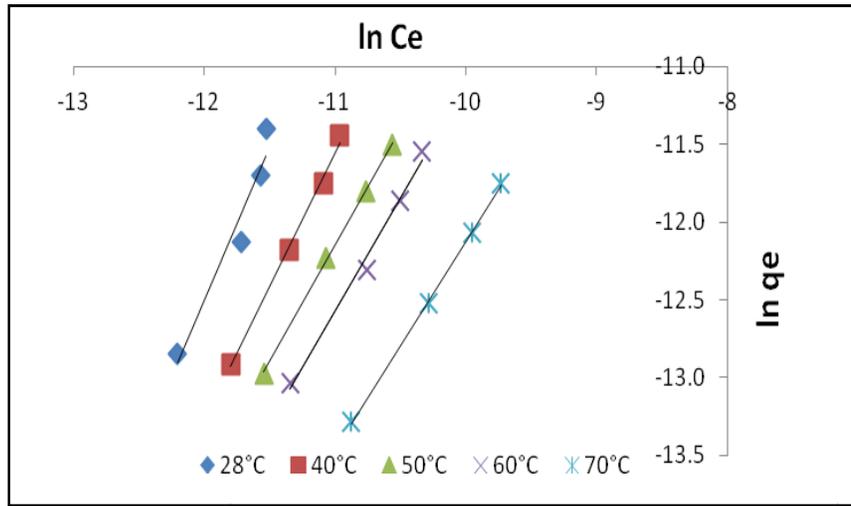
*Figure 4: Freundlich Isotherms at Different Temperatures and Concentrations.*
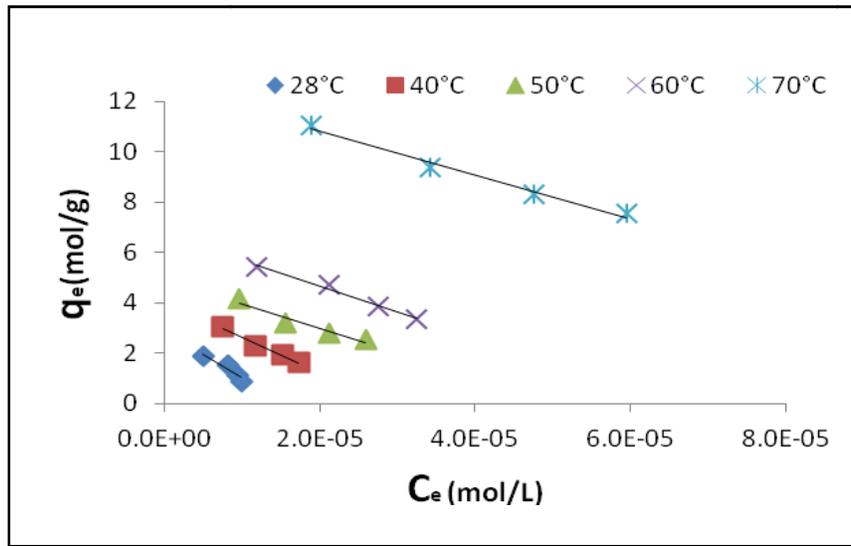


*Figure 5: Langmiur Isotherms at Different Temperatures and Concentrations.*
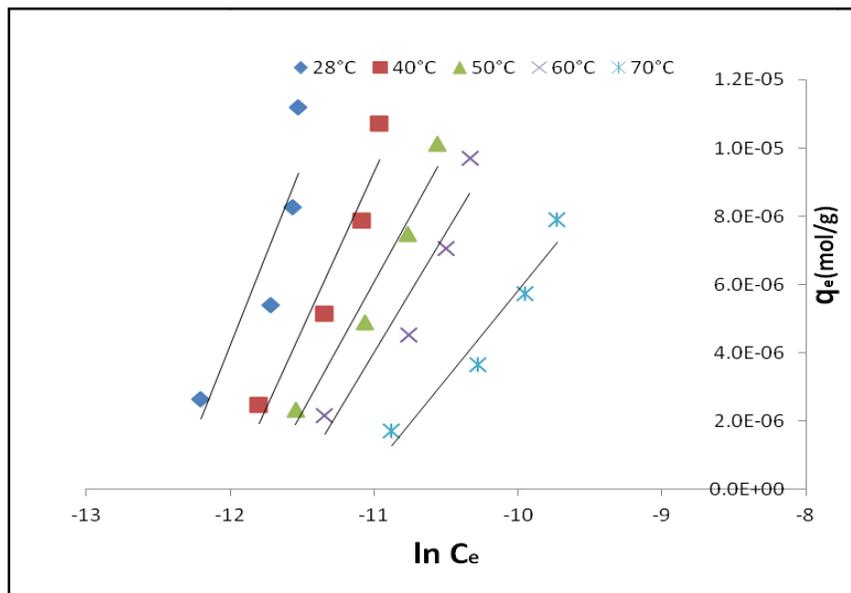


*Figure 6: Temkin Isotherms at Different Temperatures and Concentrations*
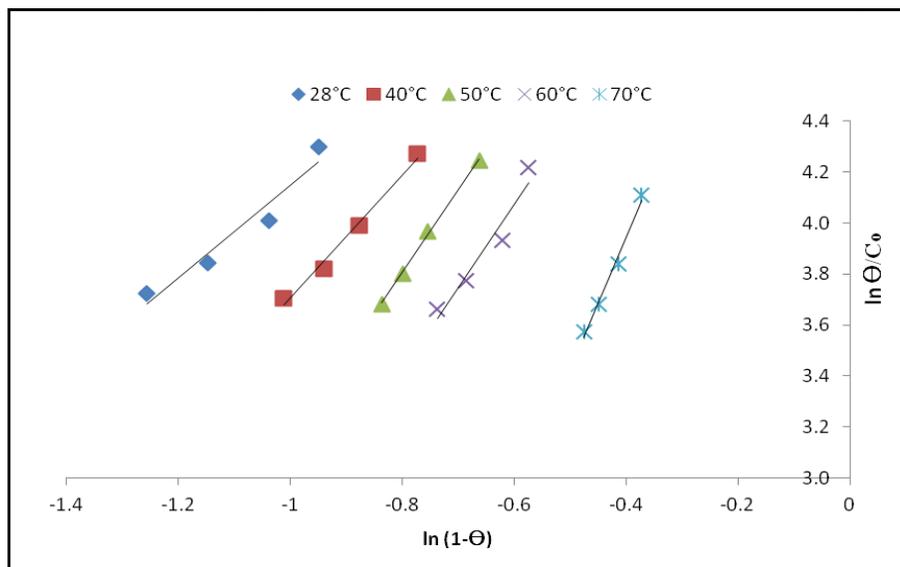
*Figure 7: Flory-Huggins Isotherms at Different Temperatures and Concentrations*

The linear equations for the four isotherm models investigated and their corresponding $R^2$ values are shown in Tables 1 and 2.The Freundlich isotherm exhibited the highest $R^2$ values from the result analysis and therefore, the model best described the adsorption process.

| Temp ($^o$C) | Langmiur | Freundlich | Tempkin | Flory-Huggins |
|---|---|---|---|---|
| 28 | y = -190563x + 2.9121 | y = 1.9438x + 10.825 | y = 1E-05x + 0.0001 | y = 1.814x + 5.9598 |
| 40 | y = -141454x + 4.0612 | y = 1.7177x + 7.3375 | y = 9E-06x + 0.0001 | y = 2.4121x + 6.1192 |
| 50 | y = -96915x + 4.9421 | y = 1.4918x + 4.2597 | y = 8E-06x + 9E-05 | y = 3.2523x + 6.4065 |
| 60 | y = -102446x + 6.7337 | y = 1.4589x + 3.4724 | y = 7E-06x + 8E-05 | y = 3.2589x + 6.0317 |
| 70 | y = -86963x + 12.554 | y = 1.3304x + 1.1793 | y = 5E-06x + 6E-05 | y = 5.1978x + 6.0249 |

*Table 1: Linear Equations of the Isotherm Models*

| Temp. ($^o$C) | Langmiur | Freundlich | Tempkin | Flory-Huggins |
|---|---|---|---|---|
| 28 | 0.9086 | 0.9397 | 0.8061 | 0.9368 |
| 40 | 0.9875 | 0.9958 | 0.9284 | 0.9896 |
| 50 | 0.9301 | 0.9995 | 0.9628 | 0.9977 |
| 60 | 0.9881 | 0.9905 | 0.9074 | 0.9415 |
| 70 | 0.9868 | 0.9993 | 0.9408 | 0.9876 |

*Table 2: Comparison of Coefficient of Determination ($R^2$) for the Isotherms*

The Freundlich isotherm model was therefore employed in resolving the parameter at different temperatures and the values presented in Table 3. The Freundlich adsorption isotherm assumes that adsorption takes place on heterogeneous surfaces and through multilayer adsorption (Mohamad *et al.,* 2013; Freundlich, 1926).

| Temp (K) | Freundlich Constants | | | |
|---|---|---|---|---|
| | n | 1/n | $K_F$ (mol/g) | $\Delta$G (kJ/mol) |
| 301 | 0.514 | 1.946 | 50261.769 | -26.090 |
| 313 | 0.582 | 1.718 | 1536.865 | -19.439 |
| 323 | 0.670 | 1.492 | 70.788 | -13.896 |
| 333 | 0.685 | 1.460 | 32.214 | -8.354 |
| 343 | 0.752 | 1.330 | 3.252 | -2.811 |

*Table 3: Freundlich Constants and ΔG Values at Different Temperatures*

The value of 1/n range between 0 and 1, and is a measure of sorption intensity or surface heterogeneity; the closer the value is to zero, the more heterogeneous the surface. Whereas, a value below unity implies chemisorption process, where 1/n above one is an indication of cooperative sorption (Foo and Hameed, 2010). Since the values of 1/n obtained at all temperatures are above one (Table 3), we therefore conclude that cooperative sorption process is at play in the removal of the Cd (II) ions using SROSE.

The plot of ln $K_F$ against 1/T is linear (Figure 8); and $\Delta H$ and $\Delta S$ were computed from the slope and intercept of the plot using equations (8) to (10) (Mohammed, 2011).
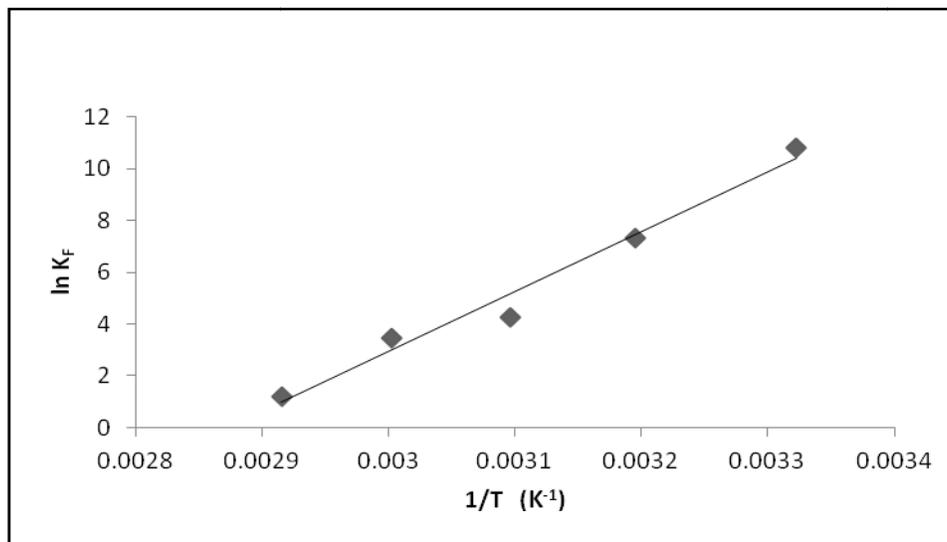


Figure 8: The Plot of ln $K_F$ against 1/T

$$\ln K_F = \Delta S/R - \Delta H/RT \qquad (8)$$

$$\Delta G = - RT \ln K_F \qquad (9)$$

$$\Delta G = \Delta H - T\Delta S \qquad (10)$$

The $\Delta H$ as determined from the slope of the graph was -19.29 KJ/mol, while the $\Delta S$ value was -554.27$JK^{-1}mol^{-1}$. The $\Delta G$ values calculated at the different temperatures are presented in Table 2.

The negative $\Delta H$ value indicates that the adsorption process is exothermic and therefore not favored by increase in temperature. The negative value of $\Delta S$ showed a decreased randomness at solid-solutions interface during the adsorption of Cd (II) ions on the modified extract.

The negative values of $\Delta G$ indicate that the metal removal process is spontaneous and feasible at the temperatures investigated.

*3.3. Sorption Mechanism*

The likely mechanism responsible for the Cd (II) ions removal was deduced using the Dubinin-Radushkevich (DR) isotherm at different temperatures. This isotherm model is reported to assume a heterogeneous adsorbent surface (Mohammed, 2011). The linear form of the DR equation is:

$$\ln q_e = \ln q_D - B_D \varepsilon^2 \qquad (11)$$

$q_D$ is the maximum ion exchange capacity, BD is the DR model constant and $\varepsilon$ is the Polanyi potential, which is equal to:

$$\varepsilon = RT \ln(1 + \frac{1}{C_e}) \qquad (12)$$

R = gas constant (8.314J/mol/K)
T = temperature (301K)

$B_D$ is related to the mean free energy E, of sorption per mole of metal ion through equation 13:

$$E = \frac{1}{\sqrt{2BD}} \qquad (13)$$

The plot of ln $q_e$ against $\varepsilon^2$ gave a linear graph, from which the slope and intercept were obtained; the values of $B_D$ and $q_D$ were deduced. E was calculated by substituting the values of $B_D$ into equation 13. These values are presented in Table 3. It can be observed that the values of $B_D$ and $q_D$ decreased with increase in temperature. Thus, the maximum ion exchange capacity of the SROSE reduces with increase in temperature, supporting the negative $\Delta H$ values obtained for the process.

| Temp. ($^o$C) | Linear equation | $B_D$ (mol$^2$/J$^2$) | $q_D$ (mol/g) | E (kJ/mol) |
|---|---|---|---|---|
| 28 | -0.000777x + 10.824788 | 0.000777 | 50251.71 | 25.37 |
| 40 | -0.000660x +  7.337734 | 0.000660 | 1537.17 | 27.53 |
| 50 | -0.000556x + 4.259999 | 0.000556 | 70.80 | 29.99 |
| 60 | -0.000527x + 3.472744 | 0.000527 | 32.23 | 30.80 |
| 70 | -0.000467x + 1.179821 | 0.000467 | 3.25 | 32.72 |

*Table 4: DR Parameters for the Adsorption of Cd (II) Ions onto SROSE*

The value of E gives us an idea of the sorption mechanism at play in the metal removal process. If the value of E is less than 8 KJ/mol, it implies that the sorption mechanism is dominated by physisorption, if the value is between 8 and 16 KJ/mol, it is dominated by ion exchange and if above 16 KJ/mol, particle diffusion is the major mechanism (Argun *et al.,* 2007; Ibezim-Ezeani and Okon, 2016).The values of E obtained are above 16 KJ/mol, indicating that within this temperature range studied, particle diffusion is the main sorption mechanism.

*3.3. Kinetic Studies*
The experimental data obtained were fitted into the pseudo-first order and pseudo-second order kinetic models in order to determine the controlling mechanism of the sorption process. Equations 14 and 15 represent the linear equations of the pseudo-first order and pseudo-second order kinetic models respectively.

$$\ln(q_e - q_t) = \ln q_e \quad - \frac{K_1}{2.303}t \qquad (14)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad (15)$$

$q_e$ = amounts of the Cd (II) ions adsorbed (mol/g) at equilibrium
$q_t$ = amounts of the Cd (II) ions adsorbed (mol /g) at time t (min),
$K_1$ = pseudo-first order rate constant adsorption (min$^{-1}$).
$K_2$ = pseudo-second order rate constant adsorption (g/ mol /min).  The plot of $\log(q_e - q_t)$ against t gave a linear relationship (Figure 9) the $k_1$ and $q_e$ were determined from the slope and intercept of the plot, while the plot of t/qt against t gave a straight line graph, from which $k_2$ was determined.
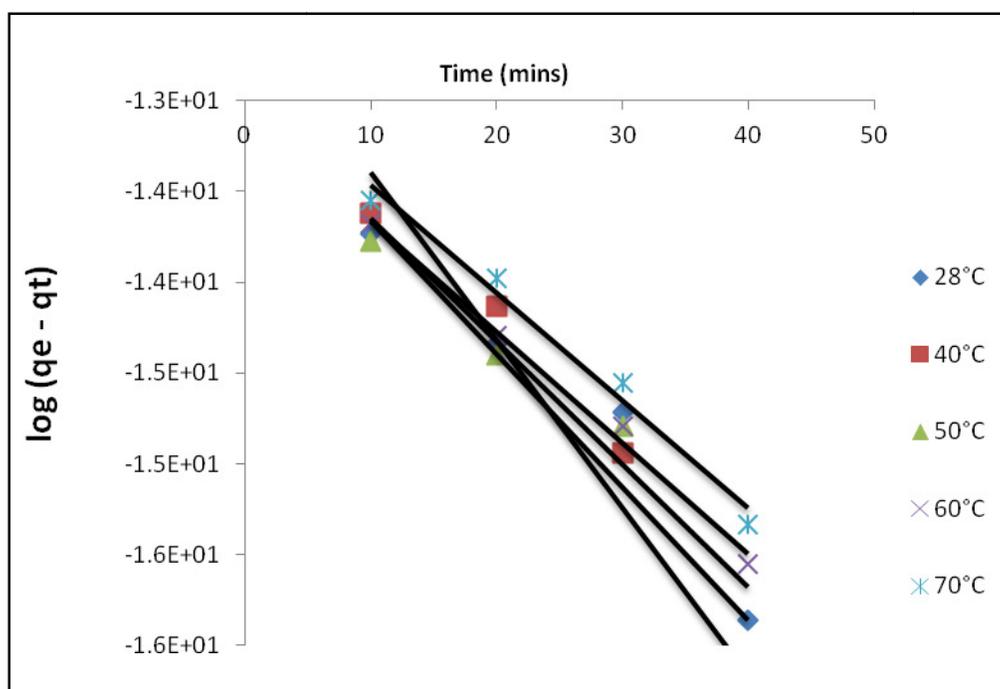


*Figure 9: The First Order Plot of log ($q_e$ - $q_t$) against t*
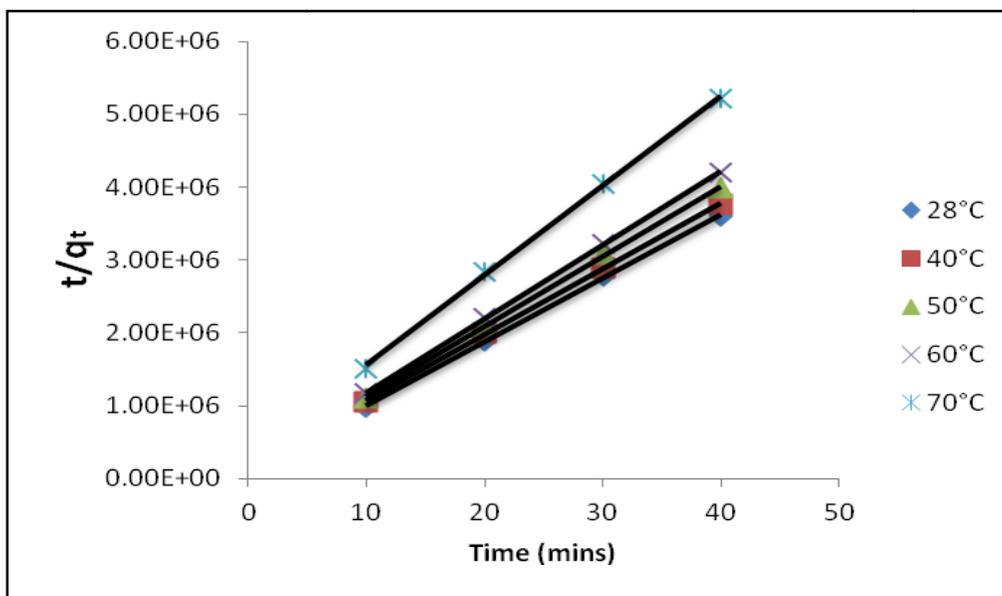
*Figure 10: The Second Order Plot of t/qt against t*

The $R^2$ values obtained by fitting the experimental data to the two kinetic models above are presented in Table 4.

| Temp (K) | Pseudo-first order | Pseudo-second order | $K_2$ (g/mol/min) |
|---|---|---|---|
|  | $R^2$ | $R^2$ |  |
| 301 | 0.9487 | 0.9997 | 61619.4474 |
| 313 | 0.9464 | 0.9996 | 46473.3052 |
| 323 | 0.9386 | 0.9996 | 62011.2863 |
| 333 | 0.9934 | 0.9999 | 60047.1846 |
| 343 | 0.9825 | 0.9992 | 45901.4566 |

*Table 5: $R^2$ Values for the Models and Rate Constants of the Second Order Models*

The higher values of regression coefficients for the second-order kinetic model indicate that the second-order kinetic model best described the sorption of Cd (II) ions onto SROSE.
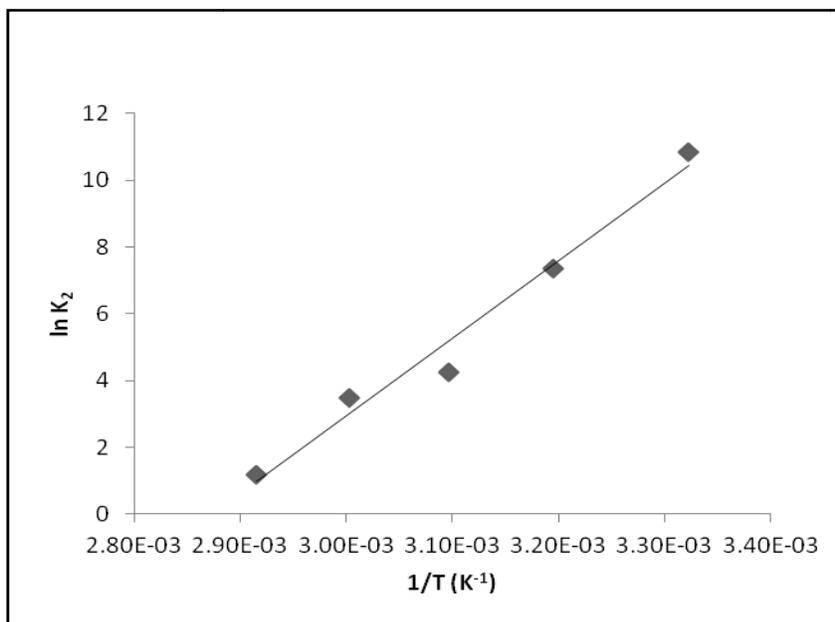


*Figure 11: The Plot of lnk2 against 1/T*

Thus, the natural logarithm of the second order rate constant ($k_2$) at different temperatures was plotted against $1/T$ (Figure 11) according to the Arrhenius equation:

$$k_2 = A \, (exp) \, \text{-}E_a/RT \qquad\qquad\qquad (16)$$

$$\ln k_2 = \ln A - \frac{E_a}{RT} \qquad\qquad\qquad (17)$$

The pre-exponential factor (A) and energy of activation ($E_a$) were determined from the slope and intercept of the plot as $1.946 \times 10^4$ g/mol/min and $\text{-}2.765$ kJmol$^{-1}$ respectively. The negative value of the activation energy ($E_a$) is in agreement with the exothermic nature of the sorption studies as earlier determined from the thermodynamic parameters.

**4. Conclusion**

The results obtained from this work indicated that succinic acid modified red onion skin extract (SROSE) has the capacity to remediate Cd (II) ions contaminated waste water. The pH of synthetic waste water, the contact time between extract and solution, as well as the initial concentration of the metal ions in solution affected the metal removal capacity of SROSE. The percentage Cd (II) ions removed, reduced with increase in temperature. Comparison of the four adsorption isotherms investigated, revealed Freundlich isotherm as the best fit for experimental data following the deductions from the regression factor. The adsorption process is spontaneous with negative ΔG values, exothermic following the negative ΔH values and there was decreased randomness at solid-solution interface during the process as revealed by the negative ΔS value. The result obtained from fitting the experimental data into the Dubinin-Raduskevich isotherm showed that the major sorption mechanism at play was particle diffusion and the pseudo-second order kinetic model best described the experimental results.

**5. Acknowledgement**

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