Preparation of Activated Carbon from Artichoke Stem by $ZnCl_2$ Activation: Application in Nickel(II) Adsorption from Aqueous Solution.

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ABSTRACT

Activated carbon is one of the most important industrial products due to its versatile applications. In this work, efficient activated carbon was produced and utilized for adsorption of nickel from simulated wastewater under varying operational parameters. The raw material (Artichoke) has been chemically modified by zinc chloride ($ZnCl_2$) to improve its surface reactivity and enhance its adsorption capacity.

The adsorbent was characterized by the FTIR analysis. The experimental data were analyzed by adsorption isotherms and kinetic models. Langmuir equation proved to be suitable to explain the adsorption process and the experimental results fit well with the pseudo-second-order model.

The performance of the prepared artichoke-based activated carbon (AAC) suggests it can be used as low coast or cheap adsorbent for the treatment of water and removal of heavy metal ions from industrial effluents.

Keywords: Heavy metal ions, nickel, Activated carbon, Artichoke.

ÖZ

Aktif karbon önemli bir sanayi ürünü olarak çok çeşitli alanlarda kullanılmaktadır. Bu çalışmada, yapay atık sulardan etkili bir şekilde nikeli arındırmakta kullanılmak üzere aktif karbon üretilmiş ve değişik şartlarda denenmiştir. Hammaddesi enginar olan aktif karbonun yüzeyi çinko klorür (ZnCl2) ile değiştirilerek reaktivitesi ve tutma kapasitesinin arttırılmaya çalışılmıştır.

Yüzey tutucu madde FTIR analiziyle karakterize edildi. Deneylerden elde edilen veriler tutma izotermleri ve kinetik modeller ile analiz edilmiştir. Langmuir denklemi tutma sürecini uygun bir şekilde açıklamaktadır ve deneysel sonuçlar pseudo-ikinci dereceden kinetik modeli ile uyumludur.

Enginardan hazırlanan bu aktif karbonun (AAC) performansı bu malzemenin düşük masraflı ve ucuz, atık sulardan ağır metal iyonlarının arındırılmasında kullanılabilecek bir tutucu olduğuna işaret etmektedir.

Anahtar kelimeler: Ağır metal iyonları, nikel, Aktif karbon, enginar.

This research dedicate it to my dear father and to my dear mother

And also dedicate it to my dear wife

And to the two candle that lights the path of my life

Omar & Lara

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LIST OF SYMBOLS ABBREVIATIONS

AAC	Artichoke Activated Carbon
AC	Activated Carbon
FT-IR	Fourier transform infrared
UV/VIS	Ultraviolet visible
ΔG^0	Gibbs free energy change (kJ mole^{-1})
ΔH^0	Enthalpy change (kJ mole^{-1})
ΔS^0	Entropy change (J mole-1 K^{-1})
K_1	Pseudo-first-order rate constant (min^{-1})
K_2	Pseudo-second-order rate constant (mg g^{-1} min^{-1})
K_{id}	Intraparticle diffusion constant (min^{-1})
K_{fd}	Liquid film diffusion constant (min^{-1})
K_f	Freundlich adsorption constant (mg g^{-1})
M	Mass of adsorption per unit volume (g L^{-1})
m	Amount of adsorbent added (g)
n	Freundlich constant
q	Amount of Adsorbate per game of adsorbent (mg g^{-1})
q_e	Amount of Adsorbate per game of adsorbent at equilibrium (mg g^{-1})
q_t	Amount of Adsorbate per game of adsorbent at any time , t
q_m	Equilibrium adsorption capacity using model
q_{max}	maximum adsorption capacity (mg g^{-1})
R^2	Linear correlation coefficient
R_L	Separation factor
r_0	Radius of adsorbent particle (cm)

t	Time (min)
T	Temperature (K)
V	Volume of the solution (mL)
Conc	concentration (mole/L)

Chapter 1

INTRODUCTION

Water is the most widespread substance in nature that is a major constituent of all living creatures. Metal pollution of the surroundings has become a serious ecological concern. Heavy metals are continuously discharged into the aquatic surroundings from natural processes like volcanic activity and weathering of rocks. Additionally, industrial processes such as electro planting, metal finishing, metallurgical, chemical industrialization and mining industries have also contributed to an increase in the concentration of heavy metal in the water (Kinhikar, 2012).

Ions of heavy metals including: copper, nickel, zinc, cadmium, lead, chromium and mercury have a significant impacts on the environment. They form very toxic ions and compounds forms; they are soluble in water and may be readily absorbed into living organisms. Out of these ions, nickel (Ni^{2+}) is the most abundant element in the earth's crust, comprising about 3% of the composition of the earth. It is the fifth most abundant element by weight after iron, oxygen, magnesium and silicon. It is released from both natural sources and anthropogenic activity, with input from both stationary and mobile sources (Kinhikar, 2012).

One of the ways to address this environmental issue is to treat the polluted water and the removal of the pollutants. Many techniques including flocculation, electrolysis, oxidation and adsorption have been employed to remove the contaminants. Among these techniques, adsorption is the most effective and cheapest method (Radenovic et al, 2011).

Figure 1.1: wastewater

1.1 Treatment Of Nickel Polluted Wastewater

Adsorption technique is excellent, easy and economic method for the removal of toxic pollutants from the aqueous solutions. Adsorption is a surface phenomenon which involves the attraction of adsorbate particles towards the surface of an adsorbent until equilibrium is attained between adsorbed particles and those freely distributed in the bulk gas or liquid. The adsorption fact is dependent upon the meeting among the surface area of the adsorbent in addition to the adsorbed types. The interaction might be as a result of either chemical or physical interactions such as (hydrogen bonding, Van der Waals forces and hydrophobic forces) (Radenovic et al, 2011).

The toxic influence of nickel within the environment has been extensively researched by several researchers. It is documented that exposure to above permitted concentration of Ni^{2+} may be carcinogenic, and that exposure can cause gastrointestinal disorder etc. Therefore it is paramount to control the release of nickel containing wastewater before been discharged to the water bodies.

Various treatment techniques have been suggested such as reverse osmosis, and electrodialysis ect, but these techniques are too expensive for developing countries and may also generate secondary pollution. Hence, agricultural remains or industrial by-products have been considered as an alternative adsorbent due to their availability and reusability of spent resources (Hasar, 2003).

Recently, agricultural waste materials have been documented to possess adsorption capability for the treatment of pollutant containing wastewaters. The biological-based adsorbent has been known to possess varying functional sites which is a key feature for heavy metal uptake from aqueous media (Hasar, 2003).

Figure 1.2: Artichoke plant

Artichoke shown in (Figure 1.2) is a native plant of Mediterranean region and can be used to prepare charcoal with the potential to treat wastewater containing pollutants (Hasar, 2003). A high surface area activated carbon with great potential for heavy metal removal can be obtained by chemical modification of charcoal with zinc chloride ($ZnCl_2$). This research work is aimed at producing effective and low-cost activated carbon from artichoke biomass for wastewater treatment under various operational parameters.

1.2 Physico-Chemical Properties Of Activated Carbon

Activated carbon/charcoal is carbonaceous adsorbent with a highly developed small porous structure and large surface area. Activated carbons possess the following features; high degree of surface reactivity, microcrystalline structure, great thermal stability, and an efficient adsorption performance.

These features confer uniqueness to activated carbon and make its a functional adsorbent (Williams & Reed, 2006).

a b

Figure 1.3: a) Granular form of AC. b) Powder form of AC

Recently, various forms of activated carbon have been produced such as fiber-based, beads-form, powder-type and granular, but granular type has been a preferred choice due to its ease of separation after use and its regeneration capability (Yeganeh et al, 2006). The adsorption potential of active carbon is based on its physico-chemical properties and this in turns is directly dependent on the sources/contents of the raw materials (Mohamad Nor et al, 2013).

Research has shown that cherry or grape-based raw material posse great number of lignin and can be used to prepare macroporous activated carbon while almond and apricot-based materials are mostly suitable for microporous activated carbon production (Suhas, 2009). Varying active groups (oxygen, hydrogen and nitrogen) are found on the surface area of most activated carbons, which are heterogeneous in nature. High number of oxygen content on the activated carbon has a prominent effect on the crystalline nature of the material and size of the pores generated (Cuhadar, 2005). Anionic activated carbon containing functional groups (carboxylic, phenolic, and lactones) can be produced at low calcination temperature (200-500^{0}C) or via chemical treatment using oxidizing chemicals such as nitric acid and hydrogen peroxide etc; while high activation temperature (800-1000^{0}C) is suitable for basic activated carbon formation (Cetinkaya et al, 2003).

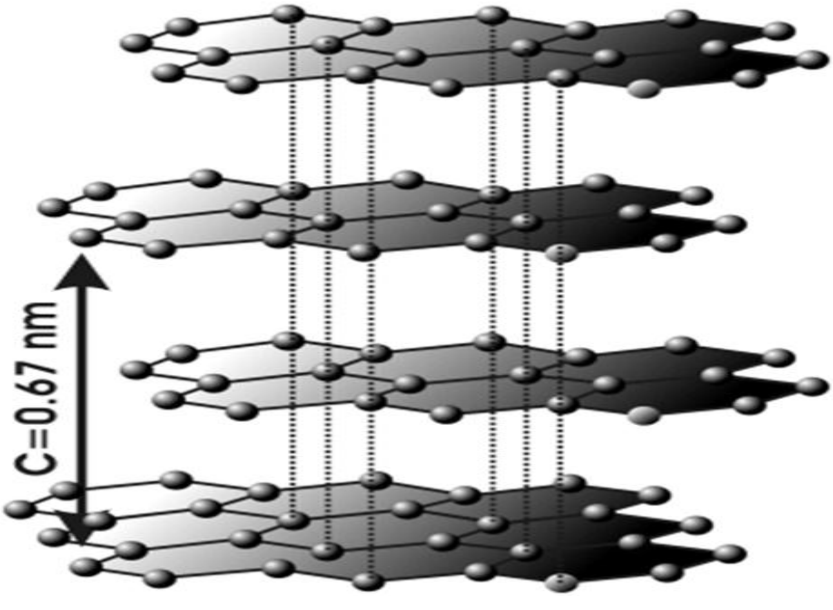


Figure 1.4 : Chemical structure of Activated Carbon

1.3 Activated Carbon From Different Sources

Ther are different sources to produce activated charcoal from carbonaceous materials such as spent fruits, wood biomass, coal, peat and biological based shells. Due to the availability and secondary waste generated, variuos new materials have been under examined as precursors for activated carbon production (Cetinkaya et al, 2003). Lignin-based biomass is huge source of agriculture waste that has been re-utilized to produce efficient activated carbon compared to other expensive and non-readily available sources of activated carbon such as peats (Mohamad Nor et al, 2013). The activated carbon used in this research is obtained from artichoke biomass via chemical activation and represented schematically in (Figure 1.5).

1.4 Research Objectives

- To prepare efficient and low cost activated charcoal from Artichoke biomass
- To investigate the Nickel cation removal potential of the prepared adsorbent.
- To examine the influence of different parameters such as contact time, pH, temperature, dosage and initial nickel concentration on the adsorption process.
- To study the kinetic and thermodynamic properties of the prepared adsorbent.

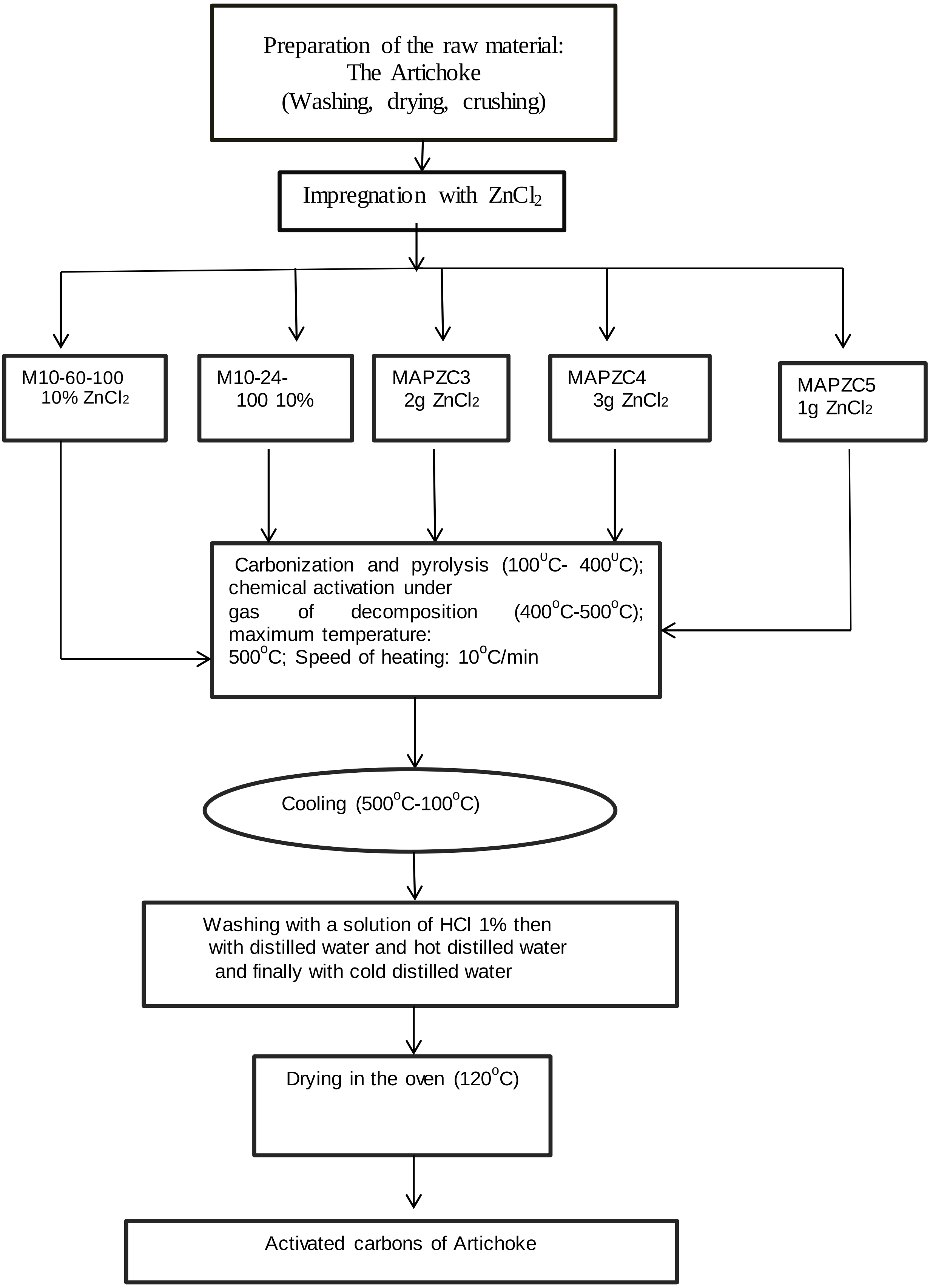


Figure 1.5: General scheme of the preparation of Activated Carbon from Artichoke (American chemical science journal, 2(4): 100-130, 2012)

Chapter 2

LITERATURE REVIEW

Heavy metal pollution is one of the main problems confronting the humankind. These contaminations emanate both from agricultural and industrial activities (Fong Lo et al, 2012). Consequently, removal of these toxic pollutants from wastewater and industrial waste has become a priority to environmentalists and technologist worldwide (Kurniawan et al, 2011). The occurrence of heavy metal ions such as copper, mercury and nickel etc within the environments at level above regulated amounts are regarded as risk to aquatic and human lives due to its kidney, gastrointestinal and nervous operation disruptions (Singh et al, 2012).

Currently, different techniques have been used such as ion exchange, precipitation, membrane separation, reverse osmosis, adsorption and evaporation to remove or recover heavy metals from aqueous media (Sekirifa et al, 2013).

Most of these methods have shown low capacity, cumbersome, expensive and have been found to be ineffective when applied to wastewater containing very low concentration of pollutants (Olorundare et al, 2012). Hence, research is focused on finding economical easily available and efficient adsorbent. The use of activated carbon lately has been popular among researchers because of its performance, economical nature and re-usability. Activated carbon has been investigated and proved to be efficient in treating polluted streams containing low concentration of heavy metals (Fong Lo et al, 2012).

The efficiency of activated carbon can be optimized by altering various production factors such as activation temperature, and the chemical used for activation. This surface improvement will further enhance the adsorption capability of the adsorbent and makes it more versatile in varying adsorption environments. For instance, mercury ions possess high solubility in aqueous solution and therefore unmodified activated carbon has limited capacity to adsorb mercury. It can, however be modified with suitable activating agent so that its capability and potential is enhanced. Thus, various modifications have been made to improve the efficiency of activated charcoal so as to combine or treat metal ions like mercury via complex or chelates formations or precipitations (Mohammad-Khah & Ansari, 2009).

2.1 Some Applications Of Activated Carbon

Activated carbon (AC) has many applications one of which is as an adsorbent for purification of water, air and many chemical products, table(2.1). AC has been an effective adsorbent for dye removal. Adsorption capacity of certain carbon is known to be a function of porous structure, chemical nature of the surface and pH of the solutions. Surface functional croup play an important role in deciding adsorption capacity and removal of the adsorbents. (Satapathy et al, 2006).

Table 2.1: Application of Activated Carbon

STATS	PURPOSE	APPLICATIONS	EXAMPLES
Gas phase	Recovery	Gasoline vapor recovery	Gasoline fuel recovery
		Solvent recovery	Cyclohexanone, Trichloroethane
	Odor removal	Odor removal in the room and Hospital	Cigar, toilet and pet odors, anesthetic gas removal
		Ozone removal	Laser printers. Carbon copiers,
	Gas separation and Harmful gas	Closed environment	CO_2 removal and Nitrogen gas separation
Liquid phase	Water treatment	Factory effluents, drinking tap water	Chlorine, Arsenate, lead removal
	Decolorization of industrial chemicals	Industrial use	pharmaceutical use and sugar refinery
	Medical applications	Medical and nursing	Kidney machine and nursing Supplies
	Mineral recovery	Gold recovery	Gold recovery

Chapter 3

EXPERIMENTAL

3.1 Reagents And Materials

Analytical grades reagents were used throughout in this work and tabulated accordingly in (table 3.1).

Table 3.1: The reagents and materials used

No	Chemicals	Company
1	Nickel sulphate hepta hydrate	Aldrich – Germany
2	Hydrochloric Acid	Riedal – deHean / Germany
3	Zinc Chloride	Sigma Aldrich – Germany
4	Pre-treated artichoke biomass	

3.2 Preparation Of Activated Carbon From Artichoke.

A pre-washed and dried of artichoke stem was used as a starting material (see figure 3.1 a) . The dried biomass was converted to charcoal in furnace at 500°C in the absence of oxygen over period of 2hr. After the sample cooled at room temperature, it was chemically treated in order achieve chemical activation. Briefly, 250 ml of $ZnCl_2$ (60% W/V) was added to 5.0 g of charcoal in beaker and heated at 60 °C under constant stirring for 24 h. The treated charcoal was separated from the solution, cooled and washed with de-ionized water, followed by soaking in a 1% hydrochloric acid solution for 2 h in order to remove the residual zinc from the pores of the carbons. The materials were washed again with hot distilled water and finally cold distilled water. Then, the material was heated at (80 °C) for 10 h to remove the moisture content. The obtained artichoke-based activated carbon (AAC) thus obtained was stored in desiccator for later use.

(a) Artichoke stem (b) Activated Carbon

Figure 3.1: Images of the Artichoke stem and the activated carbon obtained from this stem

3.3 FT-IR Analysis

The FTIR spectrophotometer (65-Perkin Elmer) was used to obtain the IR spectrum so as to determine the functional groups present on the materials used.

3.4 Adsorbate (Stock Solution) Preparation

A standard 2000 ppm Ni^{2+} stock solution of nickel was prepared by dissolving 2.38 g of nickel sulphate hexahydrate ($NiSO_4$. $6H_2O$) in 250 ml of distilled water and the subsequent working solutions were obtained by dilution from this stock solution.

3.5 Batch Adsorption Studies

Various adsorption variables such as solution temperature, pH, initial nickel concentration, and AAC dose are investigated as explained below and the nickel concentration in the supernatant was determined with a PG Instruments (T80+ model UV/VIS spectrophotometer), at 392.00 nm.

Figure 3.2: Nickel^{2+} solution before addition of adsorbent (left test tube), with adsorbent in the (middle), and after the removal of the adsorbent (right). Images clearly shows the almost complete disappearance of the blue/greenish hue due to Ni^{2+} cation.

3.5.1 Effect Of Initial Concentration

The influence of different initial nickel concentration was tested using 200mg AAC immersed into 100 ml of three separate nickel solutions (10, 20, 50 ppm). All of the samples were agitated for 1 h and then 5 ml portion were withdrawn at pre-set times and their absorbance measured at 392.0 nm using the UV/VIS spectrophotometer**.**

3.5.2 Effect Of Adsorbent Dose

The influence of AAC dosage was also tested using AAC dose rates (100, 200, 300, 400 and 500 mg) in 100 ml of 10, 20 and 50 ppm Nickel solution, then 5 ml portion were removed at one hour intervals and their absorbance at 392.0 nm were determined by UV/VIS spectrometer.

3.5.3 Effect Of The Initial Solution pH

The influence of pH on the nickel removal by AAC was examined. Buffer solutions in the pH ranging 2 to 10 were prepared. Then 50 ml of each buffer solution was mixed with 50 ml of nickel solution (50ppm) in the presence of 200 mg of activated carbon, agitated on shaker for 90 min, 5ml withdrawn and the concentration measured using the UV-VIS spectrometer.

3.5.4 Effect Of The Temperature

The effect of temperature on the adsorption behavior was investigated by taking 100 ml of (20 ppm, 50 ppm) Nickel solution each containing 200 mg activated carbon in conical flask. Each flask was then placed in a pre-set water bath at temperature of 10, 20, 30, 40 and 50 ^{0}C for 90 min. From each solution, 5 ml portion were removed periodically, and Ni^{2+} concentration measured by determining absorbance with the UV/VIS spectrometer.

Chapter 4

RESULTS AND DISCUSSION

4.1 Characterization Of AAC

The FTIR analyzer was used in order to detect the functional groups available on the surface of ACC and those responsible for the adsorption of Ni^{2+}. FTIR spectra for (a) artichoke biomass, (b) ACC (c) Ni (II) loaded ACC, are presented in (Figure 4.1).

The spectrum of raw artichoke has a broad band at 3341.8 cm^{-1} due to stretching vibration of the hydrogen bonded hydroxyl groups (-OH from carboxyls, phenols or alcohols) stretching vibration. The band at the 2923.5 cm^{-1} is due to aliphatic C-H stretching either in aromatic methoxyl group or in methyl and methylene side chains).

The adsorption band in the range 1595.6–1426.7 cm^{-1} correspond to C-C stretch, the peak at the 1242.5 cm^{-1} indicate C-O group stretch, the long band at 1027.6 cm^{-1} refers to C-N group. The weak band at the 1733.8 cm^{-1} refer to the H-C=O stretching vibration of olefins. The peak of around 1385 cm^{-1} is due to –C-H bending. The adsorption band in the range (1100-1200 cm^{-1}) is related to stretching vibration of C-O group in alcohol, ether, acid and/or ester.

For the spectrum of ACC, a reduction in hydroxyl group and –C-H group was observed and increased stretching at 1568.7 cm^{-1} which refers to C=C group was also noticed. The two peaks at 1426.7cm^{-1} and 1242.5cm^{-1} were reduced. Additionally, the spectrum of ACC show new three small peak at the 877.92 cm^{-1}, 816.5 cm^{-1} (C-H), 751.27 cm^{-1} which may be due to zinc chloride modification and due to C-CL stretch in alkyl halide. The spectrum of Ni^{2+} loaded-ACC in comparison with ACC, show decrease in the bands at 1576.4 cm^{-1} and 1158 cm^{-1}, and a new peak appeared at 1257.9cm^{-1} (C-O), this confirms the adsorption of nickel onto ACC.

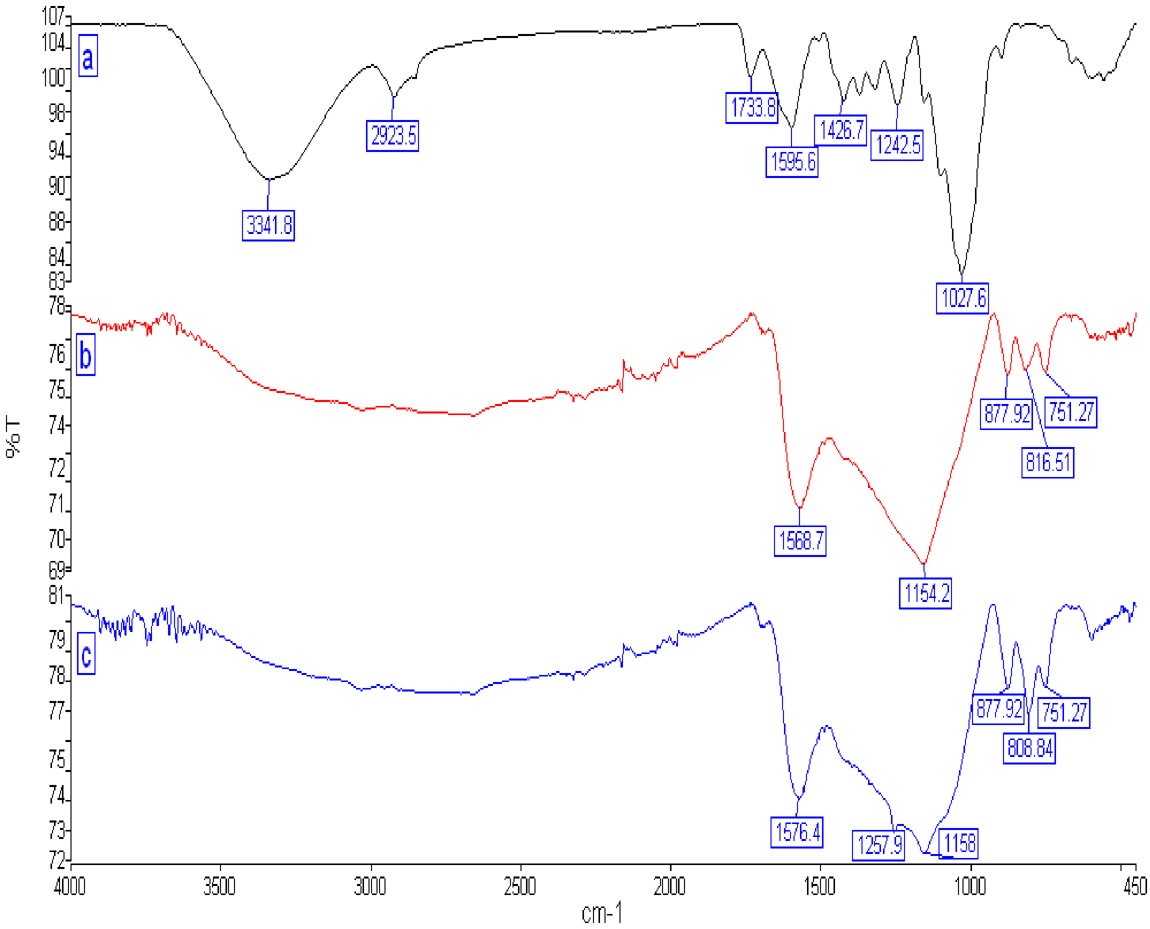


Figure 4.1: FT-IR analysis of (a) raw material (Artichoke), (b) AAC (c) nickel loaded-ACC

4.2 Adsorption Calibration

Five different nickel ion concentrations (2000, 1000, 500, 250, 125 ppm) were prepared by dilution from the 2000 ppm Ni^{2+} stock solution and their absorbance at 392.0 nm were measured using the UV-VIS spectrophotometer in order to obtain a calibration curve. Absorbance at 392.0 nm versus nickel concentration (ppm) was plotted and is presented in (Figure 4.2). The equilibrium concentration determined from the calibration curve was obtained according to the equation:

$$Y = ax + b \qquad (1)$$

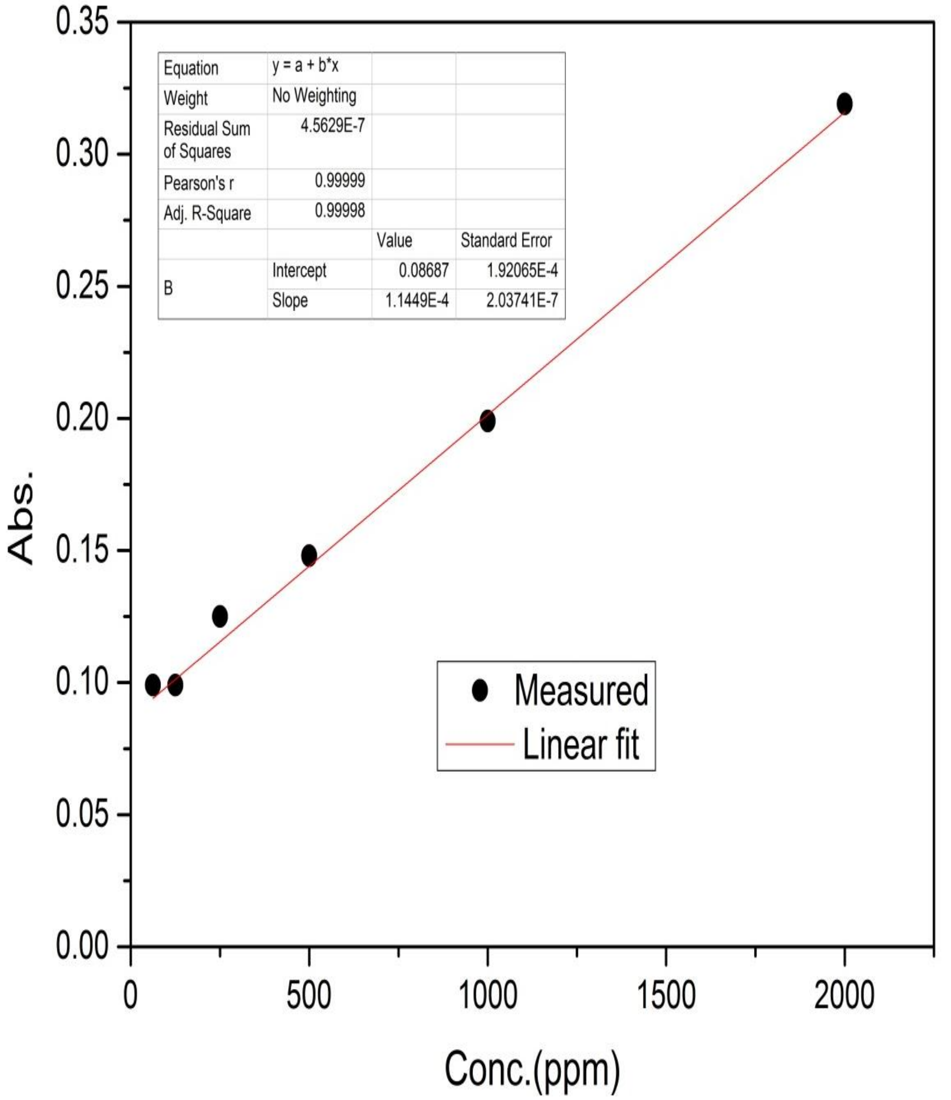


Figure 4.2: Calibration curve of nickel Ni^{2+} solution between 125 to 2000 ppm.

4.3 Batch Adsorption Experiments

The adsorption capacity and removal percent of Ni (II) from aqueous solution was investigated using the following equations respectively:

$$q_e = (C_i - C_e) \frac{V}{W} \qquad (2)$$

Where **q_e**: represent the amount of nickel adsorbed (mg/g)

C_i: initial nickel concentration in (ppm)

C_e: equilibrium nickel concentration (ppm)

W: mass of AAC in (g).

V: solution volume in (L)

$$R\% = \left(\frac{C_i - C_e}{C_i}\right) 100 \qquad (3)$$

Where: **R%=** percentage removal

C_i: initial nickel concentration, (ppm)

Ce: equilibrium nickel concentration, (ppm)

4.3.1 Effects Of Adsorption Parameters On Nickel Ion(II) Removal

4.3.1.1 Contact Time Study

The influence of contact time on nickel removal by ACC is represented in (Figure 4.3). The sorption was very fast from the first 30 min and the removal percent increased from 65, 58 and 47% to 93, 88 and 83% for nickel concentration of 10, 20, 50 mg/L respectively. A slow and steady increment was observed after 30min until the adsorption appeared to level off and attain equilibrium at around 40 min in all the cases.

No substantial increase was observed after equilibrium was achieved. The rapid adsorption at the early stage may be ascribed to enhanced concentration gradient between the nickel ions in solution and Ni^{2+} in AAC and availability of vacant sites at the early stage. The reduction in adsorption rate after 40 min could possibly be due to slower mass transfer of the Nickel ions from the bulk phase to the external layer of AAC and reduction in the free sites.

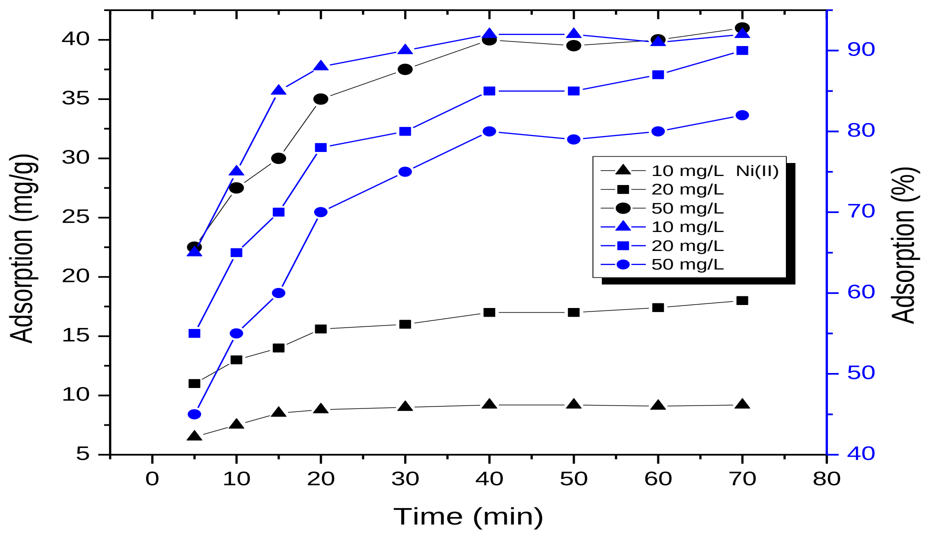


Figure 4.3: Effect of contact time on adsorption of Ni(II) (Temperature:30 ^{0}C, pH: 6.0, ACC dose: 2g/L)

4.3.1.2 Effect Of AAC Dosage

The influence of AAC dosage on the Ni (II) removal percent is presented in (Figure 4.4). As shown, removal percent increased sharply at the early stage of the adsorption with increasing AAC dose until equilibrium stage was observed with AAC dose of around 2.5-3 g/L. This phenomenon is due to increasing surface areas and surface functionalities as the AAC dosage is increased and thus Ni^{2+} adsorption increased until all available sites are completely occupied. The removal percent for Ni (II) increased from 83.9 to 95.9 and 89.1 to 97.8% at 10 and 50 mg/L initial nickel concentration respectively. Noticeable removal percent was not observed after ACC dose of 3g/L, indicating that the equilibrium has been set as all the free adsorption sites have been utilized.

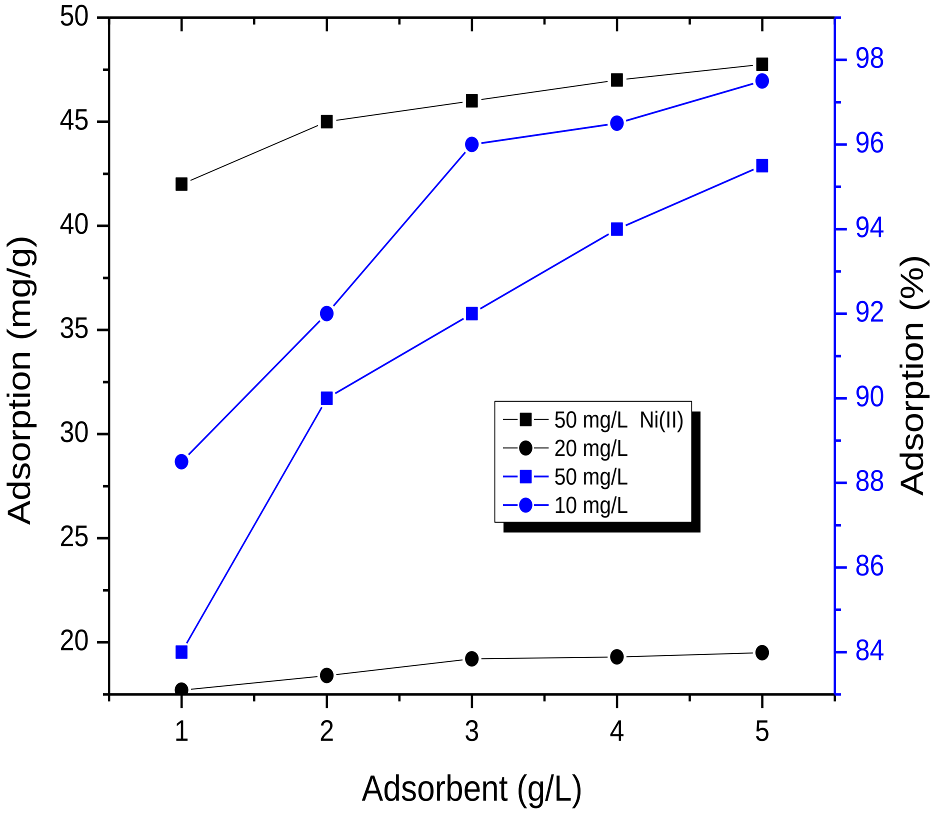


Figure 4.4: Effect of adsorbent doses on adsorption of Ni(II) (Temperature:30 ^{0}C, pH: 6.0)

4.3.1.3 Effect Of Solution pH On Nickel (II) Adsorption

The pH of the medium is a prominent factor influencing the adsorption process. Here, Ni^{2+} removal was examined in a range of pH (2.0-10.) for 50 mg/L initial nickel concentration for a fixed ACC dosage (2 g/L), (Figure 4.5) represents the obtained results. It is evident as shown in the figure that Ni(II) removal percent increased with increasing in pH from 2.0 to 6.0, no noticeable adsorption occurred after pH 6.0. This increment may be ascribed to electrostatic attraction between the negative surfaces of the adsorbent and the cationic adsorbate.

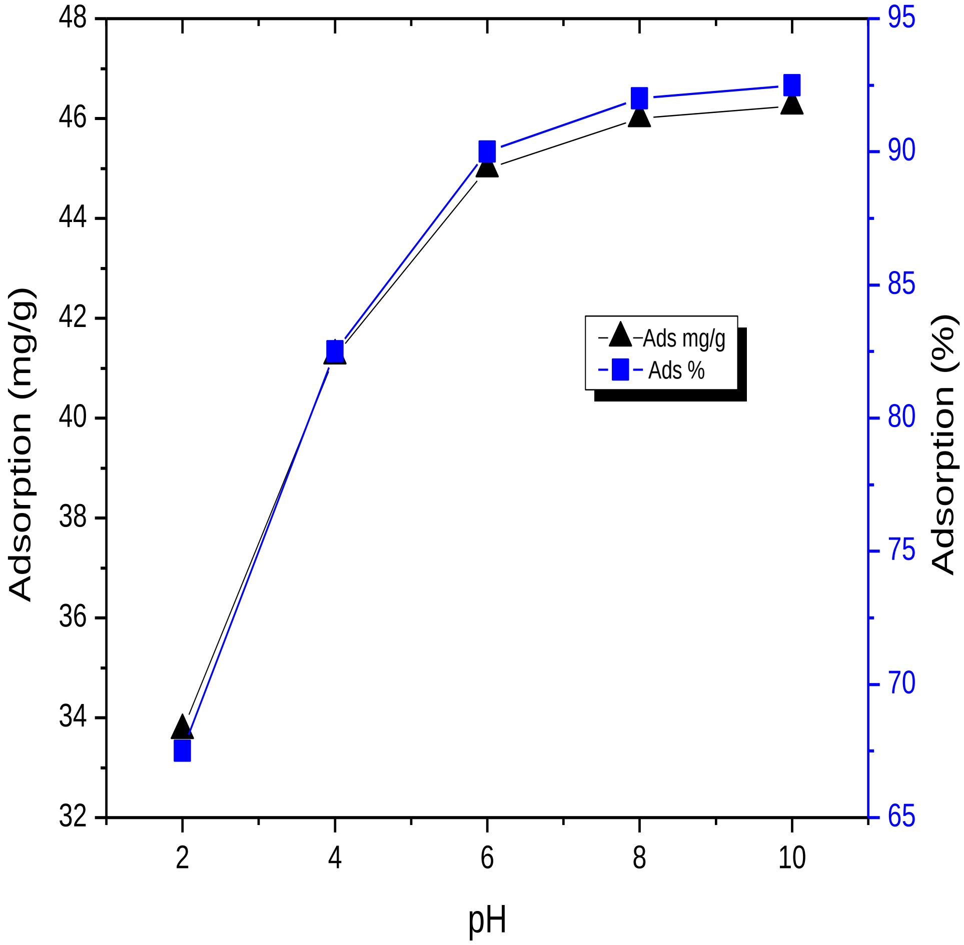


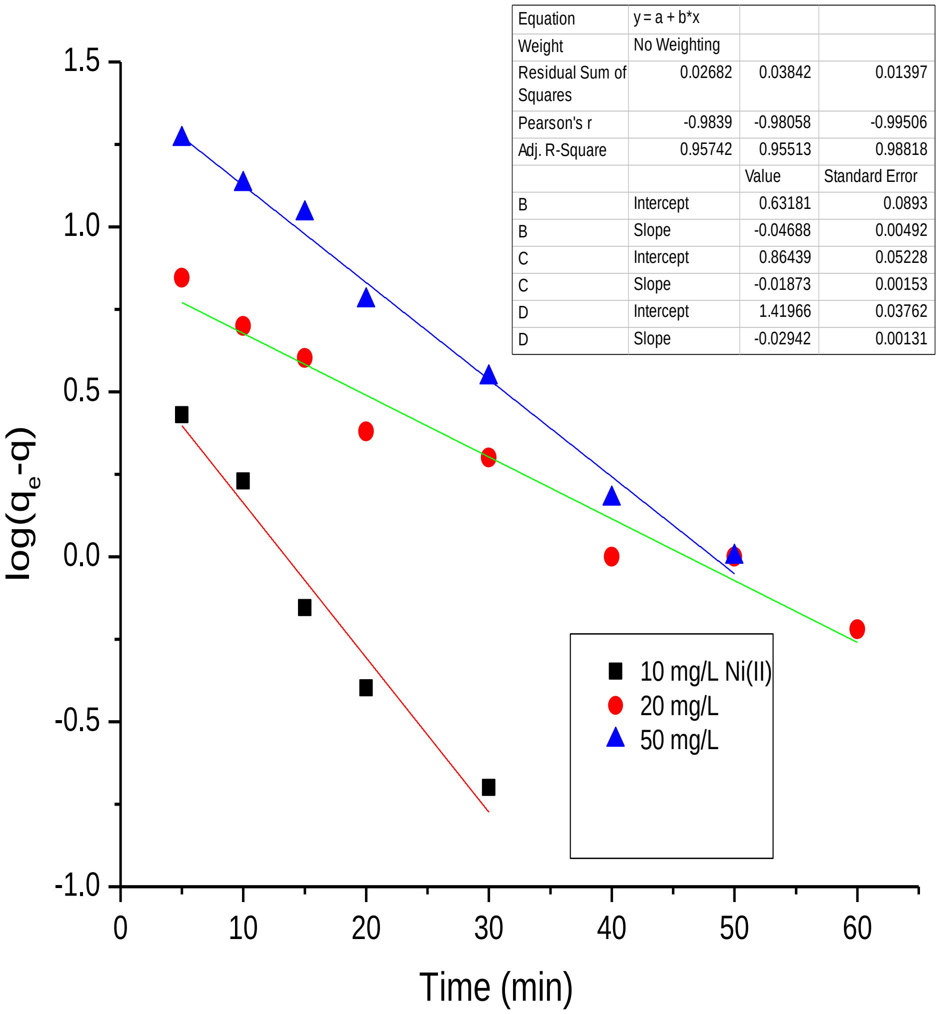
Figure 4.5. Effect of pH on adsorption of Ni(II) (Temperature:30 ^{0}C, pH: 6.0, ACC dose: 2g/l)

4.4 Adsorption Kinetics Models

Kinetic models such as the pseudo-first and pseudo-second were applied to investigate the kinetic mechanism of nickel adsorption onto AAC using the equations below. The integral form of pseudo-first-order is represented as;

$$\log(q_e - q) = \log q_e - \frac{K_{ad}}{2.303}t \qquad (4)$$

Where q, q_e represent the amount of Ni(II) removed at time t (min) and equilibrium (mg/g) respectively, and K_{ad}(min^{-1}) is rate constant of the model.



Equation	y = a + b*x		
Weight	No Weighting		
Residual Sum of Squares	0.02682	0.03842	0.01397
Pearson's r	-0.9839	-0.98058	-0.99506
Adj. R-Square	0.95742	0.95513	0.98818
		Value	Standard Error
B	Intercept	0.63181	0.0893
B	Slope	-0.04688	0.00492
C	Intercept	0.86439	0.05228
C	Slope	-0.01873	0.00153
D	Intercept	1.41966	0.03762
D	Slope	-0.02942	0.00131

Figure 4.6: Pseudo-first-order model for Ni(II) removal.

The integral form of pseudo-second-order equation is given as;

$$\frac{t}{q} = \frac{1}{k2q_e^2} + \frac{1}{q_e}\ t \qquad (5)$$

Where K_2 is the model rate constant, the experimental data were fitted into the two kinetic and obtained plots utilized to establish the various kinetic parameters. The suitability of the model was established based on the closeness of the correlation coefficient (R^2) to unity.

The linear plots obtained showed the applicability of both kinetic equations. But the higher correlation coefficient ($R^2 \approx 1.0$) is an indication of the consistency of the experimental data to the pseudo-second-order equation compared with pseudo-first-order equation ($R^2 = 0.955$–0.988). This can help us to conclude that the adsorption process may be chemisorption in nature

Table 4.1: Kinetic parameters at different Concentration

Kinetic models							
Pseudo-first-order					**Pseudo-second-order**		
Conc mg/L	**qe exp. (mg/g)**	**K_1 (1/min)**	**q_e mg/g**	**R^2**	**K_2 (g/mg min)**	**q_e mg/g**	**R^2**
50	41	0.068	26.3	0.988	248.60	44.21	0.999
20	18	0.043	7.31	0.955	85.70	18.9	0.998
10	9.2	0.11	4.3	0.957	18.60	9.5	0.998

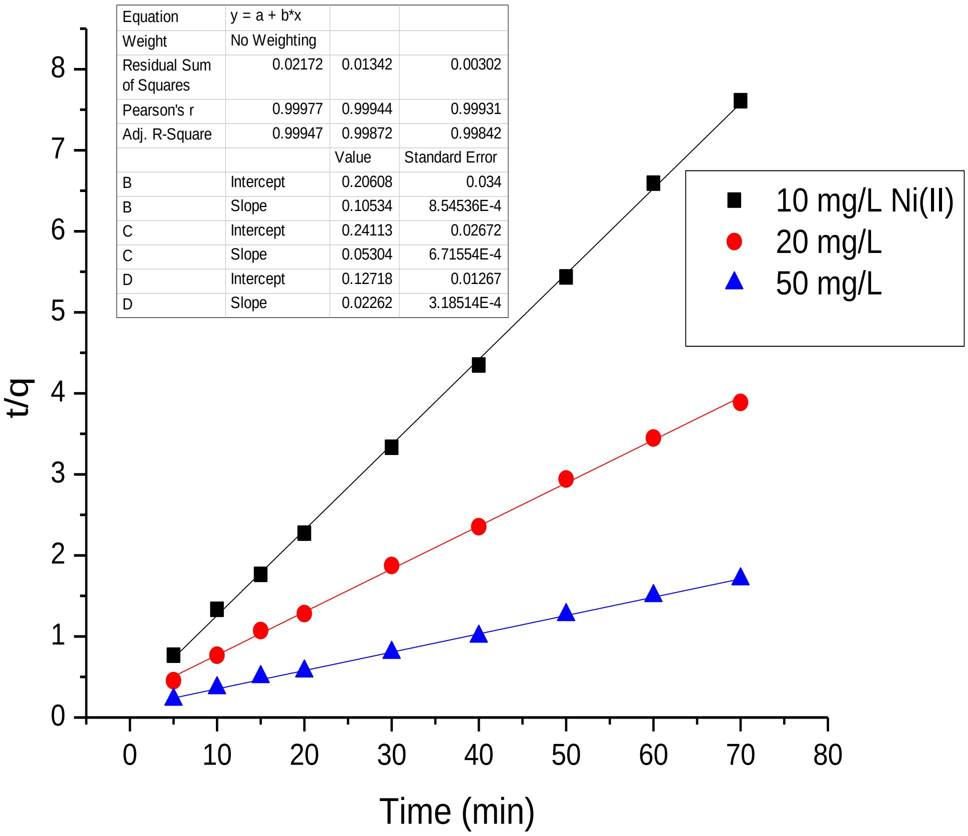


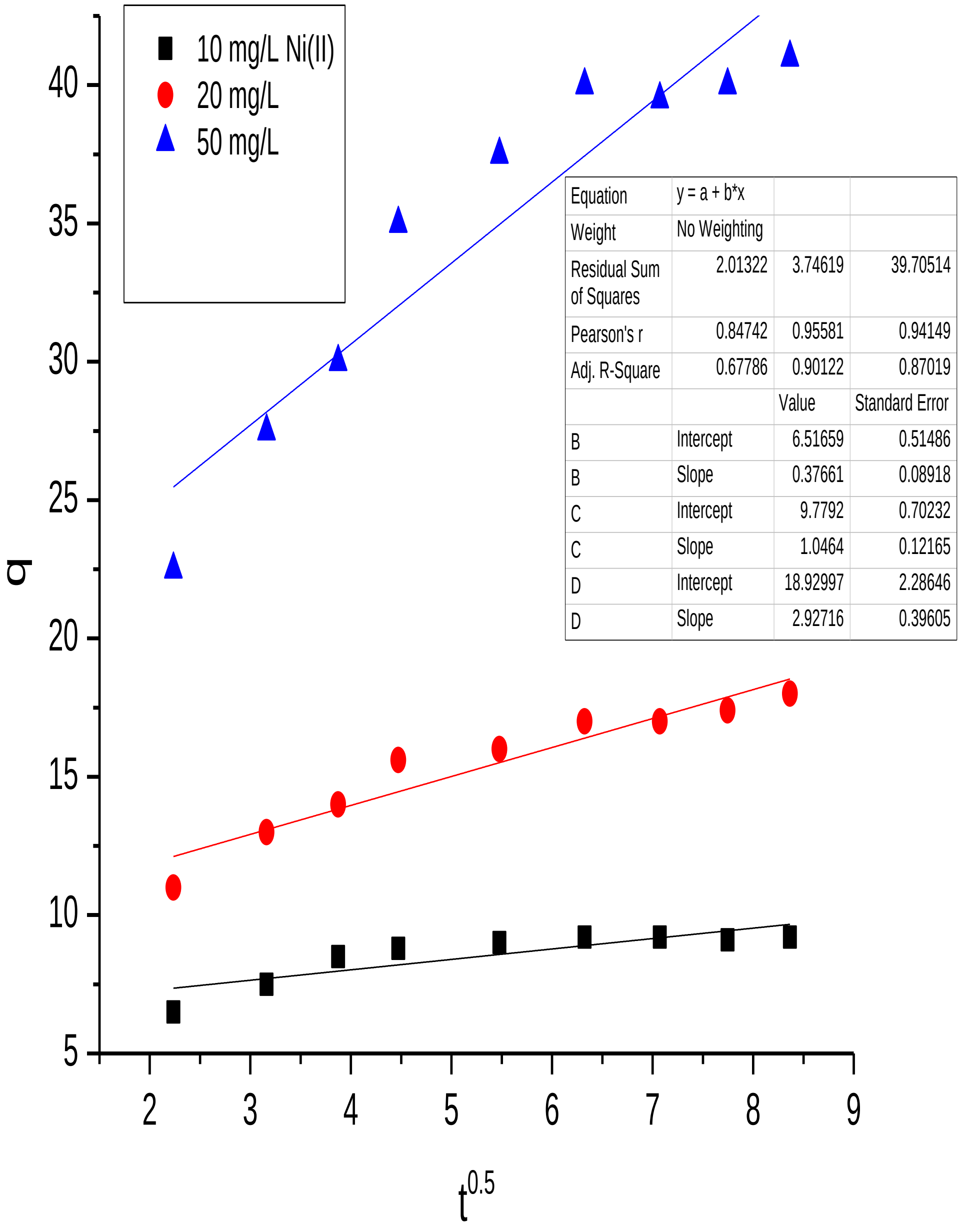
Figure 4.7: Pseudo-second-order model for Ni(II) removal.

4.5 Intraparticle Diffusion Model

In order to elucidate further the mechanism of Ni(II) removal by AAC, intra-particle diffusion model was also utilized using the following equation :

$$q = k_{id}t^{1/2} \qquad (6)$$

where q is the amount of Ni (II) adsorbed at time t. The values of the intraparticle constant (k_{id} = 0.37661, 1.0464 and 2.9271 mg/g min^{-1}) were obtained at varying nickel concentration 10, 20, 50 mg/l respectively from the plot (q versus $t^{1/2}$) presented in Figure 4.8). Multi-linear curves were obtained and do not pass through the origin. As seen, the earlier adsorption stages were due to external film transport while the later portions (linear portion of the curve) were ascribed to the intraparticle transport of nickel ions within the AAC pores. The lower R^2 value(0.67786) of the intra-particle diffusion model is an indication that the model was not the only rate controlling mechanism.



Equation	y = a + b*x		
Weight	No Weighting		
Residual Sum of Squares	2.01322	3.74619	39.70514
Pearson's r	0.84742	0.95581	0.94149
Adj. R-Square	0.67786	0.90122	0.87019
		Value	Standard Error
B	Intercept	6.51659	0.51486
B	Slope	0.37661	0.08918
C	Intercept	9.7792	0.70232
C	Slope	1.0464	0.12165
D	Intercept	18.92997	2.28646
D	Slope	2.92716	0.39605

Figure 4.8: Intraparticle diffusion plot for the adsorption of Ni(II)

4.6 Adsorption Isotherms

Two widely applied isotherm equations were applied to fit the experimental data obtained in this work. Freundlich and Langmuir equations were used and can be represented as follows:

$$\text{Ln } q_e = \ln k + \frac{1}{n} \ln c_e \qquad (7)$$

$$\frac{1}{q_e} = \frac{1}{q_m K_l C_e} + \frac{1}{q_m} \qquad (8)$$

The Ni (II) sorption by ACC obeyed the Langmuir isotherm as presented in (Table 4.2). The values of K_L (0.618 L/mg)and q_m (49.02 mg/g)were obtained from the model plot and tabulated below. The Freundlich constants k and 1/n were calculated to be 42.220 and 0.0778, respectively, indicating favorable adsorption by AAC.

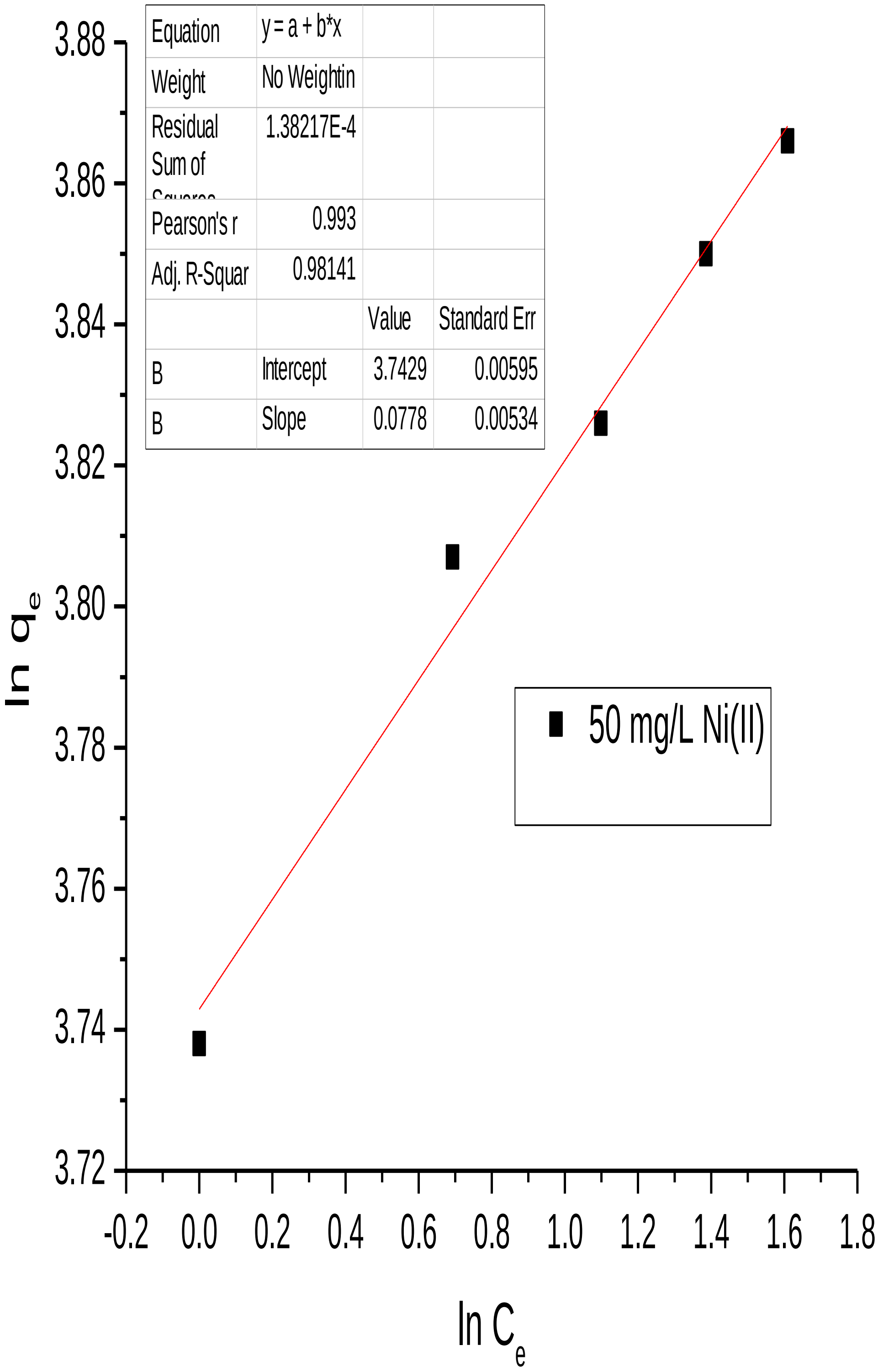
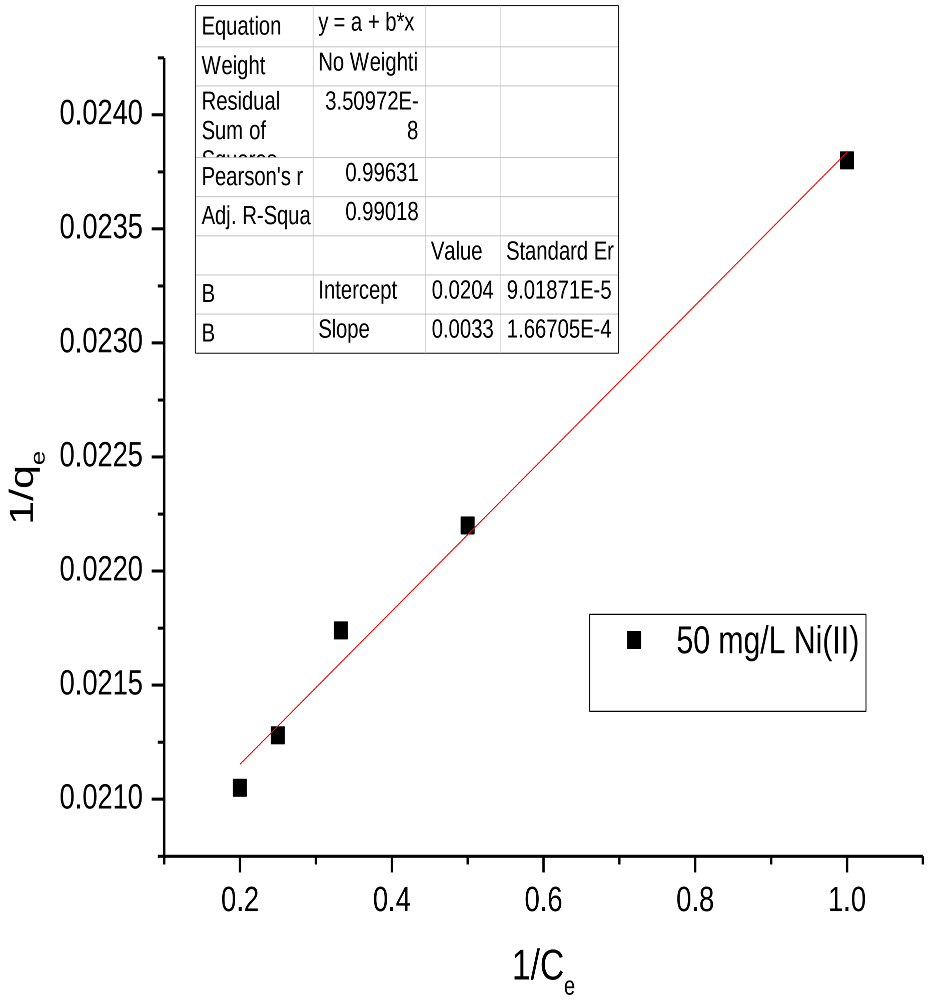


Figure 4.9: Freundlich adsorption isotherm



Equation	y = a + b*x		
Weight	No Weighti		
Residual Sum of	3.50972E-8		
Pearson's r	0.99631		
Adj. R-Squa	0.99018		
		Value	Standard Er
B	Intercept	0.0204	9.01871E-5
B	Slope	0.0033	1.66705E-4

Figure 4.10: Langmuir adsorption isotherm

Table 4.2: Adsorption isotherm parameters at pH 6.0

Freundlich	**Langmuir**
k_f = 42.22 mg/g	q_m = 49.02 mg/g
1/n = 0.0778	K_L = 0.618 L/mg
n = 12.85	R^2 =0.99018
R^2 =0.98141	

4.7. Effect Of Temperature On Nickel Adsorption

Adsorption studies were conducted at range of temperature (280-330 K) and shown in (Figure 4.11). As shown, the percentage removal increase sharply at the initial stage with increasing temperature until 300K where nickel removal percent attained equilibrium. Increasing adsorption capacity with increasing temperature is an indication of endothermic system. Due to the porous nature of AAC, diffusion of nickel through the AAC pores is highly possible as suggested by the intra-particle diffusion model, this support the endothermic nature of the adsorption process. Also, increasing temperature may generate more freely available sites via the breakage of internal bonds (Mohammad-Khah & Ansari, 2009).

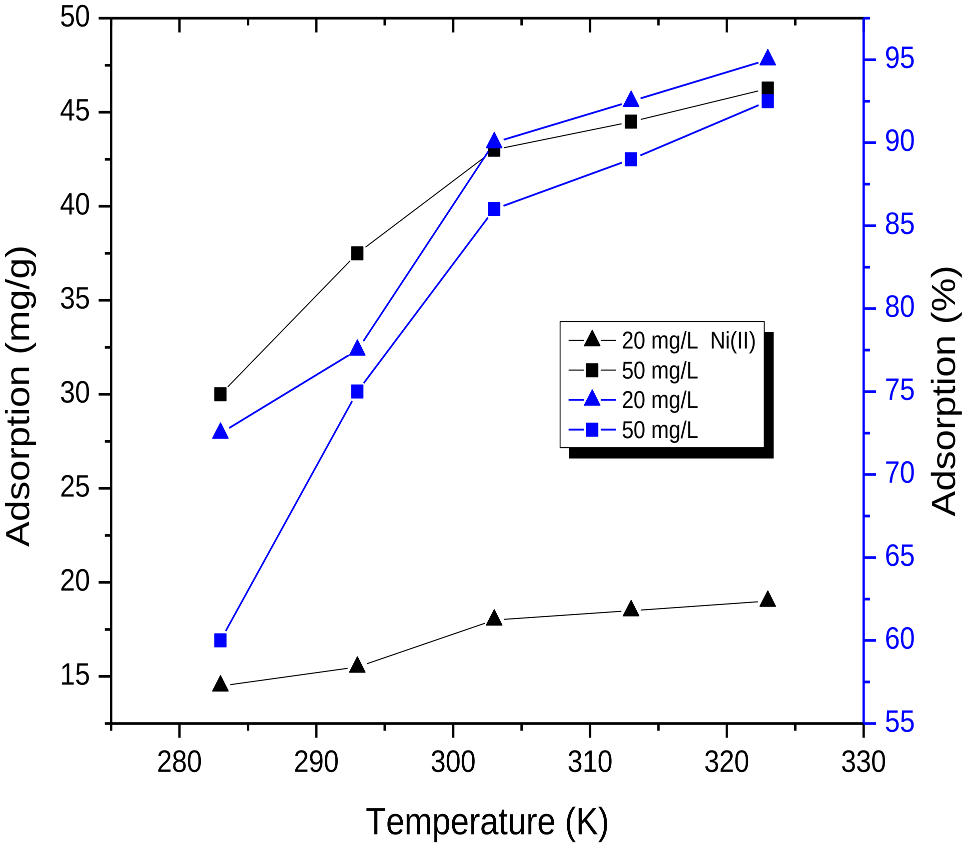


Figure 4.11: Effect of temperature as a function of initial concentration

4.7.1 Thermodynamic Parameters

Thermodynamic properties of AAC were investigated and the following parameters (ΔG^0), (ΔH^0) and (ΔS^0) were determined using the equations below so as to classify the adsorption mechanism:

$$k_c = \frac{C_{Ae}}{C_e} \qquad (9)$$

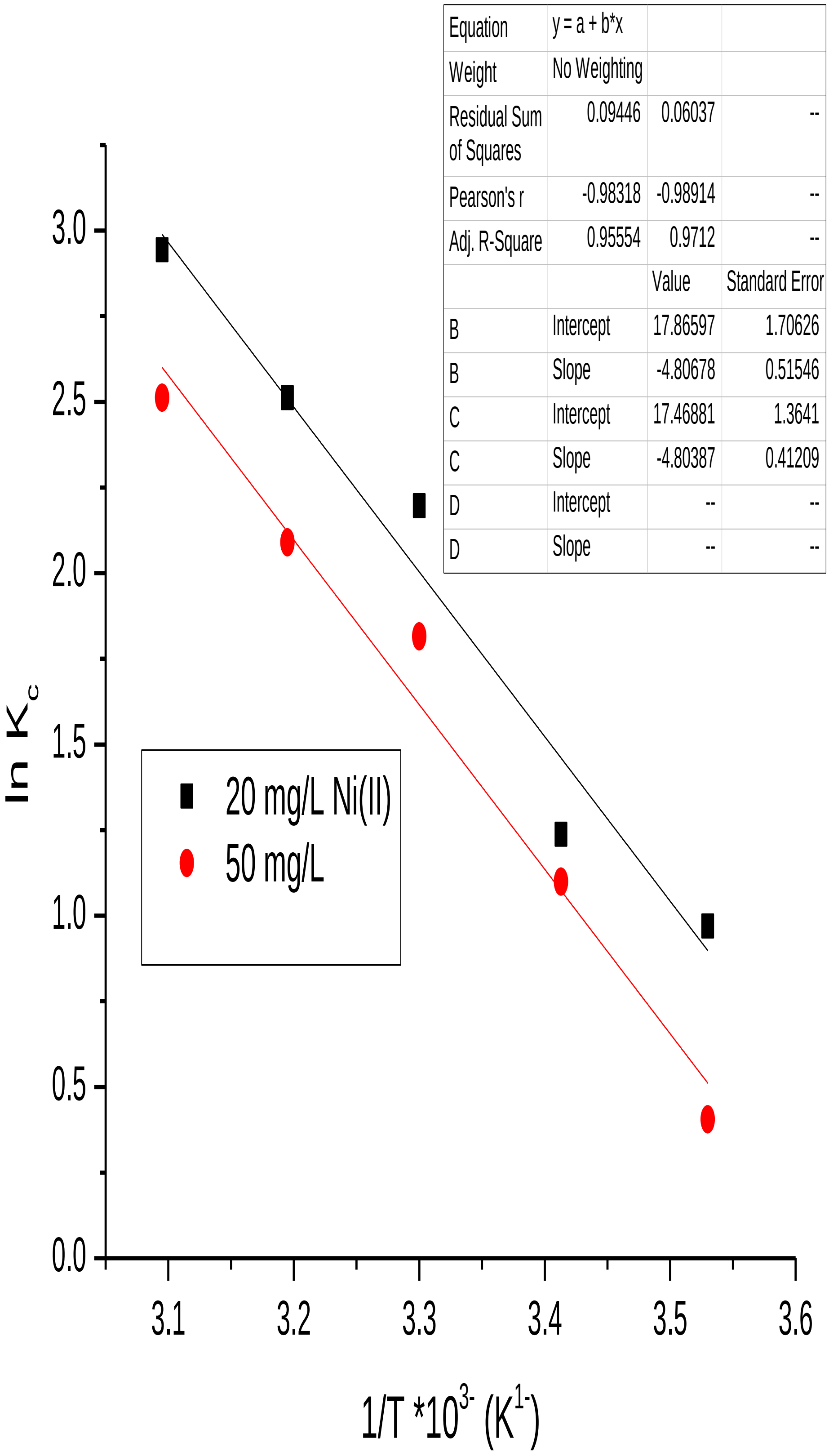
$$\Delta G_0 = - RT \ln k_c \qquad (10)$$

$$\ln k_c = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R} \qquad (11)$$

Where k_c C_e and C_{Ae} (mg/L) are equilibrium constant and equilibrium concentrations for Ni^{2+} in the solution and on the ACC surface respectively. The values of thermodynamic parameters are presented in Table (4.3). The ΔG^0 values (negatives) are an indication of spontaneous system and increasing ΔG^0 negative values with increase solution temperature is an indication of favorable adsorption at higher temperature which is consistent with the isotherm analyses. The negative and positive values of ΔS^0 and ΔH^0 represented reduced randomness of nickel ions at the AAC surface and endothermic process respectively.

Table 4.3: Thermodynamic parameters for the adsorption of Ni(II).

C_0 (mg/L)	**ΔH (kj/mol)**	**ΔS (kj/mol.K)**	**ΔG (kj/mol)**				
			10 ^{0}C	**20 ^{0}C**	**30 ^{0}C**	**40 ^{0}C**	**50 ^{0}C**
20 mg/L	39.964	0.1485	-2.281	-3.013	-5.535	-6.537	-7.906
50 mg/L	39.939	0.1452	-0.954	-2.723	-4.568	-5.439	-6.746



Equation	y = a + b*x		
Weight	No Weighting		
Residual Sum of Squares	0.09446	0.06037	--
Pearson's r	-0.98318	-0.98914	--
Adj. R-Square	0.95554	0.9712	--
		Value	Standard Error
B	Intercept	17.86597	1.70626
B	Slope	-4.80678	0.51546
C	Intercept	17.46881	1.3641
C	Slope	-4.80387	0.41209
D	Intercept	--	--
D	Slope	--	--

Figure 4.12: A plot of ln k_c against 1/T for Ni(II) adsorption for different initial concentration

Chapter 5

CONCLUSION

This study demonstrated that efficient adsorbent can be prepared from the chemical activation of artichoke biomass using zinc chloride as activation agent. The adsorption potential of the as-prepared adsorbent was investigated towards Ni (II) removal from simulated nickel containing water. The following conclusions were reached;

- FT-IR analysis confirmed the calcination and activation of the prepared adsorbent compared with the raw biomass.
- The experimental data are consistent with Langmuir adsorption isotherm model, and the adsorption kinetic of Ni^{2+} adsorbing on to $ZnCl_2$ activated charcoal obeys the pseudo-second-order model.
- The adsorption process was found to be feasible, spontaneous and endothermic in nature as described by the thermodynamic properties of the process.
- The manufactured $ZnCl_2$ activated charcoal from Artichoke biomass has been shown to be effective in adsorbing Ni^{2+} ions from very dilute aqueous solution and therefore needs to be investigated further to enhance and optimize adsorption conditions.

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