Removal of Ni (II) From Aqueous Water Using A Mixture (50: 50) of Bentonite and China Clay As An Adsorbent

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Abstract: ***Waste water contains heavy metals as toxic pollutants; Nickel is one of them which need to dispose carefully in the environment. A potential adsorption of nickel from various aqueous solutions was performed. Parameters such as pH, interaction of different cations like K(I), Na(I), Mg(II), Ca(II), contact speed RPM; contact time and the concentrations of adsorbent and adsorbate were studied to optimize the conditions to be utilized on a commercial scale for the decontamination of effluents using a batch adsorption technique. Adsorption parameters were determined using Langmuir isotherm. The optimum pH for nickel removal was 6, the percentage of nickel removal at equilibrium increases with increasing the amount of wastes. The removal of Ni(II) ions attained 74-77 %., this means that Ni(II) can be effectively removed from aqueous solutions by wastes. The mechanisms for adsorption of Ni(II) ions from wastes involved complex formation of nickel with rubeanic acid which was estimated spectrophotometrically.***

Keywords: Absorption, Ni (II) ion, Bentonite clay, china clay, Spectrophotometer

1. Introduction

The industrial effluents rich in heavy metals cause contamination of soil and aquatic bodies have attracted intense interest. The higher concentration of inorganic nickel compound causes: "lungs cancer, myocardial infarction, headache," "dizziness, nausea and vomiting, chest pain, tightness of the chest, dry cough and shortness of breath, rapid respiration, cyanosis, extreme weakness". chronic bronchitis, emphysema, reduced vital capacity, urinary excretion of proteins suggesting tubular dysfunction in the kidneys in human[12] .Highest risk of mortality due to cancer of respiratory tract, chronic fatigue and muscle pain, mucosal irritation, asthma, (Nickel and nickel compounds, 1990), reversible renal effects [13], immune system damage are found among nickel mine workers involved in roasting, smelting, and electrolysis..Short-term exposure of nickel to animals are reported to cause: laboured breathing, pneumonia, degeneration of nasal airway surfaces and atrophy of the nasal smell receptor tissue, significant decreases in body weight, chronic active inflammation of the lungs, and death. (ALBERTA 2004)

However many metals in small amounts are necessary for the completion of biological cycles, but they can cause toxicity when their concentration is increased. The aquatic environment is adversely affected by the harmful effects of heavy metals because aquatic organisms are in close and prolonged contact with the soluble metals [1-3]. Heavy metals are readily absorbed by the animals and they cannot be degraded by the micro-organisms like organic molecules, so they must be removed.

Conventional methods for the removal of toxic heavy metals from industrial effluents includes chemical precipitation, filtration, electrochemical treatment, electro-dialysis is an electrically driven process involving the use of ion-selective membranes [4] ion exchange [5] coagulation [6], solvent extraction [7], electrolysis [8], membrane separation [8], absorption [9] and inclusion [10], solid formation [11] which were all distinguished by the type of association between metal and host mineral. These processes have many disadvantages such as incomplete removal, high energy and reagents coasts and disposal of toxic sludge. Adsorption as an alternative method, to be a highly effective, cheap and easy method among the physicochemical treatment processes [12].The present study of adsorption is to remove Ni (II) from aqueous solution using Bentonite clay as adsorbent and effect of different parameters, such as contact time of adsorbent and adsorbate, effect of pH change. Equilibrium modeling was carried out by Langmuir Adsorption isotherms. Nickel (II) was estimated spectrophotometrically.

2. Material and Methods

2.1. Selection of Adsorbent:

Adsorbent used for the study of adsorption of nickel (II) was a mixture of Bentonite Clay and China clay in equal proportions, selected after extensive experimental work. Both the clays were taken from the market.

2.2. General Methods Used for Batch Adsorption Studies

As a first step, in all experiments, a known weight of clay (0.4g) was put into the shaking flask. A known quantity of Nickel solution (12 cm^3) except otherwise mentioned was added to it. At room temperature its pH was adjusted (7.0) expect otherwise mentioned was added to it. The sample was equilibrated at room temperature by shaking for 30 minutes. Complete separation of two phases was achieved within 10 minutes of centrifugation as was confirmed by experiments varying the time of centrifugation.

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2.3. Preparation of Stock Solution

Weighed amount of Nickel (II) Chloride (2.0g) of analytical grade was dissolved in distilled water and made the volume up to 500 cm^3 in measuring flask. It was 1000 ppm solution. 100 ppm stock solution was prepared by dissolving 10 cm^3 of 1000 ppm solution in distilled water and made the volume up to 100 cm^3 in measuring flask. Further dilutions were made from the above mentioned 100 ppm stock solution.

2.4. Preparation of Standard Solutions

Standard solutions of 4-20 ppm of nickel (II) were prepared by taking 4-20 cm3 of 100 ppm solution in separate 100 cm^3 measuring flasks and made volume up to the mark with distilled water. Six test tubes were labeled, added 5 cm^3 of standard solution in each test tube, then added 1.0 cm^3 of rubeanic acid as complexing agent and 1.0 cm^3 of ammonium hydroxide to maintain pH almost 8-9,agitated well, allowed them to stand for 15 minutes, after 15 minutes orange to blue coloured complex was obtained. Then noted the absorbance of each solution by adjusting the wavelength of spectrophotometer at 540nm and plotted a calibration curve, after running reagent blank solution which contains 5 cm^3 of distilled water along with 1.0 cm^3 of rubeanic acid and1.0 $cm^3$of ammonium hydroxide.

2.5. Batch Adsorption Studies

All experiments were carried out at room temperature (25^0). Solutions were placed in glassware apparatus and gently agitated on an electric shaker. The effect of Contact time (2-90 minutes), pH(1-11), concentration of Ni (II) (2-20 ppm), concentration of clay (0.05 – 0.6 g), resolution speed (25-300 RPM) and Initial concentration of different cations (Na^+, K^+, Ca^{++}, Mg^{++}) (2-10 ppm solutions of each) were investigated by varying any one of the process parameters and keeping the other parameters constant.

Distribution Coefficient (K_d) and %age adsorption (P%) were calculated according to the following equations**[reference]**

$K_d = \frac{C_0 - C_e}{Ce} \times \frac{V}{M}$ cm^3/g	(1)
$P\% = \frac{100 \times K_d}{K_d + \frac{V}{M}}\%$	(2)

Whereas

C_0 = initial concentration of Ni(II) (ug)
C_e = concentration in supernatant after filtration (ug)
V = volume of solution added (cm^3)
M = weight of adsorbent (g)

The Langmuir isotherm is represented by the following equation:

$$\frac{C_e}{q_e} = \frac{1}{Q_o b} + \frac{C_e}{Q_o} \quad (3)$$

Where C_e is the equilibrium concentration (mg/L), q_e is the amount (µg) adsorbed at equilibrium time and Q_o and b are Langmuir constants related to the adsorption capacity and energy respectively. The model (3) was fitted by using regression analysis and significance is checked at 5% level of significance. The model adequacy is determined on the basis of coefficient of determinant (R^2).

3. Results and Discussion

The adsorption of Ni(II) in aqueous solutions was examined by optimizing various parameters such as contact time, shaking speed, pH and amount of adsorbent and adsorbate using spectrophotometric technique. The criterion for the optimization was the selection of parameters where maximum adsorption occurred. All the reported results are the average of at least triplicate measurements.

3.1. Effect of pH on Adsorption Rate

The removal of nickel from waste water is highly dependent on the pH level of the solution which affects the surface charge on the adsorbent and the degree of ionization. The adsorption behavior of nickel ions was studied in aqueous solutions of different pH values from 1 to 11. The figure 1.1 and figure 1.2 depicts the plots of pH versus percent adsorption of Ni (II) and pH versus distribution coefficient (K_d) respectively. It was observed that the maximum adsorption of nickel on clay mixture occurred at pH 6.0, which gradually decreased with an increase in pH. Our results are also in agreement with the results obtained previously for the adsorption of heavy metals. The decrease in adsorption of nickel noted at alkaline pH is probably due to the formation of hydroxide.

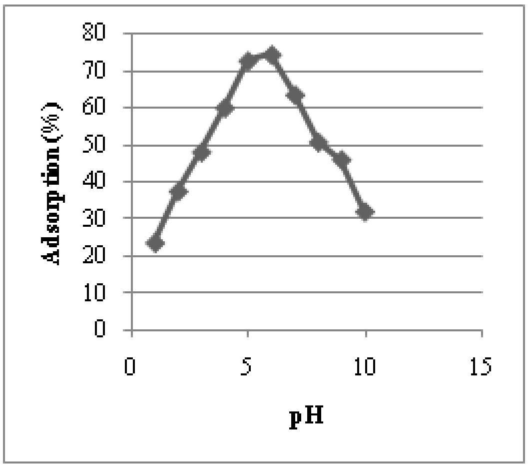

Figure 1.1: Graph between pH and% Adsorption

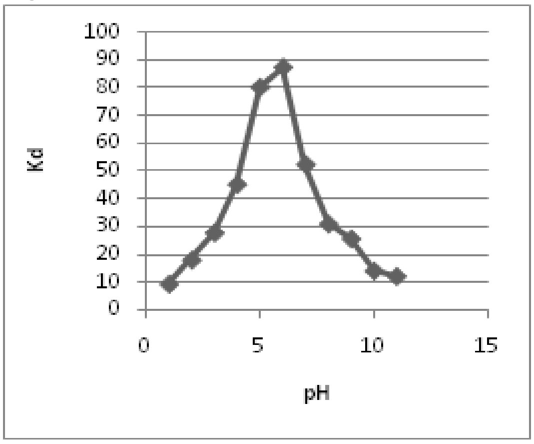

Figure 1.2: Graph between pH and K_d

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The adsorption data of pH were further analyzed with Langmuir isotherm model. The regression model is fitted taking dependent variable as equilibrium concentration of nickel and amount of nickel adsorbed as independent variable keeping amount of nickel, contact time, contact speed and amount of clay as fixed at 300 µg, 30 minutes, 200 RPM and 0.4 g. The variables are transformed by dividing C_e to q_e and C_e to Q_o respectively to form the linear relation and to fit a linear model. The regression model between equilibrium concentration of nickel and the amount of nickel adsorbed is significant ($p<0.05$) with F-statistic is 42.896.

Table 1

Model	Coefficients		t	Sig.
	B	Std. Error		
Constant	-1.613	.488	-3.305	.009
c	5.929	.905	6.549	.000

Table 1 shows the significance of individual variable. The value of regression coefficient is 5.929which is significant ($p<0.05$) with t-value 6.549. This value also indicates that there is positive relationship between the transformed independent and dependent variables. Furthermore, the constant term of the regression model is also significant.

On the basis of these results, the form of the fitted model is as,

$$\frac{C_e}{q_e} = -1.613 + 5.929\frac{C_e}{Q_0} \quad (4)$$

Table 2

Q_o	300
b	-2.0665
R^2	0.827
Adjusted R^2	0.807

The high value of R^2 and adjusted R^2 is high which indicates that the fitted model is good enough to explain the variation of dependent variable on the basis of independent variable.

3.2 Effect of Contact Time on Adsorption Rate

The variation of percent adsorption of nickel (II) with shaking time was studied using 12 cm^3 of 10 ppm nickel solution with 0.4 g of mixture of bentonite clay and china clay at 6.0 pH with varying contact time from 2 to 90 minutes. The figure 1.3 and 1.4 shows the plots of contact time versus percent adsorption of Ni (II) and contact time versus distribution coefficient (K_d) respectively. It is seen that the percent adsorption increases with shaking time. Maximum adsorption was observed at 30 minutes, beyond which there was no further increase in the adsorption. Therefore, 30 minutes contact time was considered to be sufficient for the adsorption of nickel (II) on mixture of bentonite clay and china clay and was used for all subsequent experiments.

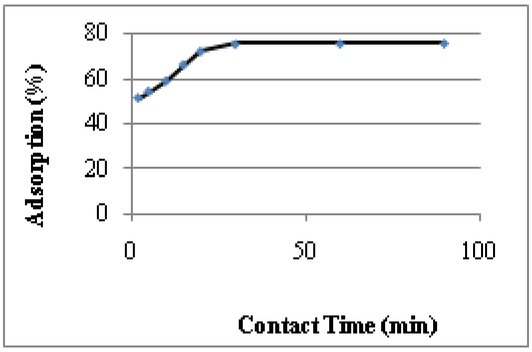

Figure 1.3: Graph between Contact Time and% Adsorption

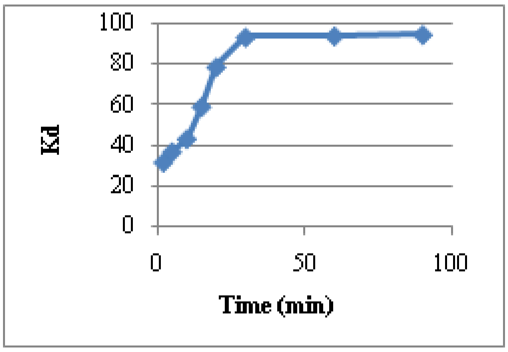

Figure 1.4: Graph between Contact Time and Distribution Coeficient (k_d)

The Langmuir isotherm model is fitted through regression model considering equilibrium concentration of nickel as dependent variable and amount of nickel adsorbed as independent variable, keeping amount of nickel, pH, contact speed and amount of clay as fixed at 300 µg, 6.0, 200 RPM and 0.4 g respectively. The variables are transformed by dividing C_e to q_e and C_e to Q_o respectively to form the linear relation and to fit a linear model. The regression model between is found significant ($p<0.05$) with F-statistic is 700.729 with significant regression coefficient ($p<0.05$).Furthermore, the constant term of the regression model is also significant.

Table 3

Model	Coefficients		t	Sig.
	B	Std.		
Constant	-.296	.033	-8.993	.000
c	2.487	.094	26.471	.000

On the basis of these results, the form of the fitted model is as,

$$\frac{C_e}{q_e} = -0.296 + 2.487\frac{C_e}{Q_0} \quad (5)$$

Table 4

Q_o	300
b	-0.0113
R^2	0.992
Adjusted R^2	0.990

Table 4 presents the information about the parameter of actual model i.e., Langmuir model. The high value of R^2

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indicates that the fitted model is significant and confirms the relationship between the variables.

3.3 Effect of Contact Speed

The variation of percent adsorption of nickel (II) with contact speed was studied using 12 ml of 10 ppm nickel (II) solution with 0.4 g of clay at 6.0 pH with varying contact speed over 50-300 RPM. The plots of contact speed versus percent adsorption of nickel and contact speed versus distribution coefficient (K_s) are shown in fig 1.5 and fig 1.6 respectively which shows the increase in percent adsorption due to increase in contact time with maximum adsorption.

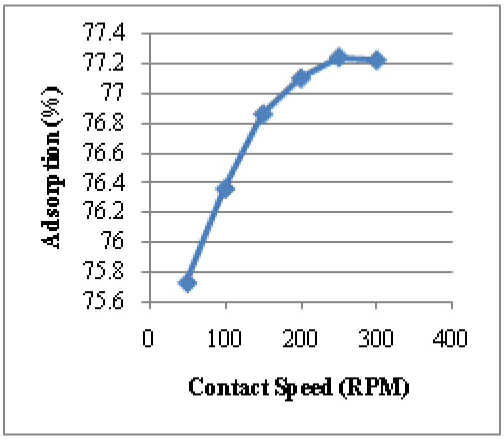

Figure 1.5: Graph between Shaking Speed and % Adsorption

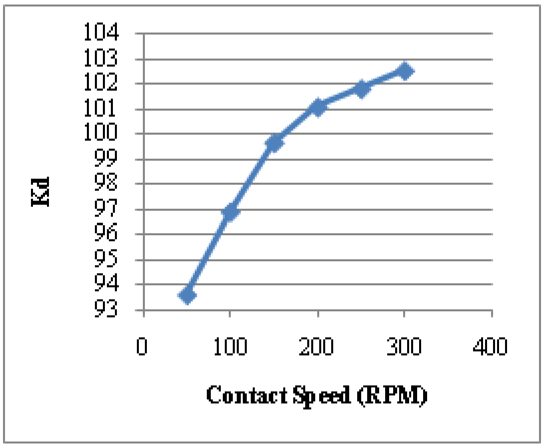

Figure 1.6: Graph between Shaking Speed and Distribution Coffiecient (K_d)

The adsorption data on the basis of contact speed was further correlated with Langmuir isotherm model. The regression model is fitted taking dependent variable as equilibrium concentration of nickel and amount of nickel adsorbed as independent variable, after transformation, keeping amount of nickel, Ph, contact time and amount of clay as fixed at 300 µg, 6.0, 30 minutes and 0.4 g respectively. The regression model is found significant with significant regression coefficient. The high value of R^2 (0.941) also confirm the relationship between the independent and dependent variables.

Table 5

Model	*Coefficients*		*t*	*Sig.*
	B	*Std. Error*		
Constant	-.139	.055	-2.533	.064
c	1.897	.236	8.021	.001

On the basis of these results, the form of the fitted model is as,

Table 6

Q_o	300
b	-0.0239
R^2	0.941
Adjusted R^2	0.927

3.4Effect of Different Cations

The effect of different cations concentration like Na^+, K^+, Ca^{++} and Mg^{++}, under the optimized conditions was studied. The plots of concentrations of different cations versus percent adsorption of Ni (II) and distribution coefficient (K_d) are shown in Figure 1.7 and 1.8 The results show that the sorption of Ni (II) on mixture of bentonite and china clay (adsorbent) is somewhat influenced by the cations in the suspension. This indicates that cations can alter the surface properties of clay and hence influence the sorption of Ni (II) on clay surface. The effect of these cations in reducing the adsorption of nickel (II) followed the order $K^+ > Ca^{+2} > Na^+ > Mg^{+2}$ at ph 6.0.

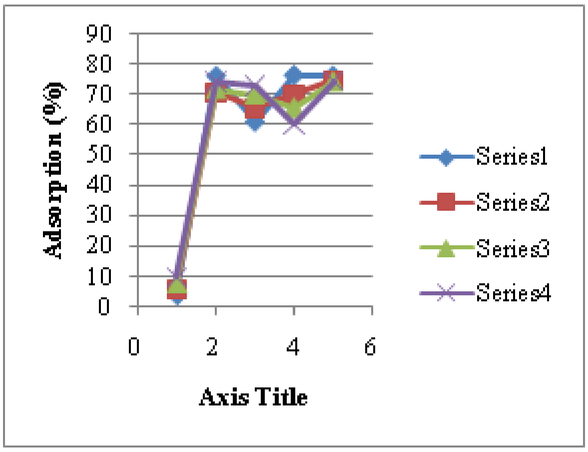

Figure 1.7: Graph between Different Cations Concentration and % Adsorption

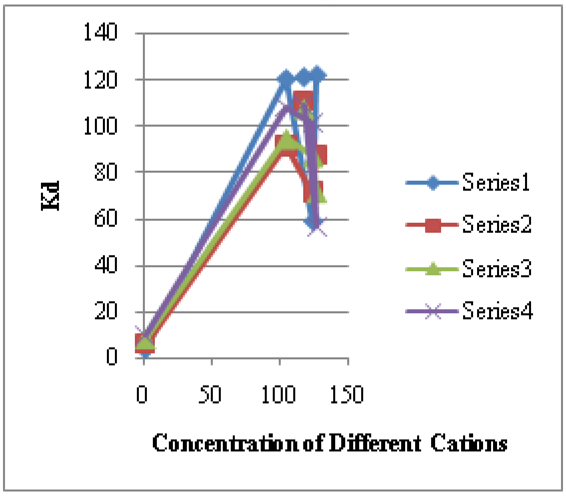

Figure 1.8: Graph between Different Cations Concentration and Distribution Coefficient (K_d)

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The data obtained by effect of different cations were further analyzed by Langmuir isotherm model. The regression model for Na^+, K^+, Ca^{++} and Mg^{++} is fitted under optimized conditions by transforming variables by dividing C_e to q_e and C_e to Q_o respectively to form the linear relation. All the models were found significant ($p<0.05$) with F-statistic as 1.169E4, 656.288, 581.367 and 1.428E4 respectively. Furthermore the regression coefficients for all regression models are significant at 5% level of significant.

3.4.1 Na+ Cation

Table 7

Mo del	Coeffici		t	Sig.
	B	Std.		
Co	-	.005	-	.00
c	1.	.017	108.	.00

$$\frac{C_e}{q_e} = -0.129 + 1.853\frac{C_e}{Q_0}$$ (For Na^+)

Table 8

Q_o	300
b	-0.0258
R^2	1.000
Adjusted R^2	1.000

3.4.2 K^+ Cation

Table 9

Model	Coefficients		t	Sig.
	B	Std. Error		
Constant	-.203	.008	-7.807	.004
c	2.136	.028	25.618	.000

On the basis of these results, the form of the fitted model is as,

$$\frac{C_e}{q_e} = -0.203 + 2.136\frac{C_e}{Q_0}$$ (for K^+)

Table 10

Q_o	300
b	-0.0164
R^2	0.995
Adjusted R^2	0.994

3.4.3 Ca^{++} Cation

Table 11

Model	Unstandardized Coefficients		t	Sig.
	B	Std. Error		
Constant	-.195	.027	-7.202	.006
c	2.122	.088	24.112	.000

On the basis of these results, the form of the fitted model is as,

$$\frac{C_e}{q_e} = -0.195 + 2.122\frac{C_e}{Q_0}$$ (for Ca^{++})

Table 12

Q_o	300
b	-0.0171
R^2	0.995

3.4.4 Mg^{++} Cation

Table 13

Model	Coefficients		t	Sig.
	B	Std. Error		
Constant	-.109	.004	-29.471	.000
c	1.769	.015	119.516	.000

$$\frac{C_e}{q_e} = -0.109 + 1.769\frac{C_e}{Q_0}$$ (for Mg^{++})

Table 14

Q_o	300
b	-0.0306
R^2	1.000
Adjusted R^2	1.000

3.5 Effect of Amount of Clay (Adsorbent)

The amount of the adsorbent (clay) affects the efficiency of the adsorption, and this parameter was optimized by shaking 10 cm^3 of 10 ppm Ni (II) solution using the optimized conditions of contact time, contact speed, pH, and the amount of adsorbate. The amount of mixture of bentonite and china clay (adsorbent) was varied from 0.05 to 0.6 g. The results are shown in fig. 1.9 and fig. 1.10 that give indication that the values of % adsorption increases with increasing the amount of clay up to 0.4 g and then remains constant up to 0.6 g. These results match with the results obtained by (Nasir Khalid *et al.*,) using Rice Husk for the adsorption of nickel. The results show that just 0.4 g of (adsorbent) is sufficient for the quantitative removal of Ni (II) from the aqueous solution used.

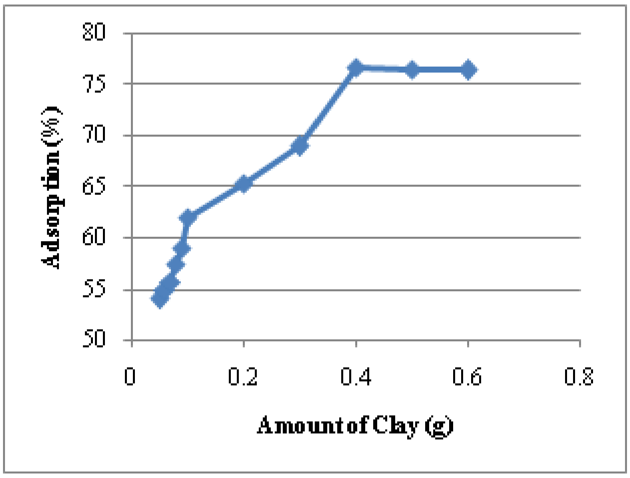

Figure 1.9: Graph between clay concentration and % Adsorption

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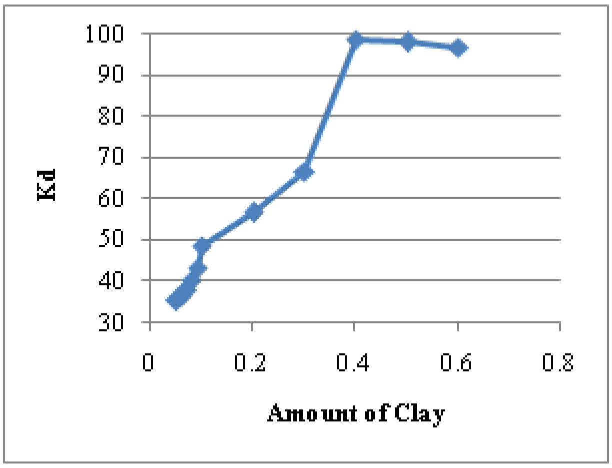

Figure 1.10: Graph between amount of clay and Distribution Coefficient (K_d)

3.6 Effect of Amount of Nickel (II) Solution (Adsorbate)

The effect of nickel concentration on the adsorption process was studied under the optimized conditions with varying concentration of nickel from 2 ppm to 20 ppmand the results are shown in figure 1.11 and 1.12. The plots depicts that the adsorption of nickel was almost constant up to 10 ppm of nickel. Beyond this concentration the adsorption gradually decreased with an increase in the concentration of nickel.

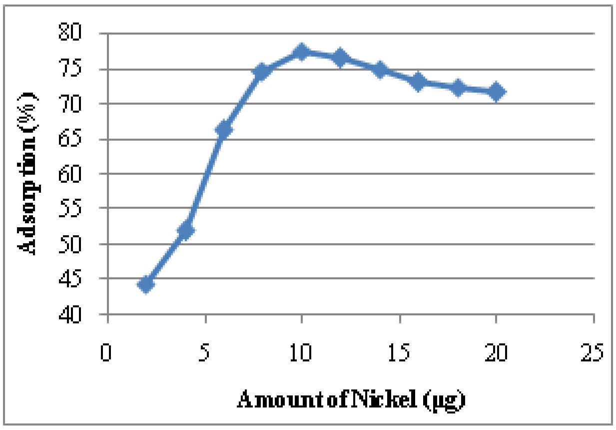

Figure 1.11: Graph between Amount of Nickel and % Adsorption

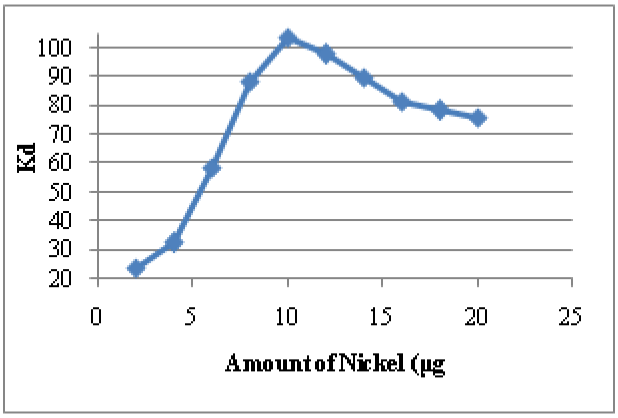

Figure 1.12: Graph between Amount of Nickel and Distribution Coefficient

4. Conclusion

Pollution of aquatic environment with toxic value able heavy metals is widespread. Consideration of mode of purifying these contaminations must be given to strategies that are designed to high through put methods while keeping cost at minimum. The adsorption technique was found rapid, simple and selective in the present study hence it could be used for removal of Ni(II) from aqueous water using a mixture (50 : 50) of bentonite and china clay as an adsorbent. The effect of pH, contact time, contact speed, different cations (Na^+, K^+, Ca^{++}, Mg^{++}), amount of adsorbent and amount of adsorbate were studied and their results were significant.

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