Isotherm, Thermodynamic and Kinetic Studies on the Adsorption of Cu(II), Cd(II) and Ni(II) Ions from Aqueous Solution onto Coconut Shell Activated Carbon

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Abstract: ***This study throws light on the use of coconut shell in the removal of heavy metal ions Cu(II), Cd(II) and Ni(II) from the aqueous solution.The adsorption parameters were determined using both Langmuir and Freundlich isotherm models. The adsorption kinetics followed the pseudo-second-order model.This model gives the best-fit to experimental data for heavy metal ions.The second order kinetics give highest correlation coefficient values 0.989, 0.993, 0.995 for Cu^{2+}, Cd^{2+}, Ni^{2+}respectively.Thermodynamic parameters such as change in Gibbs free energy (ΔG^0), enthalpy change (ΔH^0), and entropy change (ΔS^0) were also evaluated. The values showed that the adsorption process for Cu(II), Cd(II) and Ni(II) ions was endothermic.The negative value of ΔG^0 suggests the spontaneity of the reaction.The final result of the study suggests that the coconut shell carbon (CNS) has a good efficiency to remove Cu(II), Cd(II) and Ni(II) ions from aqueous solution and it is a cost effective adsorbent too.***

Keywords: Activated carbon, Adsorption, Isotherm, Kinetic, thermodynamic, Heavy metal ions, coconut shell

1. Introduction

Water pollution is a serious and undesirable environmental problem in the world. Therefore, water needs to be treated to make it safe for humans and other living organisms. People are increasingly concerned about contaminants in their drinking water that cannot be removed by water softeners or physical filtration[1]. Heavy metals find their way into natural water bodies because of establishment and development of some industries such as smelting and electric battery manufacturing, alloy preparation, paint, coating, corrosion inhibition and wood preservation.

Adsorption finds its application in industries as activated charcoal, purification of water, in synthetic resin etc. It is operative in most physical, chemical and biological systems.It is considered to be very suitable for waste water treatment because of its simplicity and cost effectiveness[2-3].Adsorption on activated carbon is considered to be a particularly competitive and effective process for the removal of heavy metals in trace quantities. However, the use of activated carbon is not suitable in developing countries due to the high costs associated with the production and regeneration of spent carbon [4-5].

Activated carbon is a non-graphite from of carbon which can be produced from any carbonaceous material.Agricultural byproducts such as coconut shell[6], paddy husk, bamboo wood, sawdust[7], rice husk[8], nut shells[9], fruit pits and charcoal, brown and bituminous coals, lignite peat bone, almond shell, and olive are some common raw materialsused for manufacturing active carbon. Any carbonaceous material (nature or synthetic) with high carbon content can be used as raw material for preparation of activated carbon. In fact, any carbonaceous low–cost material (of animal, plant, or mineral origin) with high carbon and low ash content can simply be changed in to activated carbon by proper thermal decomposition process.

Studies on the use of coconut shell as adsorbent are limited. Coconut shell is hard and high carbon content material so, shells are superb raw material for the production of activated carbon.Raw material for activated carbons that are produced using coconut shells ismostly found in geographic regions where coconuts are harvested which include India, Philippines, Sri Lanka and the Malaysia.

Coconut shell activated carbon has a tighter, more microporous structure than the activated carbon produced from coal and therefore,effective for organic chemical adsorption.Coconut shell-based carbon is the least dusty and is harderthan most types of activated carbons. Due to these properties, it is a good choice for use as a potential adsorbent.

The aim of this paper is to assess the ability of coconut shell carbon to adsorb Cu(II), Cd(II) and Ni(II) ions from aqueous solutions. The effects of the solution pH, adsorbent dosage, contact time and temperature on the removal of Cu(II), Cd(II) and Ni(II) ions were studied. The equilibrium data has been analyzed using Langmuir and Freundlich isotherm models. Further, the adsorption kinetics and thermodynamic parameters for adsorption process of heavy metal ions on CNS were also investigated.

2. Materials and Methods

A. Preparation of activated carbon from coconut shell (CNS):

The raw material of present research work i.e. coconut shell was obtained from fruit market in Shahdol. To remove dirt and sand present in the coconut shell, it was washed with tap water. This washed sample material was then left for 2-5 days in sun light and crushed to reduce the size. Smaller pieces (250gm) were carbonized at 400ºC for 15 mins and then using 1 M $ZnCl_2$ activated at 500ºC for approximately three hours. Using desiccator, the sample was cooled and then washed several times with distilled water until a pH between 6 and 7 was obtained. Adsorbent was then put in an oven at 105ºC for a period of one day. Further, the dried shell was burned in a furnace at temperature 650ºC for approximately two hours. The charcoal was soaked in chemical solution of $ZnCl_2$ for 8 hours, to become activated carbon. The activated carbon was further treated by HCl.

B. Aqueous solution of heavy metal

For the study, analytical grade reagents were used. 1000 mg/L aqueous solutions of the metal were prepared as stock solutions from their salts ($CuSO_4$, $CdSO_4$, $NiSO_4$). From aliquots ofthese stock solutions, working solutions of different concentrations were prepared of the desired concentration.

3. Experimental Procedure

For the adsorption studies, 100 ml of these heavy metal solutions was taken with 0.5gm of the adsorbent in a shakerfor 1 hour at temperature 303K. The speed of the shaker was 100r/min. At the end of each experiment, the contents of each glassware were filtered using a Whatman No. 14 filter paper after which the concentration of residual metal ions in each filtrate was determined by AAS.

4. Results and Discussion

A. Adsorption Isotherm

The equilibrium data obtained were analysed in the light of Freundlich and Langmuir isotherm.

The Freundlich equation is given by –

$$\frac{x}{m} = k_e C_e^{1/n}$$

Taking the logarithmic form of the equation

$$\log\left(\frac{x}{m}\right) = \log k_e + \frac{1}{n}\log C_e$$

Langmuir equation is given by[10]-

$$\frac{x}{m} = \frac{abC_e}{(1 + bC_e)}$$

Or

$$\frac{x}{m} = \left(\frac{1}{ab}\right)\cdot\left(\frac{1}{C_e}\right) + \frac{1}{a}$$

Where:

x/m= amount of heavy metal ions in mg/gm adsorbed per unit mass of adsorbent

'K_e' and 'n'=Freundlich constant

'a' and 'b'= Langmuir constant

C_e=Equilibrium concentrationof heavy metal ion (mg/l)

Here, 'a' is measure of adsorption capacity expressed in mg/g and 'b' is a measure of energy of adsorption expressed in l/mg. The value of constants 'a' and 'b' can be calculated from the slope and intercept of the plot drawn between $1/C_e$ and 1/(x/m). Similarly, the value of K_e and 1/n in Freundlich adsorption isotherm can be obtained from the intercept and slope of the plot of log x/m verses log C_e. The adsorptions studied were conducted at fix adsorbent dosage of CNS by varying initial metal ion concentration.

The surface heterogeneity of the adsorbent (CNS) is suggested by the Freundlich isotherm model i.e. it has small heterogeneous adsorption patches that are homogenous in themselves. The activation of adsorption site takes place, heading to increase adsorption probably through the surface exchange mechanism. The linear plots of log X/m versus log Ce. (Figure 1, 3, 5, 7, 9, 11) suggest the applicability of Freundlich model for Cu(II), Cd(II), and Ni(II). The value of Freundlich constant for Cu(II), Cd(II) and Ni(II) at two temperatures vic. 303K and 313K is shown in Table-1. It is observed that the experimental data obtained was inaccordance with the Freundlich isotherm. The Freundlich isotherm data had a reliability (r) of over 95% in all cases.

Value of k and n calculated from the intercept and slope of the plots are presented in Table-1. The Freundlich exponent and n, give an indication of the favorability of adsorption. A value of n > 1.0 represents a favorable adsorption condition. The values of n obtained in this study for the adsorption of Cu(II), Cd(II), Ni(II) on CNS are greater than unity, indicating favorable adsorption of the metal ion on CNS. The values of Langmuir constants 'a', 'b' and 'r' are presented in Table-2. Adsorption capacity as indicated by value of 'a' is seen to be quite high for CNS i.e. Cu(II) 15.601, Cd(II) 9.898, and Ni(II) 8.799 at 303K. Whereas the value of 'a' is found to be18.729, 18.454 and 9.715 at 313K for Cu, Cd, and Ni metal ions respectively. The energy of adsorption as indicated by 'b' is found to be highest for Ni(II)(1.767 L mol^{-1} at 303K, 1.678 L mol^{-1} at 313K).At 313K,Cu(II) and Cd(II) have values 0.821L $mol^{-1}$and 0.771 L mol^{-1}whichare one of the lowest.

The results of the Langmuir isotherm model achieved from the data show that the correlation coefficient values for Cu(II), Cd(II), and Ni(II) are 0.987, 0.999, and 0.993 at 303K and 0.993, 0.953, and 0.989 at 313 Krespectively. These values are best fit for the Langmuir isotherm model. They indicate monolayer adsorption nature of these metal ions on CNS.

On the basis of regression analysis of the experimental data, it may be inferred that the adsorption behavior of metal ions on coconut shell is in good agreement with Langmuir model. This can be attributed to three main causes-

1) The formation of monolayer coverage on the surface of CNS with minimal interaction among molecules of substrate.
2) All sites having equal absorption energies
3) Immobile and localized adsorption.

R_L –

The separation factor R_L is usually employed to describe the favorability of the adsorption.It is based on the Langmuir adsorption constant.

$$R_L = 1/(1+ bc)$$

Where,
c is the initial concentration of heavy metal ions; and
b is Langmuir constant which indicates the nature ofadsorption.
If R_L>0 but <1, the Langmuir isotherm is favorable which is the case in our study.

B. Thermodynamic studies

The effect of temperature on the adsorption of Cu(II), Cd(II) and Ni(II) ions on to CNS was studied at two temperatures - 303K and 313K. These studies were carried out at the optimum pH values. The thermodynamic parameters of adsorption such as Gibbs free energy change ΔG^0 (Kcal mol^{-1}), standard enthalpy change ΔH^0(Kcal mol^{-1}) and standard entropy change ΔS^0 (Kcal mol^{-1}) were calculated using the following equation(s):

$$\Delta G^0 = -RT \ln k$$

$$\Delta H^0 = \left(\frac{T_2 T_1}{T_2 - T_1}\right) \ln\left(\frac{k_2}{k_1}\right)$$

$$\Delta S^0 = \left(\frac{\Delta H^0 - \Delta G^0}{T}\right)$$

Where,
k_1 and $k_2$are the equilibrium constants;
T is the absolute temperature;
R is the universalgas constant.

Table-3 shows the values of ΔG^0, ΔH^0 and ΔS^0 determined in this study for the adsorption of Cu^{2+}, Cd^{2+} and Ni^{2+} on CNS. The negative values of Gibbs free energy show the thermodynamic favourability of the adsorption process.

Generally speaking, increase in adsorption rate with temperature was observed within the temperature range of our study, which may be attributed to the increase in the mobility and diffusion of ionic species into the pore sites of the activated carbons.

The obtained ΔH^0 values are positive, which indicate the endothermic nature of the adsorption on to CNS. The change in entropy is positive, indicating the entropy of the system increased during the adsorption. It should also be noted that the entropy of the surroundings might increase because the adsorption reaction is not an isolated process.

The negative ΔG^0 demonstrates that the adsorption process on CNS is a spontaneous process, and the increase (depreciation) of ΔG^0 values with the increase of temperature indicated that the adsorption became more favourable at high temperature.

C. Kinetic studies

The sorption kinetics of sorbent depend on the properties of the sorbate, experimental condition, concentrations, temperatures and pH values. The pseudo-first-order rate model equation given by Lagergren in 1898 is[11]:

$$\frac{dq}{dt} = k_1(q_e - q)$$

Where,q_e is the amount of solute adsorbed at equilibrium per unit weight of adsorbent (mg/g) and q the amount of solute adsorbed at any time (mg/g) and $k_1$is the adsorption constant.

The above equation can be integrated for the boundary conditions t = 0 to > 0 (q = 0 to >0) and then rearranged to obtain the following linear time dependence function:

$$\log(q_e - q) = \log(q_e) - (k_1/2.303)t$$

or

$$k_1 = \left(\frac{2.303}{t}\right)\log\left(\frac{q_e}{q_e - q}\right)$$

This is the most popular form of pseudo-first-order kinetic model equation. Figure-13, 14, and 15 show an example for these plots. The correlation coefficient in this model lies between (0.891) and (0.929). It shows that pseudo-first-order-model has very poor correlation coefficient for best fit data. Therefore, it can be concluded that this model is not satisfactory to be used as a suitable model. Constant k_1 and correlation coefficient have been calculated and summarized in Table- 5.

Lagergren equation was later modified by Ho and Mckayand to[12-14]:

$$dq/dt = k_2 (q_e-q)^2$$

Integrating this equation for the boundary condition, t = 0 to > 0 and q = 0 to > 0 and rearranging to obtain the linearized form gives us:

$$\frac{t}{q} = \left(\frac{1}{k_2 q_e^2}\right) + \left(\frac{1}{q_e}\right)t$$

Hence

$$\frac{t}{q} = \left(\frac{1}{h}\right) + \left(\frac{1}{q_e}\right)t$$

Here h, is the initial adsorption rate (mg/(g min)). The above equation is pseudo-second order equation. From equation, the plot of t/q vs t has a linear relationship from which k_2 and h can be determined from the slope and intercept of the plot. The plot for coconut shell at 30ºC for Cu(II), Cd(II) and Ni(II) ions is given in figure-16, 17, 18 and values for k_2 and h were calculated and reported in Table-1. The correlation coefficient values for this model lie between 0.989 and 0.995 which are veryclose to ideal correlation coefficient value making it a perfect model. So, it may be concluded that the adsorption of Cu^{2+}, Cd^{2+} and Ni^{2+} ions onto coconut shell perfectly follows the pseudo-second-order.

It can also be concluded from the values of k_2 of different metal ions that the reaction taking place is of the pseudo-second-order. The preferential adsorption of different heavy metal ions on coconut shell, which can be predicted by the value of k_2 is $Ni^{2+} > Cd^{2+} >$ and Cu^{2+}.

5. Conclusion

Toxic heavy metals are not bio-degradable and do not degrade in to harmless end products either. The presence of toxic heavy metals in industrial effluents has become a matter of environmental concern. Chemical, metallurgical, tannery, mining, jewelry, electrical and electronics are large scale industries in industrial nations and developing countries and are the main source for metal containing waste.Thermodynamic study of Cu(II), Cd(II) and Ni(II)

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revealed the adsorption of metal ions was spontaneous, feasible and endothermic in nature. It was found that Freundlich and Langmuir adsorption models fit well to the study. The Langmuir and Freundlich constant values indicate the beneficial adsorption of metal ions, the linear Langmuir plots indicate monolayer coverage of adsorbates at the outer surface of the adsorbent.The value of R_L is found to be greater than 0 but smaller than 1 clearly indicating that the Langmuir isotherm is more applicable for the adsorption of Cu(II), Cd(II) and Ni(II) metal ions. Positive value of entropy reflects the affinity of adsorbent for heavy metals.The adsorption kinetics of Cu(II), Cd(II) and Ni(II) on the CNS follows the pseudo-second-order model.

Table 1: Value of Freundlich constants for Cu(II),Cd(II) and Ni(II) ions

Metal ion	log K		1/n		r(corr.coefficient)	
	303K	313K	303K	313K	303K	313K
Cu(II)	-1.111	-1.183	0.667	0.725	0.979	0.984
Cd(II)	-1.005	-1.135	0.571	0.671	0.991	0.954
Ni(II)	-0.962	-0.980	0.511	0.524	0.977	0.975

Table 2: Values of Langmuir isotherm constants for sorption of Cu(II), Cd(II) and Ni(II) metal ions

Metal ion	b value related to the equilibrium constant (L mol^{-1})		a (L mol^{-1})		R (corr.coefficient)	
	303K	313K	303K	313K	303K	313K
Cu (II)	1.013	0.821	15.601	18.729	0.987	0.993
Cd(II)	1.657	0.771	9.898	18.454	0.999	0.953
Ni(II)	1.767	1.678	8.799	9.715	0.993	0.989

Table 3: Thermodynamic parameters

S.No.	Metal ion	Δ G^0		Δ H^0	ΔS^0
		303K	313K		
1	Cu (II)	-9.034	-11.204	3.312	0.0436
2	Cd (II)	-5.732	-11.039	11.291	0.0638
3	Ni(II)	-5.095	-5.811	1.795	0.0235

Table 4: Equilibrium parameters, R_L calculated from Langmuir adsorption isotherm-

Metal concentration (mg/L)	Cu(II)		Cd(II)		Ni(II)	
	303K	313K	303K	313K	303K	313K
50	0.0012	0.00107	0.0020	0.0010	0.0022	0.0020
100	0.0006	0.00053	0.0010	0.0005	0.0011	0.0010
150	0.0004	0.00036	0.0006	0.0003	0.0007	0.0006
200	0.0003	0.00027	0.0005	0.00027	0.0005	0.0005
250	0.0002	0.00021	0.0004	0.00022	0.0004	0.0004

Table 5: Kinetic parameter for adsorption of Cu(II), Cd(II) and Ni(II) ions on coconut shell.

Models	Parameters	Cu^{2+}	Cd^{2+}	Ni^{2+}
Pseudo-first order kinetic	K_1	0.031	0.034	0.024
	q_e (mg g^{-1})	5.262	5.682	3.482
	R^2	0.916	0.929	0.891
Pseudo-second order kinetic	h (mg/ (g min))	25.812	29.254	42.167
	K_2 (g mg^{-1}min^{-1})	0.070	0.064	0.078
	R^2	0.989	0.993	0.995

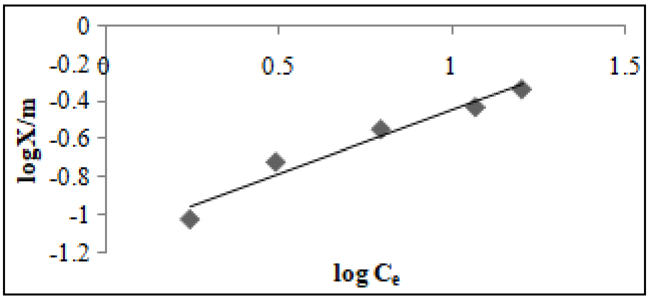

Figure 1: Freundlichadsorption isotherm of Cu(II) at 303K on CNS

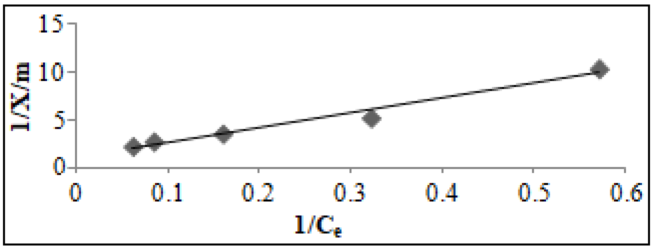

Figure 2: Langmuiradsorption isotherm of Cu(II) at 303K on CNS

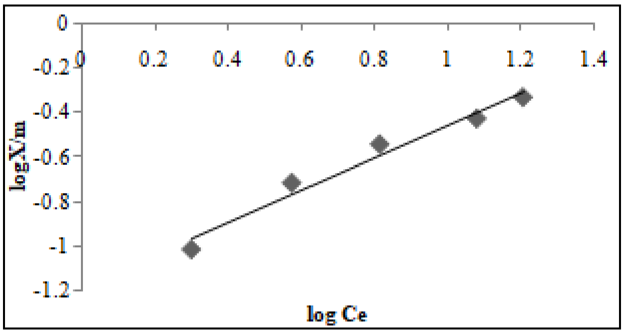

Figure 3: Freundlichadsorption isotherm of Cu(II) at 313K on CNS

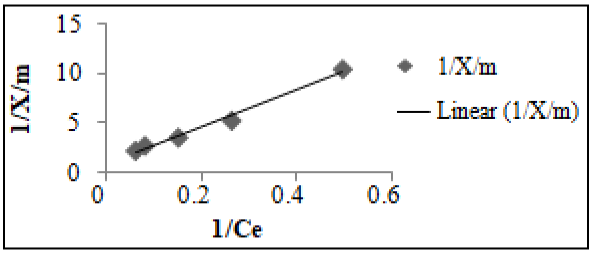

Figure 4: Langmuiradsorption isotherm of Cu(II) at 313K on CNS

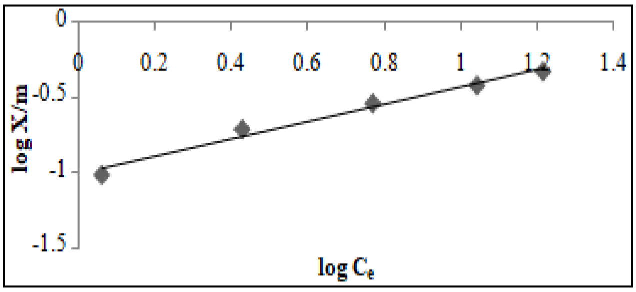

Figure 5: Freundlichadsorption isotherm of Cd(II) at 303K on CNS

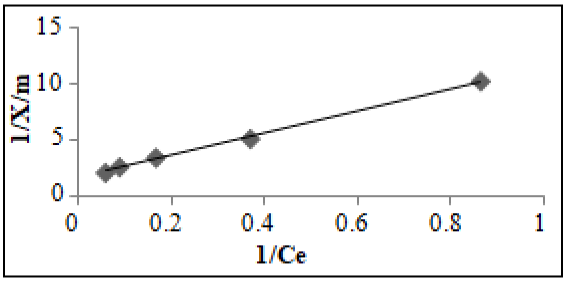

Figure 6: Langmuiradsorption isotherm of Cd(II) at 303K on CNS

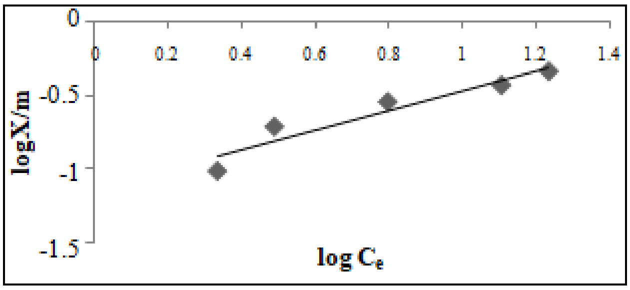

Figure 7: Freundlichadsorption isotherm of Cd(II) at 313K on CNS

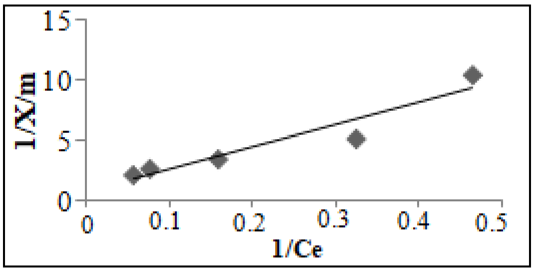

Figure 8: Langmuiradsorption isotherm of Cd(II) at 313K on CNS

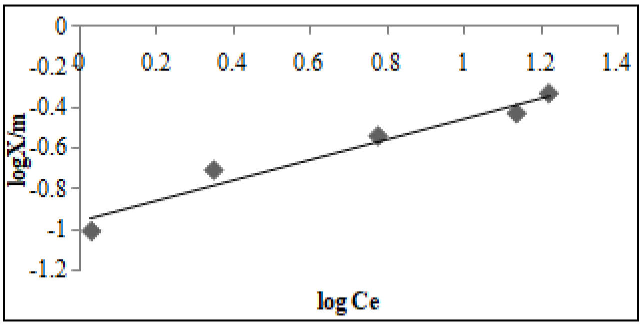

Figure 9: Freundlichadsorption isotherm of Ni(II) at 303K on CNS

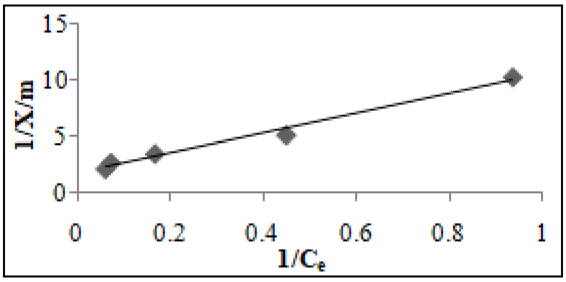

Figure 10: Langmuiradsorption isotherm of Ni(II) at 303K on CNS

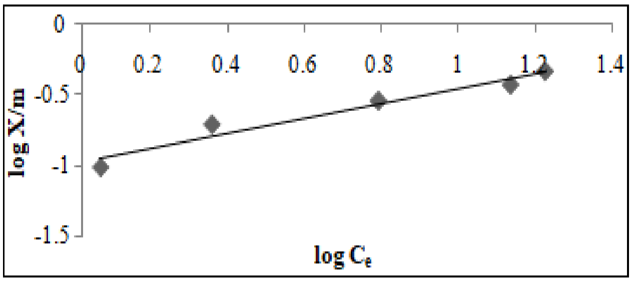

Figure 11: Freundlichadsorption isotherm of Ni(II) at 313K on CNS

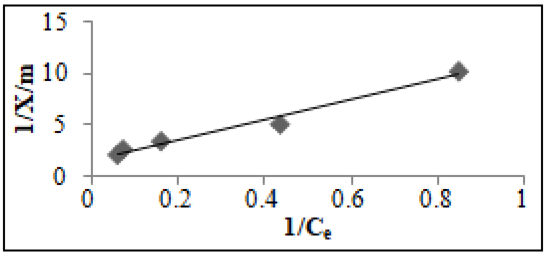

Figure 12: Langmuiradsorption isotherm of Ni(II) at 313K on CNS

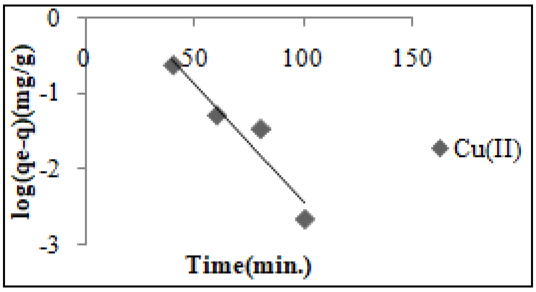

Figure 13: Pseudo-first-order kinetic of Cu(II) ion adsorption onto CNS.

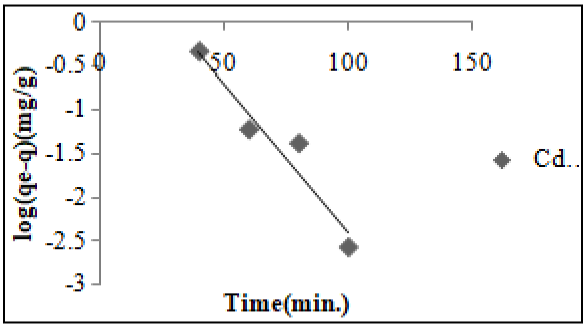

Figure 14: Pseudo-first-order kinetic of Cd(II) ion adsorption onto CNS.

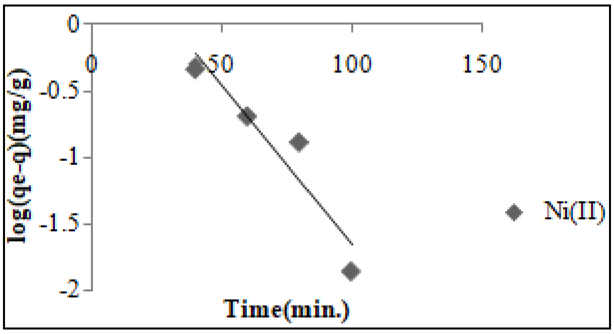

Figure 15: Pseudo-first-order kinetic of Ni(II) ion adsorption onto CNS.

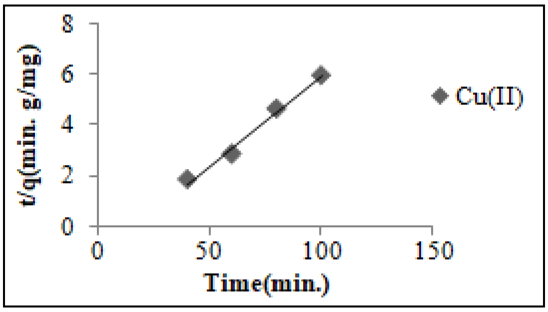

Figure 16: Pseudo-second-order kinetic of Cu(II) ion adsorption onto CNS.

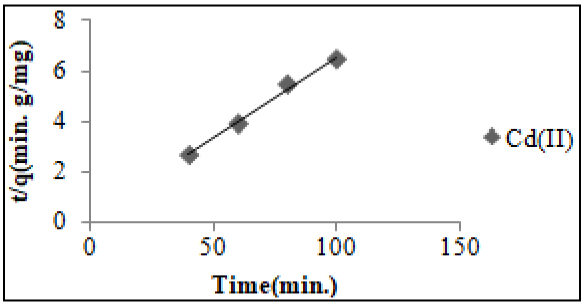

Figure 17: Pseudo-second-order kinetic of Cd(II) ion adsorption onto CNS

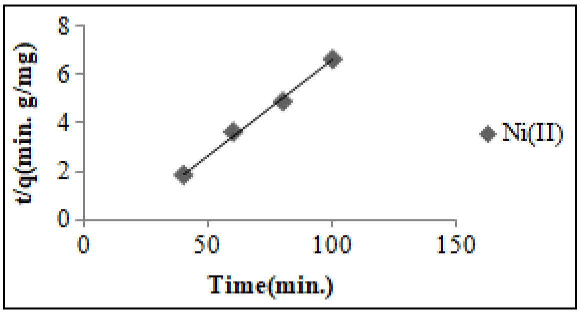

Figure 18: Pseudo-second-order kinetic of Ni(II) ion adsorption onto CNS

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