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REMOVAL OF NICKEL IONS FROM AQUEOUS SOLUTIONS USING FLY ASH:EQUILIBRIUM AND KINETIC STUDIES

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ABSTRACT

In the present study, adsorptive capacity ofcoal fly ash (CFA) for the removal of Ni(II) ions in aqueous medium has been studied. Batch studies has been conductedto investigate the effects of various adsorption 0parameters such as contact time (5-120 min), pH (1-10) of solution, metal ions concentration (5-200 mg/L) and adsorbent dose (0.1-1.5 g) on adsorption ofNi(II) ions onto CFA. The optimum set of conditions for maximum adsorption of Ni(II) ions were found to be initial concentration 50mg/L, dosage 0.1 g and pH 6. The maximum adsorption of Ni(II) ions by CFA was found to be 91.8 %. The adsorption data was fitted best to the Langmuir model (R^2 = 0.9818) and monolayer adsorption capacity of CFA for Ni(II) was found to be 3.2499 mg/g. These results suggested that CFA can be effectively used as efficient adsorbent for the removal of Ni(II) from industrial wastewaters and inorganic effluent..

Key words: Adsorption, Coal Fly Ash (CFA), Nickel,Langmuir, Freundlichetc.

I. INTRODUCTION

Heavy metals are generally referred to as those metals which possess a specific density more than 5 g/cm^3 and adversely affect the environment and living organisms [1]. Environmental pollution by heavy metal ions has received worldwide attention due to their long-term toxicity, non-biodegradability and accumulation in living organisms [2]. They are non-biodegradable and their concentration gets accentuated through bioaccumulation via food chain in living tissues, causing various diseases and disorders [3]. Nickel is a nutritionally essential trace metal for at least several animal species, micro-organisms and plants, and therefore either deficiency or toxicity symptoms can occur when, respectively, too little or too much Ni is taken up. Most nickel is used for the production of stainless steel and other [4]. Several treatment methods such as membrane filtration, chemical precipitation, ion exchange, and filtrationhave been reported for the removal of metal ions from water and wastewater.The shortcomings of most of these methods are high operational and maintenance costs, high-energy consumption and complex design [5]. Among several chemical and physical methods, the adsorption has been found to be superior to other techniques due to its simplicity of design, low investment cost and high efficiency. The application of low cost and easily available materials in wastewater treatment has recently attracted the interest of researchers [6, 7]. In this study, CFA was utilized for the removal of Ni(II) ions from aqueous solution.

II. METHODOLOGY

2.1 Collection and Preparation of adsorbent

Raw sample of coal fly ash was collected from Kasimpur Thermal Power Plant, Aligarh in powder form.The raw sample obtained was taken in a beaker and washed several times with double distilled water to remove any impurities present in the sample. The supernatant was thrown and clean sample was retained. After cleaning the sample was kept in sun light for drying. Then sample was sieved through 150 µ size of ASTM mesh to obtained particles of uniform diameter and stored in an air tight container to be used as an adsorbent for the removal of lead ions from aqueous solutions.

2.2Adsorbate solution

For preparing stock nickel solution of 1000 mg/L lead ions concentration the required amount of Nickel sulphate ($NiSO_4.5H_2O$) was dissolved in a standard flask of 1000 ml in double distilled water. These stock solutions were used to prepare the working solutions of desired concentrations for different experiments

2.3 Determination of point of zero charge

The point of zero charge (pH_{pzc}) of the CFA was determined by solid addition method with DDW and 0.1 N KNO_3 solutions . The 50 ml DDW (Double distilled water) was transferred into a series of conical flasks and the initial pH (pH_i) of these solutions were roughly adjusted between 2 to 10 by adding either 0.1 N HCl or 0.1 N NaOH solutions. The initial pH (pH_i) of these solutions was than measured accurately by using pH meter. After that 0.5 gm of adsorbent was added into each flask and allowed to equilibrate for 24 hours with intermittent manual shaking. After attaining equilibrium solution was filtered and the final pH (pH_f) of the supernatant liquid was then noted. The difference between initial and final values ($pHe = pH_i – pH_f$) were plotted against pH_i, the point of intersection of resulting curve with abscissa at which pH_i is zero, gave the point of zero charge (pH_{pzc}). The same procedure was repeated using 0.1 N KNO_3 solutions.

2.4 Adsorption studies

Batch experiments for adsorption of Ni(II) ions on CFA were conducted by varying pH, contact time, adsorbent dose and adsorbate concentration. The experiments were carried out by contacting 0.4g of the adsorbent with 50 ml solution of 50 mg/L concentration of Ni(II) ions except for the effects of contact time in which concentration range from 5 to 200 mg/L were used. The flasks were shaken for the required time period on a rotary shaker at 120 rpm at room temperature at pH 6. The effect of contact time was studied for the time period of 5 to 180 minutes. At predetermined times, the flasks were withdrawn from the shaker and the reaction mixtures were filter and filtrate samples were analysed for residual concentration of Ni(II) ions by AAS. The amount of metal adsorbed (mg/g), q_e and removal efficiency, R % was calculated using the formula given below:

$$q_e = \frac{(C_i - C_e)}{W} \times V \qquad R\% = \frac{(C_i - C_e)}{C_i} \times 100$$

where q_e is the amount of metal adsorbed (mg/g), R % is the adsorption percentage of metal ions, V is the volume of the adsorbate solution (L), C_i is the initial metal ions concentration (mg/L), C_e is the metal ions concentration at equilibrium (mg/L) and W is the weight of the adsorbent in gram (g).

2.5 Adsorption isotherms

The adsorption capacity of the system was studied by analysing obtained data with the Langmuir, Freundlich, Temkin & D-R isotherm models. The equilibrium sorption of Ni(II) ions was carried out by contacting 0.5g of the CFA with 50 ml solutions of Ni(II) ions of concentrations ranging from 5 – 200 mg/L in 100 ml conical flasks with intermittent shaking for 2 hours on the rotary shaker.

2.6Adsorption kinetics

The obtained experimental data was analysed with pseudo first order, second order and intra particle diffusion model to investigate the validity with kinetic data which help in determining the kinetics of adsorption process.

III. RESULTS AND DISCUSSION

3.1 Adsorption studies

3.1.1 Effect of pH

The pH of the solution affects the surface charge of the adsorbents as well as the degree of ionization and speciation of adsorbate particles [8]. It is known that metal species [M(II)=Cd(II)] are present in deionized water in the form of M^{+2}, M(OH)(s), $M(OH)_2$(s) etc. [9]. It is obvious that adsorption of M(II) must be higher in alkaline medium. At high pH, precipitation of metal ions as metal hydroxides plays an important role in removing metal ions. The optimum pH of Ni(II) ions solution and its influence on the extent of adsorption onto CFA was studied by varying pH in the range of 1-10 which is shown in “Fig. 1”. It was observed that adsorption ofNi(II) ions increased with an increase in pH and reaches maximum, 91.8 % at pH 6. At lower pH value H^+ions compete with Ni(II) ions for adsorption on sites. The increase in adsorption with increasing pH is gradual becauseincreasing pH reduces the competition of H^+ ions present in the solution with Ni(II) ions for adsorption sites. It may be due to the fact that increase in pH makes the adsorbent surface more negatively charged due to protonation of adsorbent and thus become more accessible for the adsorption of metal ions (positively charged) through electrostatic force of attraction [10, 11].At higher pH i.e, after pH6, the removal percentage decreases due to precipitation of metal ions in form of hydroxides due to higher pH.

Moreover, the pH of point of zero charge, pH_{zpc} has an important influence on adsorption processes. The surface of adsorbent was positive when pH <pH_{zpc}, neutral when pH = pH_{zpc} and negative at pH >pH_{zpc}. The data plotted in “Fig. 5” indicated that the pH_{zpc} value of CFA was 5.8, showing that the surface was negatively charged above this pH and hence fairly large amount of Ni(II) ions (91.8% at pH 6) were adsorbed.

3.1.2 Effect of contact time

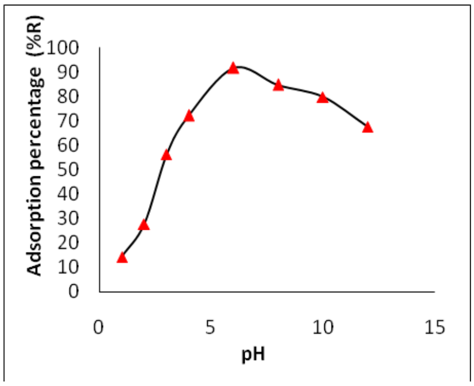
Batch studies was conducted to order optimize the contact time for the maximum removal of Ni(II) ions. Contact time was varied between 5-120 minutes for the removal of Ni(II) ions from aqueous solutions of 50 mg/L of Ni(II) ions with adsorbent dose of 0.4 g at optimum pH 6. The effect of contact time on adsorption of Ni(II) ions is shown in “Fig. 2”. It was observed that adsorption of Ni(II) ions increases with increase of contact time until it reaches equilibrium. The rate of Ni(II) ions removal was very rapid during initial 20 minutes (55.8%) which may be due to the availability of large number of vacant sites on the adsorbent surface during initial stages of adsorption. Thereafter, the rate of adsorption of Ni(II) ions increased slowly and reached maximum (91.2%) in 120 minutes and then became almost constant. This showed that equilibrium was established in 120 minutes.

3.1.3 Effect of concentration

The effect of initial Ni(II) ions concentration was studied by varying initial Ni(II) ions concentration from 5 – 200 mg/L on the removal of Ni(II) ions with adsorbent dose of 0.4 g at an optimum pH 6.0 and shown in “Fig. 3”. It was observed that adsorption efficiency of Ni(II) ions gradually decreased with the increase in initial metal ion concentration but adsorption capacity of the adsorbent increase. Fig. 3 shows that an increase in the initial Ni(II) ion concentration resulted in decreased nickel ions uptake appreciably from 85.36% to 42.415%. The increase in C_i also enhances the interaction between the metal ions in the aqueous phase and the adsorbent surface which results in increasing the driving force of the concentration gradient and thus facilitates the higher adsorption of metal ions on adsorbent surface.

3.1.4 Effect of adsorbent dose

The effect of adsorbent dosage from 0.1 to 1.5 g on the uptake of nickel ions onto CFA was studied and is shown in “Fig. 4”. It was found that the removal efficiency of metal ions increased from 16.8% to 98.4% with an increase in the adsorbent dosage from 0.1 g to 1.5 g. Increase in adsorption by increase in adsorbent dose is due to increase in ion exchange sites, surface area and number of available adsorption sites. Adsorption capacity was found to be maximum, 4.2 mg/g and then decrease gradually to 1.67 mg/g with increase of adsorbent dose up to 1.5 g. It may happen due to the overlapping of adsorption sites as result of adsorbent particles overcrowding [12].



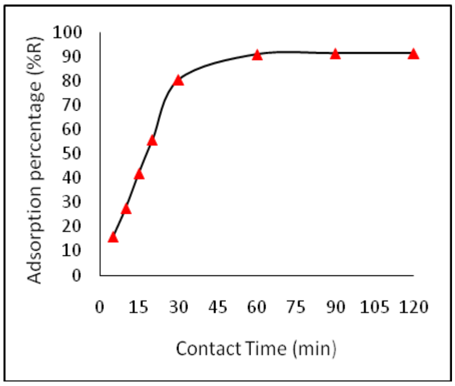
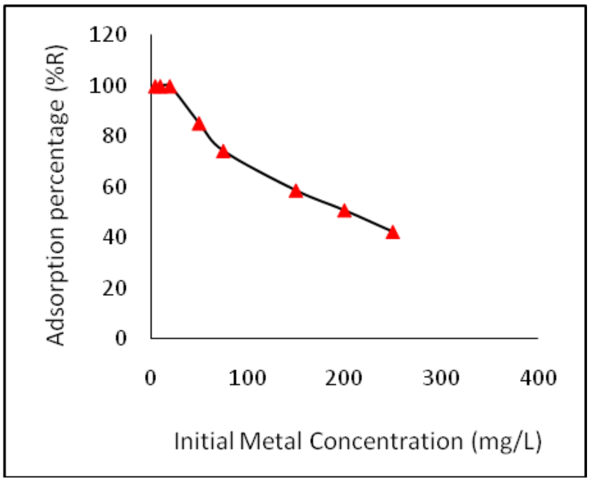


Fig. 1 Effect of pH

Fig. 2 Effect of contact time



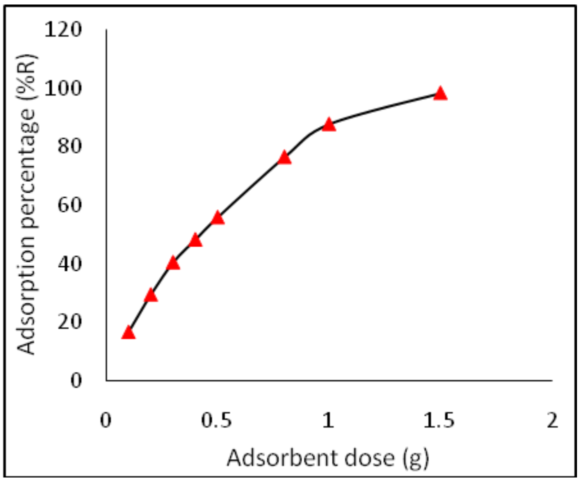


Fig. 3 Effect of Ni(II) ions concentration

Fig. 4 Effect of adsorbent dose

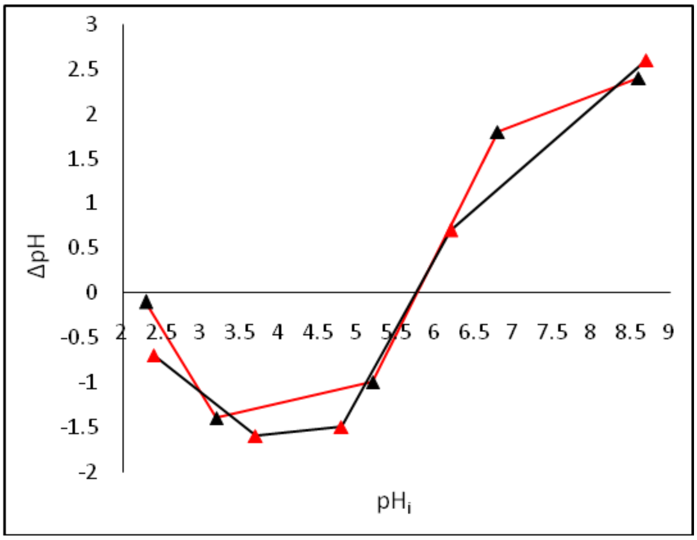


Fig.5 Point of zero charge of CFA

3.2 Adsorption isotherms studies

The variation in the amount of gas adsorbed by the adsorbent with pressure at constant temperature can be expressed by means of a curve termed as adsorption isotherm.In order to model the adsorption behaviour and calculate the adsorption capacity of adsorbent for the removal of Ni(II) using CFA, adsorption isotherms were studied. The obtained experimental data was analysed with Langmuir, Freundlich, Temkin& D-R adsorption isotherm and shown in "Fig. 6, 7, 8 & 9". The values of correlation coefficients, R^2 and constants of these isotherms shown in table 1 indicated that Langmuir model dominates with $R^2 \approx 0.9818$ in the applicability of experimental data on isotherm models. The monolayer adsorption capacity, q_m of CFA for Ni(II) ions calculated from Langmuir plot of Ce/$q_e$vsC_e shown in "Fig. 6" was found to be 3.2499 mg/g. The values of K_F, 1/n and R^2 obtained from the graph of log $q_e$vs log C_e for Freundlich isotherm shown in "Fig. 7" are listed in "Table 1". The value of n was found to be 4.1169 which is greater than 1 and indicates that the adsorption of Ni(II) ions on CFA occurred through chemisorption process. The values of A, B & R^2 obtained from graph of qe&lnCe from

Temkin isotherms are shown in fig. 8. The values of q_m, β & R^2 were obtained from D-R isotherm as shown in fig. 9.

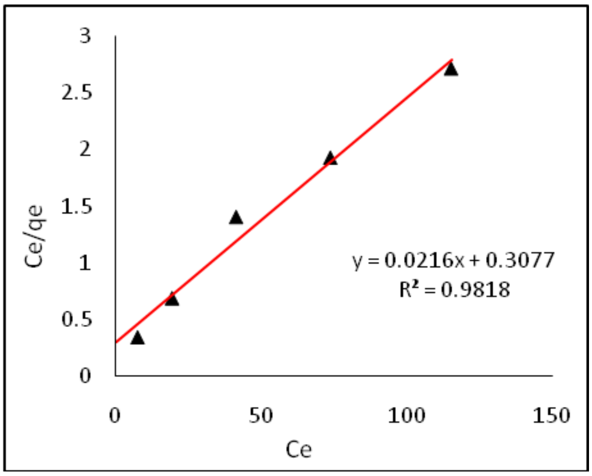


Fig. 6 Langmuir adsorption isotherm

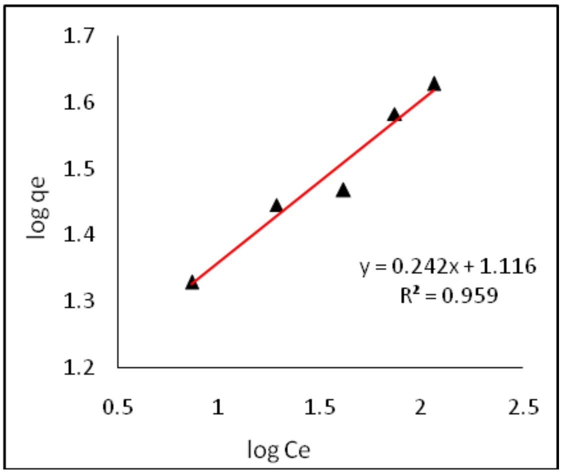


Fig. 7 Freundlich adsorption isotherm

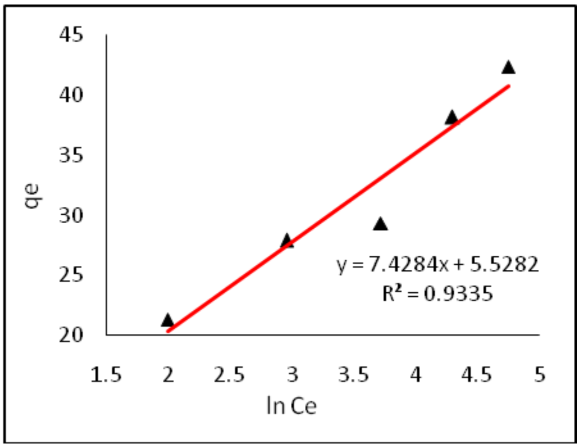


Fig. 8 Temkin adsorption isotherm

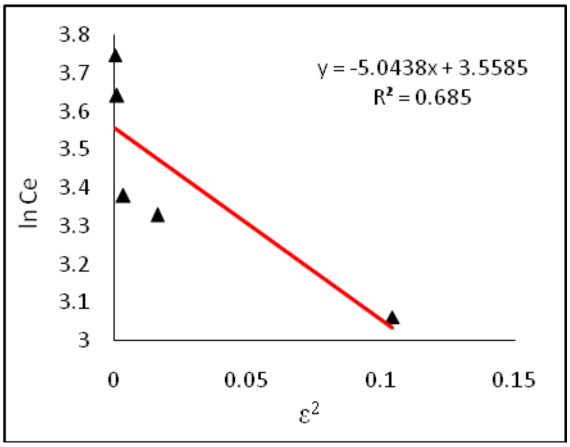


Fig. 9 D-R adsorption isotherm

Table: 1 Langmuir, Freundlich, Temkin & D-R isotherm constants for the adsorption of Ni(II)

Metal	**Langmuir isotherm**				**Freundlich isotherm**			
Ni^{+2}	**q_m**	**b**	**R^2**	**R_L**	**1/n**	**n**	**K_F**	**R^2**
	3.2499	14.2454	0.9818	0.000519	0.2429	4.1169	13.0828	0.9595
	Temkin isotherm				**D-R isotherm**			
	A	**B**	**R^2**		**q_m**	**β**	**R^2**	
	2.10475	7.4284	0.9335		35.110049	5.0438	0.685	

3.3 Kinetic Studies

In order to investigate the mechanism of adsorption of Ni(II) on CFA, the kinetic studies were carried out by Pseudo- first order, pseudo second order kinetic model and intra-particle diffusion model. The graphs plotted for the models mentioned above are shown in fig.10, 11 and 12. The values of R^2 and other parameters for pseudo first order ($R^2 \approx 0.991$), pseudo second order ($R^2 \approx 0.9921$) and intra-particle diffusion ($R^2 \approx 0.8143$) listed in table 2 indicated that adsorption of Ni(II) ions by CFA was best described by pseudo second order kinetic model. The calculated values of q_e from the model were in good agreement with experimental values. Moreover the applicability of pseudo second order model implies that adsorption of Ni(II) on CFA is a chemisorption process which involves the formation of single layer of Ni(II) ions on the surface of adsorbent by chemisorption and may be followed by additional layer of physically adsorbed Ni(II) ions.

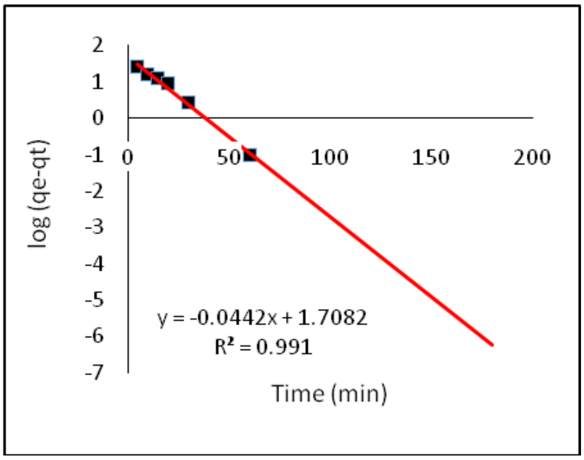


Fig. 10Pseudo first order model

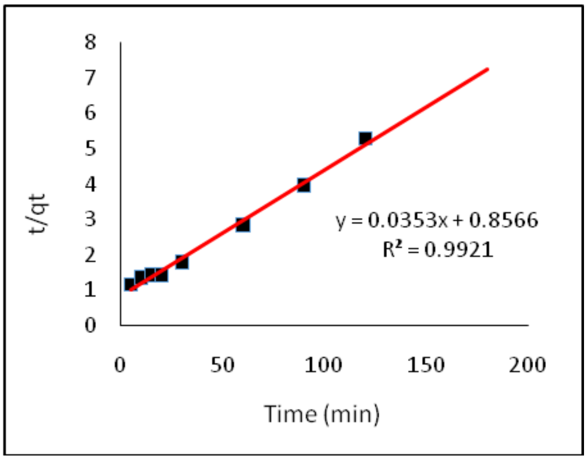


Fig. 11Second first order model

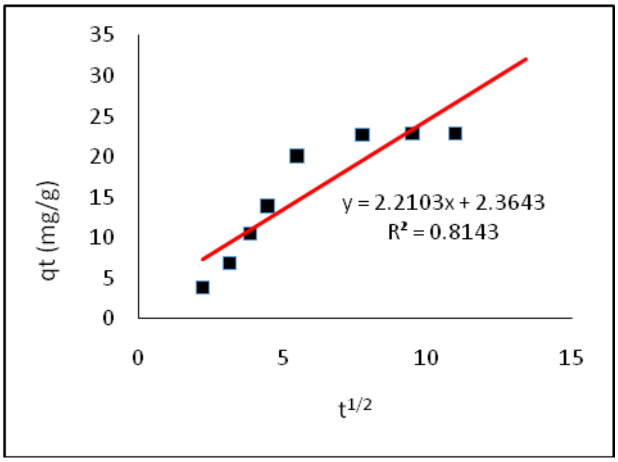


Fig. 12 Intra-Particle Diffusion

Table: 2 pseudo first order, pseudo second order and Intra-particle Diffusionconstants

Metal	**Pseudo- First Order**			**Pseudo- Second Order Model**			**Intra-Particle Diffusion**		
Ni^{2+}	**qe**	**k_1**	**R^2**	**qe**	**k_2**	**R^2**	K_d	**I**	**R^2**
	51.074	0.1018	0.991	28.386	0.00145	0.9921	2.2103	2.3643	0.8143

IV. CONCLUSION

The present investigation shows that CFA is an excellent free of cost available adsorbent used for the removal of Ni(II) ions from aqueous solutions. The adsorption parameters such as solution pH, adsorbent dose, initial Ni(II) ions concentration and contact time were studied in the experiment and the maximum adsorption of Ni(II) ions was found 91.8 % at pH 6 using 50 mg/L of Ni(II) ions solution with 0.4 g of adsorbent dose. Adsorption equilibrium data is best fitted to Langmuir model. The maximum adsorption capacity, q_m obtained from Langmuir model was 3.2499mg/g. The adsorption process was found to be chemical in nature and occurred by forming monolayer of Ni(II) ions. From these observations it can be concluded that CFAhas a high potential, inexpensive and non-hazardous industrial waste which could be used as an effective indigenous material for treatment of wastewater stream containing nickel ions.

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