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Adsorption Kinetics of Ni(II) Using Kaolinite Clay Part-I

ANIMA S. DADHICH*, SHAIK KHASIM BEEBI, MISS G.V. KAVITHA and K.V.K. CHAITANYA

Department of Environmental Studies, College of Engineering
Gandhi Institute of Technology and Management, Visakhapatnam-530 045, India

The present work involved Ni(II) removal by a non-conventional adsorbent, Kaolinite clay. The effect of contact time, adsorbent dosage, pH and initial concentration of the metal ion on the kinetics of adsorption was studied. It was observed that Ni(II) removal increases with increasing contact time and becomes constant after 5 h. As the adsorbent dosage is increased from 2 to 4 g percentage reduction increase continuously. The effect of pH on the removal of Ni(II) showed that percentage adsorption increases with increasing pH up to 9. The adsorption data was fitted will in Freundlich isotherm, Langmuir isotherm, Langergran's equation and also Weber Morris equation.

Key Words: Adsorption, Ni(II), Kaolinite clay, Batch technique, Langmuir isotherm.

INTRODUCTION

As the human population is increasing by leaps and bounds, there is need for more production in all spheres. Many industries are coming up polluting more and more while leaving the biosphere foul and unpleasant. The incidence of air and water pollution from metals has reached such an alarming level that environmentalists are finding it difficult to enforce control measures. All these pollutants seriously interfere with bioenvironmental process and thereby posing a menace to the life on this planet. Metals have been classified into essential and non-essential group. The former consists of Ca, Mg, K, Fe, Mn, Zn, Cu and the latter of Hg, Pb, Cd, Ni, As and Se. The metals of the second group, directly or indirectly, have adverse consequence on biological activities. Wastewater, which contains heavy metal pollutants cause direct toxicity, both to human and other living beings due to their presence beyond specified limits.

The main goal today is "To adopt appropriate methods and to develop suitable techniques either to prevent the metal pollution or to reduce it to very low levels". Various physical and chemical methods like precipitation, electrodialysis, reverse osmosis, ion exchange and adsorption are involved in the removal of heavy metals[1]. Conventional adsorbents like activated carbon are effective in removal of heavy metals. But they are costly when compared to the non-conventional adsorbents like kaolinite clay, bentonite clay, etc. The use of low cost adsorbents in the wastewater treatment is recommended since they are relatively cheaper and available locally. In the present investigation an attempt is made to adsorb Ni(II) on kaolinite clay. Nickel is present in the wastewaters of electroplating industry. In India there are over 50,000 large, medium and small electroplating units, mostly scattered in the urban areas. Most of the industries are not able to meet standards for the discharge of their effluents. WHO has prescribed a maximum concentration of Ni(II) in drinking water as 0.1 mg/L, whereas in electroplating effluent water it may be up to 50 mg/L[2]. Thus the effluent water has to be treated for the removal of Ni(II).

EXPERIMENTAL

The procedures and methods followed to investigate the adsorption of nickel using nonconventional adsorbent, kaolinite clay, have been described in detail. All the chemicals used were of analytical grade and double distilled water was used for all experimental work. Nickel was analyzed spectrophotometrically using standard methods[3]. Batch experiments were carried out to study the kinetics of adsorption of Ni(II) from aqueous solution using kaolinite clay as adsorbent. The effect of following parameters on the adsorption of Ni(II) was studied:

- Effect of contact time
- Effect of adsorbent dosage
- Effect of pH
- Effect of initial concentration

The contact time was varied from 30 to 420 min. The adsorbent dosage was varied from 2 to 10 g/L and pH was varied from 1 to 9. The initial metal concentration was varied from 5 to 100 ppm.

RESULTS AND DISCUSSION

The adsorption kinetics for removal of nickel from aqueous solution of Ni(II) was studied using a non-conventional adsorbent, Kaolinite clay. The results of these studies are presented below:

Effect of contact time: It was shown that the contact time has a great effect on nickel removal. By increasing the contact time, the adsorption percentage also increases up to 5 h. Afterwards it decreases (Fig. 1). 50% reduction was observed in first 30 min of contact time due to the availability of vacant sites. As the contact time is increased further, the % reduction increases at a slower rate up to 4 h. Then it becomes constant up to 6 h. Thereafter, the % reduction decreases with increasing the contact time, probably due to desorption of metal ions back to that solution. The maximum removal was noted at 5 h (300 min) and the per cent reduction in the metal ion observed was 85%.

Effect of adsorbent dosage: It is necessary to determine the dosage of adsorbent required to achieve a desired level of treatment with a view to economize on the amount of adsorbent to be used. It has been shown by several workers that the extent of adsorption at solid solution interface is a strong function of adsorbent dosage. In the present study, the effect of various adsorbent dosages of kaolinite clay on nickel removal was studied. It was observed that as the adsorbent dosage is increased from 2 to 4 g, the % reduction of the metal ion also increased continuously

(Fig. 2). After 4 g while applying more dosages, *viz.*, 5, 6, 8, 10 g it was observed that the per cent reduction decreased continuously, might be due to less contact of the adsorbent with the adsorbate when present in bulk. The maximum removal was noted for 4 g dosage.

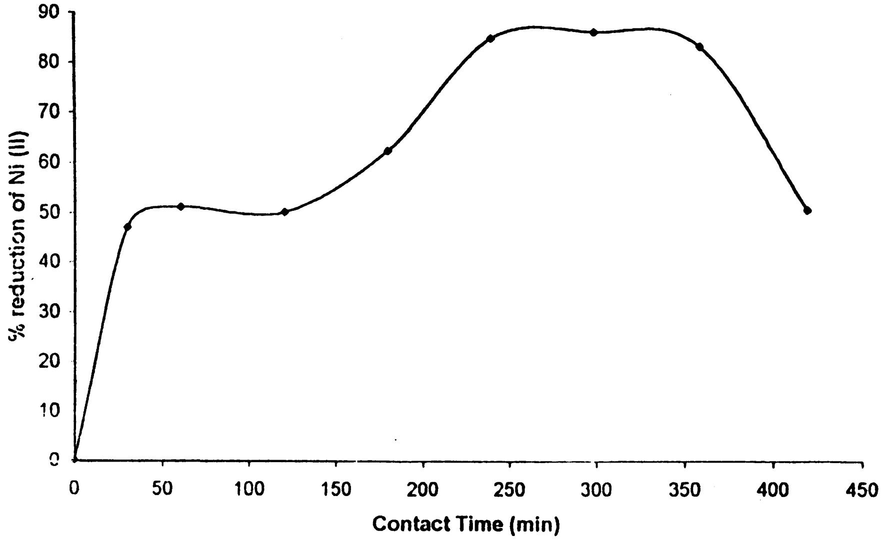

Fig. 1. % reduction *vs.* contact time

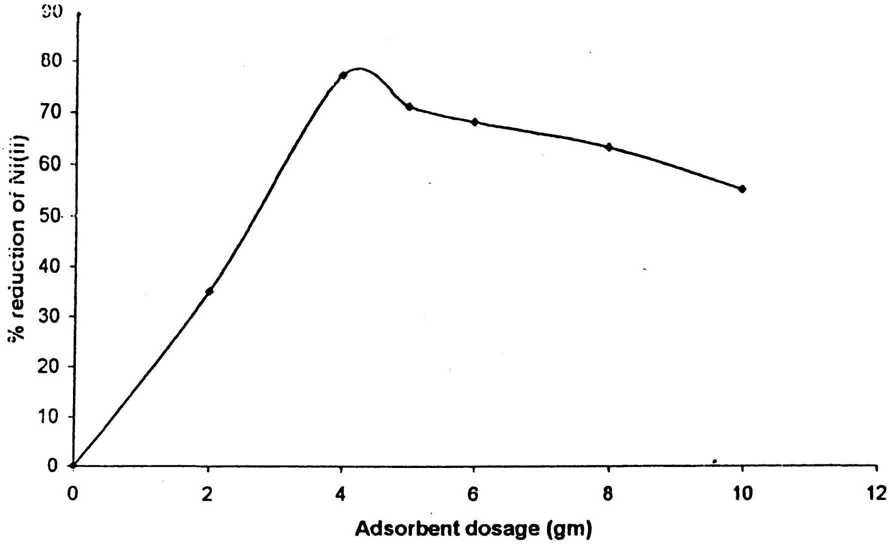

Fig. 2. Reduction of Ni(II) *vs.* adsorbent dosage

Effect of pH: The pH of a solution from which adsorption occurs may affect the extent of adsorption for several reasons. Due to strong adsorption of hydrogen from the solution and hydroxyl ions, the adsorption of the ions is strongly influenced. The pH of the solution also affects the degree of ionization and in turn affects the extent of adsorption. Increase in hydrogen ion concentration also results in neutralization of negative charge at the surface of the adsorbent thereby reducing hindrance to diffusion and making available more of the active surface of the adsorbent.

The % reduction was found to be increased with increasing pH up to 9 due to less competition offered by H^+ ion (Fig. 3), which is of smaller size as compared with Ni(II). Since adsorption is affected by the presence of free metal ion concentration as pH increased above 7 towards alkaline side, the solution was observed to be turbid probably due to formation of metal hydroxides. The higher percentage of reduction may be due to precipitation along with adsorption or adsorption of monodental metal complex formed due to hydrolysis. Though, higher percentage of reduction was observed at pH 8, the optimum value chosen for futher batch studies was pH 6 due to the lack of crystal structure of the adsorbent to show the hydroxide complex asdorption.

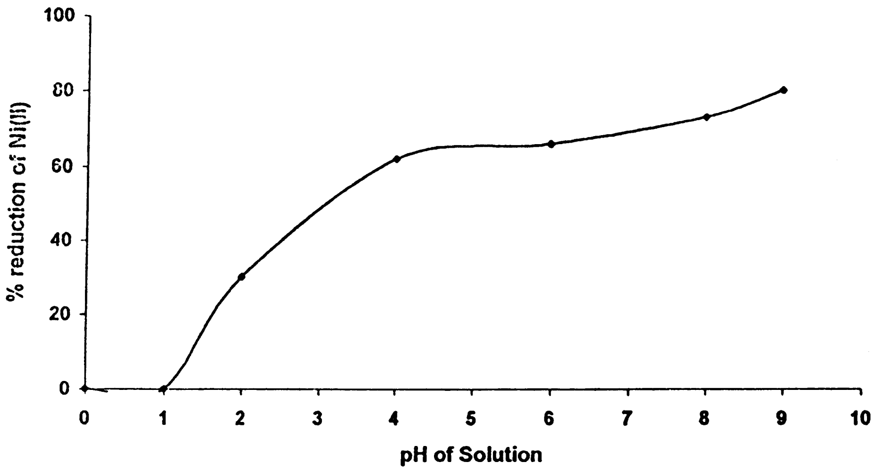

Fig. 3. Reduction of Ni(II) *vs.* pH

Effect of concentration: The effect of concentration on adsorption of solute is dependent on several factors such as pH, temperature, ionic strength of solution, particle size, dosage *etc.*, of the adsorbent. Several investigations have reported reduction in percentage adsorption with increase in metal ion concentration. A similar observation is reported from the data obtained from removal of Ni(II) using Kaolinite clay as absorbent.

The Ni(II) cocnetrations taken as 5, 15, 20, 30, 40, 50, 60 and 100 ppm with adsorbent dosage of 4 g, pH 6 and for a contact time of 5 h. It is observed that by increasing concentrations, the percentage removal of Ni(II) is decreasing simultaneously (Fig. 4). The rate constant K *vs.* ln C_i/C_e was plotted (Fig. 5) for varying metal concentrations which shows it to be a first order kinetics.

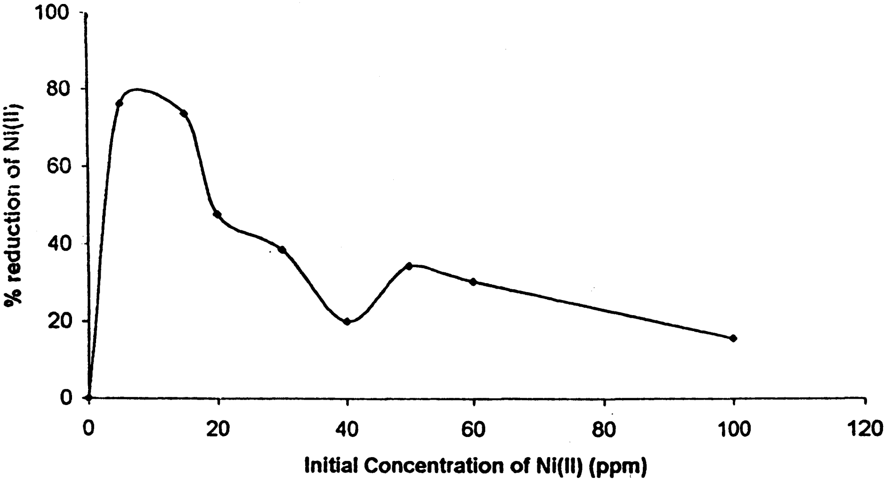

Fig. 4. Percentage reduction of Ni(II) *vs.* initial concentration

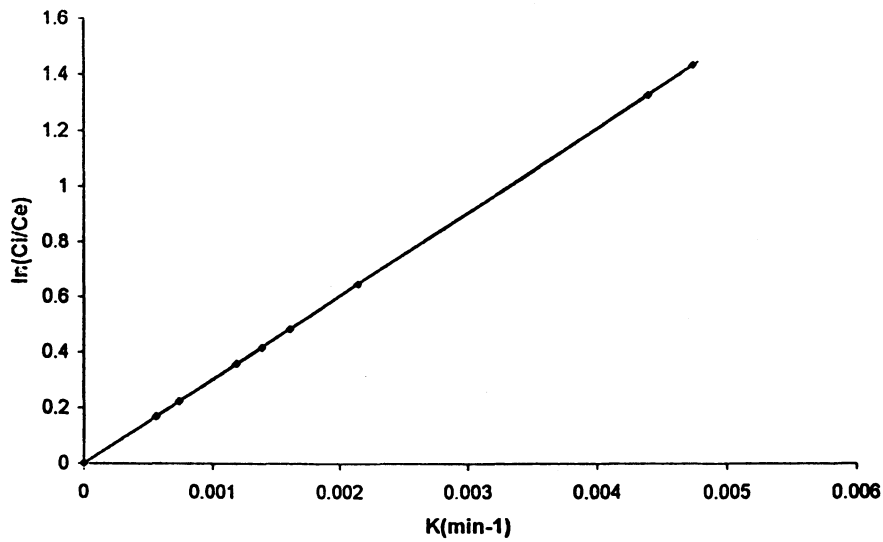

Fig. 5. Rate constant (K) *vs.* ln (C_i/C_e)

Adsorption isotherms: Models for characterizing the equilibrium of a solute among the phases and interfaces of a system typically relate the amount of solute, Q_e, adsorbed per unit of an adsorbing phase or interface to the amount of solute concentration, C_e, retained in the solvent phase. This type of expression at constant temperature is known as "isotherm". The isotherm, plotted between log C_e and log Q_e, is found to be linear over a wide range of concentrations (Fig. 6). The values of Freundlich constants K and 1/n are given in Table-1.

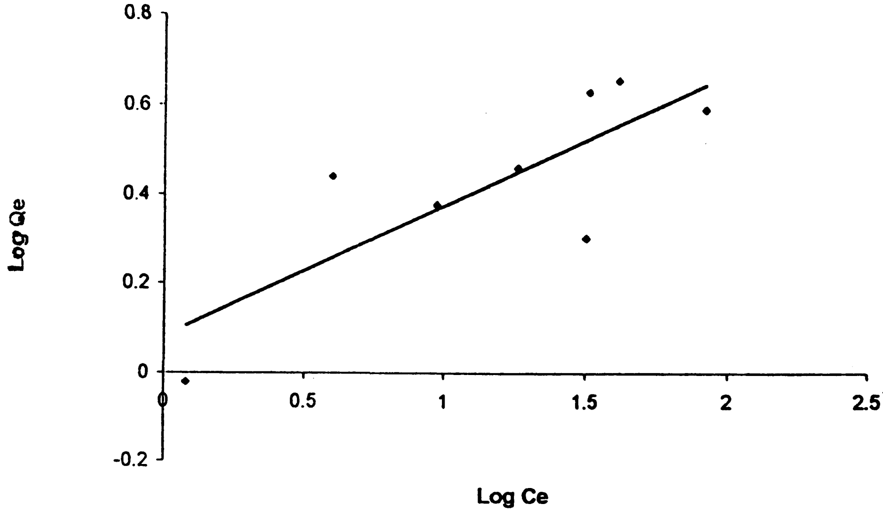

Fig. 6. Freundlich adsorption plot for log C_e *vs.* log Q_e

TABLE-1
FREUNDLICH ISOTHERM CONSTANTS

Adsorbent used	K	1/n
Kaolinite clay	0.2912	0.0820

The langmuir isotherm plotted between C_e and C_e/Q_e was found to be linear over a wide range (Fig. 7). The values of the Langmuir constants C_0 and b are given in the

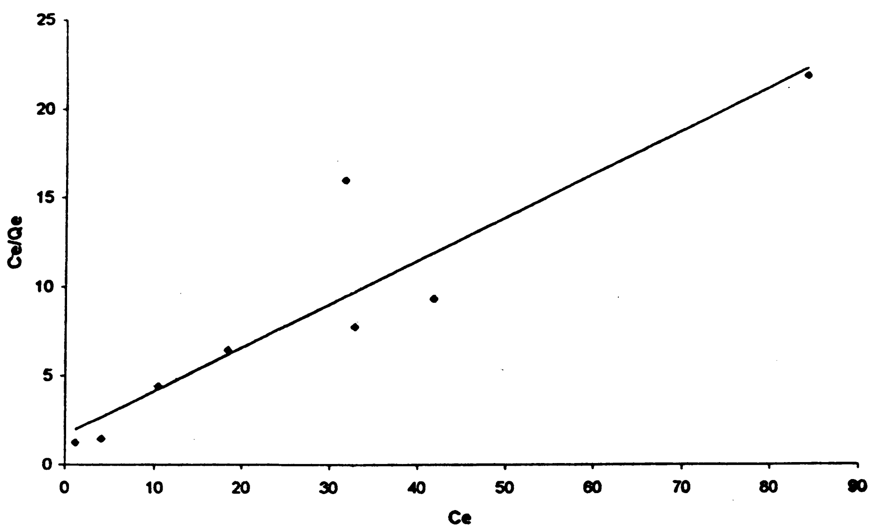

Fig. 7. Langmuir plot of C_e *vs.* C_e/Q_e

Table-2, which were calculated from slopes and intercepts of the Langmuir plot. The essential characteristics of the Langmuir isotherm may be expressed in terms of a dimensionless equilibrium parameter R_L^1. The value of $R_L > 1$ shows unfavourable adsorption, the value of $R_L = 1$ shows linear adsorption and the value of $R_L < 1$ shows favourable adsorption.

TABLE-2
LANGMUIR ISOTHERM CONSTANTS

Adsorbent used	Qo	b
Kaolinite clay	0.2430	1.7052

An attempt has been made to analyze the results in the light of the Lagergren model[2] with a view to evaluate the mechanistic parameter associated with the adsorption process. This equation suggests linearity for the plot of log $(C_e - Q_e)$ against time. A linear relationship was observed among the plotted parameters indicating the applicability of the above equation and the first order value of the uptake of the adsorbate (Fig. 8). It is of interest to study the probability of the adsorbate species to diffuse into the interior sites of the particles of the adsorbent. For this purpose, Weber Morris equation[4] was tested.

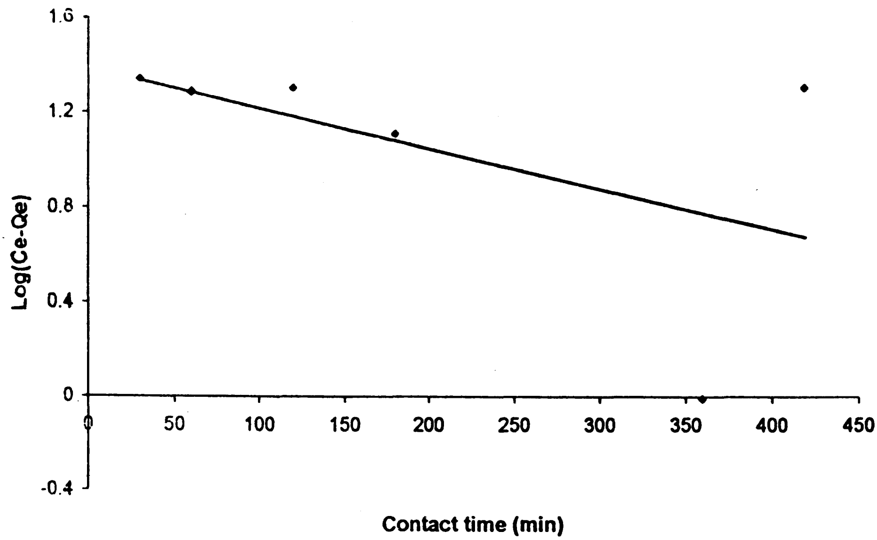

Fig. 8. Lagergren adsorption plot for contact time *vs.* log $(C_e - Q_e)$

The linear plot indicates the diffusion of the adsorbate species from the surface film into the micro pores. The line is not passing through the origin thereby indicating that intraparticle diffusion is not the only rate-determining step (Fig. 9).

The molar free energy[5] changes were calculated for varying concentrations at 27°C. The magnitude of such negativity of G varied from –3559.51 to –420.07. The decrease in G provides a measure of decrease in the concentration of adsorbate in the solute phase. The negative value indicates the spontaneity of adsorption.

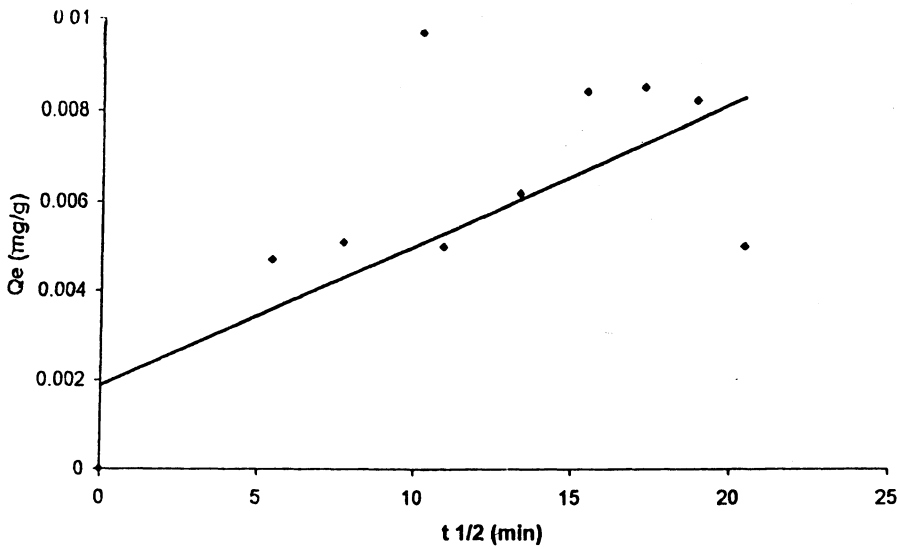

Fig. 9. Weber and Morris plot of $t_{1/2}$ *vs.* Q_e

TABLE-3
% REMOVAL OF Ni(II) USING KAOLINITE CLAY FOR VARIOUS INITIAL CONCENTRATIONS

Adsorbent used:	kaolinite clay	Contact time	5 h
Adsorbent dosage	4 g	pH	6
Temperature	Room temperature		

S. No.	Concentration (ppm)	Remaining concentration, C_e (mg/L)	Amount of metal ion adsorbed $(C_i - C_e)$ (mg/L)	$Q_e = \frac{C_i - C_e}{\text{Wt. of adsorbent}}$ (mg/g)	log C_e	log Q_e	K (min^{-1})	G ($J K^{-1} mol^{-1}$)	% Reduction
1	5	1.2	3.5	0.950	0.079	0.022	0.00475	–3559.51	76.0
2	15	4.0	11.0	2.750	0.602	0.439	0.00441	–3296.72	73.3
3	20	10.5	9.5	2.375	0.978	0.376	0.00215	–1607.16	47.5
4	30	18.5	11.5	2.875	1.267	0.459	0.00161	–1205.76	38.3
5	40	32.0	8.0	2.000	1.505	0.301	0.00074	–556.56	20.0
6	50	33.0	17.0	4.250	1.519	0.628	0.00139	–1036.38	34.0
7	60	42.0	18.0	4.500	1.623	0.653	0.00119	–889.62	30.0
8	100	84.5	15.5	3.875	1.927	0.588	0.00056	–420.07	15.5

Conclusion

- The optimum contact time for removal of Ni(II) using Kaolinite clay was 5 h (300 min).
- The optimum adsorbent dosage for removal of Ni(II) was found to be 40 g/L.

- The optimum pH for adsorption of Ni(II) from aqueous solution using kaolinite clay was found to be 6.
- The percentage removal for an intial concentration of 5 ppm for a dosage of 40 g/L of kaolinite clay at pH 6 and for a contact time of 5 h (300 min) was found to be 76%, whereas for an initial concentration of 100 ppm under the same optimum conditions, it was found to be 15.5% indicating that at high concentration of metal ions, the efficiency of the adsorbent has been decreased.
- The adsorption of Ni(II) using kaolinite clay follows Freundlich isotherm. It was found to be linear over a wide range.
- Langmuir isotherm was fitted well into the adsorption of Ni(II) using kaolinite clay.
- The limitless separation factor (R_L) for Langmuir isotherm was found to be < 1, hence it predicts a favourable adsorption.
- The molar free energy was found to be in the range for varying metal concentration. The negative value of the free energy indicates the spontaneity of the adsorption of Ni(II) using kaolinite clay.
- The plot of ln (C_i/C_e) *vs.* K (min^{-1}) was found to be linear indicating the first order value of the adsorption process.
- Lagergren equation and Weber-Morris equation were fitted well for the adsorption data and was found to be linear, further supporting the first order kinetics of the adsorption.

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