

Comparative Study of Adsorption Kinetics of Ni (II) Using China Clay and Flyash as Adsorbents

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Abstract: The present study was aimed to compare the study of adsorption kinetics and percentage removal of Ni (II) using China clay and Fly ash as adsorbents. The effect of contact time, adsorbent dosage, pH of system and initial concentration on the kinetics of adsorption was studied. The rate constants for the removal of Ni (II) with both adsorbents for varying metal ion concentration showed it to be a first order kinetics. Adsorption data was fitted well into Freundlich adsorption isotherm.

Keywords: Adsorption, Nickel, China clay, Fly ash, Batch adsorption technique, pH, Kinetics

1. Introduction

The presence of heavy metals in the aquatic ecosystem has been of increasing concern because of increase in discharge, their toxic properties and other adverse effects of receiving water uses. Heavy metal pollutants seriously interfere with bioenvironmental process and thereby posing a menace to the life on this planet. Due to rapid growth of populations and industrialization throughout the world water is highly polluted and has thus become undesirable for all living beings. A metal such as Lead, Cadmium, Copper, Arsenic, Nickel, Chromium, Zinc and Mercury has been recognized as hazardous heavy metals [1]. Nickel and its compounds are widely used in many industries such as metal plating industry [2], silver refineries [3], automotive plating of zinc base castings [4] and plating plants [5]. The permissible limit of nickel in drinking water is 1.0 mg/l [6]. Nickel affects the air pockets of lungs resulting in respiratory symptoms and causing lung cancer. Doses of Nickel sulphate induce myocardial and liver damage [7].

In the present study a comparison of the adsorption kinetics of Ni (II) using China clay and Fly ash was made.

2. Experimental

The procedure and technique followed to investigate the adsorption using two adsorbents ie, China clay and Fly ash. The chemical analysis of both the adsorbents are given below:

Table 1: Chemical analysis of China clay as Adsorbent

Constituents	Percentage by weight
SiO ₂	46.22
Al ₂ O ₃	38.40
CaO	0.86
Fe ₂ O ₃	0.68
MgO	0.37
Loss of ignition	13.47

Table 2: Chemical analysis of Fly ash as Adsorbent

Constituents	Percentage by weight
SiO ₂	56.04
Al ₂ O ₃	25.90
CaO	2.22
Fe ₂ O ₃	1.26
MgO	0.94
Loss of ignition	13.64

Batch adsorption technique was conducted to calculate the effect of concentrations of adsorbate Ni (II) solution, contact time, adsorbent dosage, pH of solutions were prepared from nickel sulphate in 250ml flask. Nickel samples were prepared by dissolving a known quantity of nickel sulphate in distilled water and used as stock solutions. Known amount of adsorbent was mixed with 100 ml of aqueous solutions of various initial concentrations (1.0gm/l, 2.0gm/l, 3.0gm/l, 4.0gm/l and 5.0gm/l) of Ni (II) in each flask. The stirring speed was kept constant at 120 rpm. Dimethylglyoxime method was used and absorbance was measured at 445 nm with spectronic-20 spectrophotometer. The concentration of Ni (II) at different time adsorbed onto adsorbent was calculated by the equation.

$$Q_t = (C_o - C_e) V/M$$

Where, Q_t is the amount of Ni (II) adsorbed on the surface of Red mud at different time t . C_o is the initial concentration of Ni (II) and C_e is the aqueous phase concentration of Ni (II) at time t . V is the volume of aqueous phase. M is the weight of adsorbent. The experiments were repeated by taking both the adsorbents. The equilibrium data was fitted into Freundlich adsorption isotherm.

3. Result and Discussion

3.1 Effect of contact time

It was observed that the contact time has a great effect on the removal of Ni (II) solution. The result indicates that the percentage adsorption increases as the contact time increases and become constant after 120minutes for both the adsorbents. This indicates that the equilibrium was attained up to 120minutes, as there was no further significant change in equilibrium concentrations. The percentage removal of Ni (II) observed was 90 for China clay, whereas 87 for Fly ash

(Figure: 1).

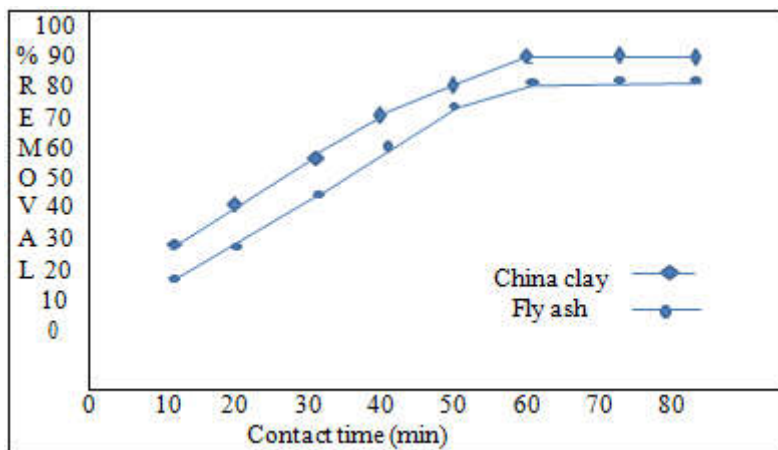


Figure 1: Percentage removal of Ni(II) vs Contact time

3.2 Effect of Adsorbent Dosages

The effect of various adsorbent dosages of China clay on Ni(II) removal was studied. It was observed that as the amount of adsorbents dosage increased from 0.4, 0.8, 1.2, 1.6, 2.0 gm, the percentage of removal of Ni(II) ion increased continuously. Similar observation was also made for Fly ash as adsorbent (Figure: 2). It is due to presence of more

adsorption sites on the outer surface of adsorbent. As the adsorbent dosage increased, more active sites and surface area of the adsorbent become available for adsorption [8]. The adsorbent dosage is an important parameter for adsorption studies because it determines the capacity of adsorbent for a given initial concentration of Ni(II) solution [9].

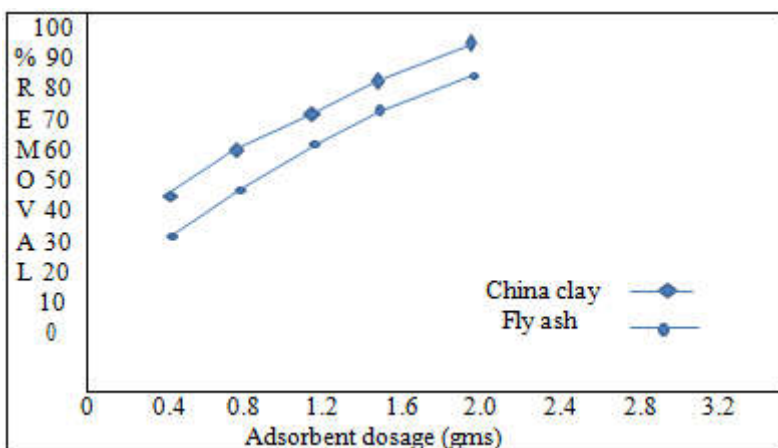


Figure 2: Percentage removal of Ni(II) vs Adsorbent dosage

The percentage adsorption for initial concentration of 3.0 mg/l of Ni(II) for contact time of 120 min with a dosage of 2.0 gm of China clay and Fly ash were 77.87 and 74.40 respectively.

3.3 Effect of pH

The batch adsorption experiments were conducted at different pH values and evaluated the effect of pH on the adsorption of Ni(II) with China clay and fly ash.

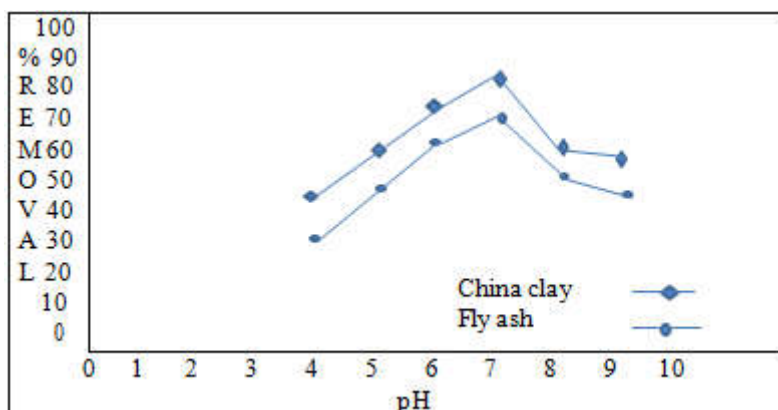


Figure 3: Percentage removal of Ni(II) vs pH

It affects the surface charge of the adsorbent, degree of ionization and speciation of aqueous Ni (II) solutions. Three types of mechanism were suggested by Mac-Naughton and James [10] for heavy metals removal from aqueous solutions.

- 1) Ion exchange reactions.
- 2) Metal ion adsorption at hydrated oxides of the surface.
 - (iii) Metal hydroxyl species adsorption at hydrated oxide surface.

The effect of pH on adsorption of Ni (II) on China clay was studied at pH 4.0, 5, 0, 6.5, 7.0, 8, 0 and 9.0. The maximum adsorption capacity of China clay was found to be at pH 7.0 (Figure: 3). It was observed that Ni (II) adsorption increases with increasing pH value in the range 3.0 to 7.0 and thereafter adsorption decreases up to 9.0 pH. The decrease in percentage removal at high pH value may be due to the fact that Ni (II) generally form hydroxides at higher pH. Metal ion adsorption is mostly governed by the free metal ion concentration. At high pH hydroxyl ions complete with the metal ion for the adsorption.

The increase in hydrogen ion concentration at low pH of 7 may be result in neutralization of negative and positive charges at the surface of the adsorbent thereby reducing hindrance to diffusion and making more of the active surface

of the adsorbent [11].

3.4 Effect of Concentration

It was reported that percentage removal decrease with increase in metal ion concentration. Similar observation was made from the data obtained for removal of Ni (II) ion by using China clay and Fly ash as adsorbents. The initial concentration was taken from 1, 2, 3, 4 and 5mg/l with adsorbent, dosage of 2gm at ph 7.5 for a contact time 120 minutes. The percentage removal of Ni (II) continuously decreased from 90.20, 81.6, 77.87, 72.85 and 60.64 as Ni (II) ion concentration increased for China clay. In case of Fly ash the percentage removal decreased from 87.20, 79.90, 74.40, 67.90 and 62.04 with increase in Ni (II) ion concentration (Figure: 4).

Generally, adsorption follows first order rate kinetics. The rate constant for the adsorption of Ni (II) ion were calculated from the equation.

$$K = \frac{1}{t} \ln \frac{C_i}{C_e}$$

Where t is the contact time, Ci is the initial concentration of metal ion, Ce is the final concentration after adsorption. The results have been given in table 3 and 4.

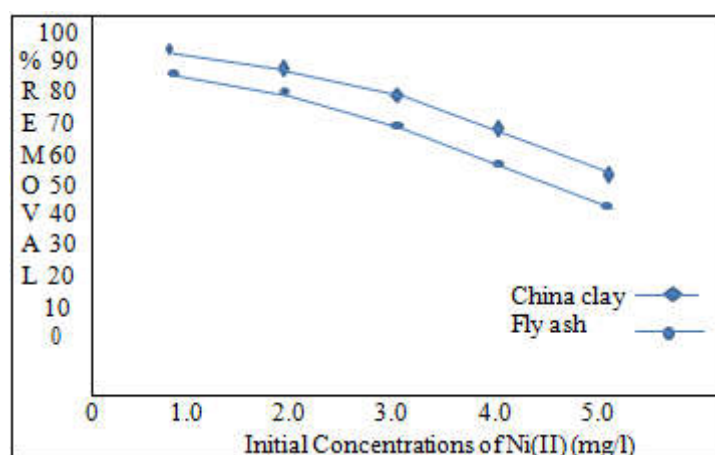


Figure 4: Percentage removal of Ni (II) vs Initial Concentration.

Table 3: Percentage removal of Ni (II) using China clay at various initial concentrations

S. No	Initial conc of Ni (II) (mg/l)	final conc of Ni (II) (mg/l)	Amount of Ni (II) adsorbed	qe	log Ce	log qe	K (min ⁻¹)	% Removal
1	1.0	0.098	0.902	0.049	-1.09	-1.31	0.019	90.20
2	2.0	0.368	1.632	0.184	-0.43	-0.74	0.013	81, 60
3	3.0	0.664	2.336	0.332	-0.18	-0.48	0.012	77.87
4	4.0	1.086	2.914	0.543	0.04	-0.27	0.010	72.85
5	5.0	1.968	3.032	0.984	0.30	-0.01	0.007	60.64

Table 4: Percentage removal of Ni (II) using Fly ash at various initial concentrations

S. No	Initial conc of Ni (II) (mg/l)	final conc of Ni (II) (mg/l)	Amount of Ni (II) adsorbed	qe	log Ce	log qe	K (min ⁻¹)	% Removal
1	1.0	0.128	0.872	0.064	-0.89	-1.19	0.016	87.20
2	2.0	0.402	1.598	0.201	-0.39	-0.70	0.013	79, 90
3	3.0	0.768	2.232	0.384	-0.11	-0.42	0.011	74.40
4	4.0	1.284	2.715	0.642	+0.11	-0.19	0.009	67.90
5	5.0	1.898	3.102	0.949	+0.28	-0.02	0.007	62.04

The equilibrium data fitted into Freundlich adsorption isotherm and were found to be linear over a wide range of concentrations (figure: 5 and 6).

Straight line graphs were obtained when $\ln \frac{C_i}{C_e}$ were plotted against K, which passes through origin indicate first order rate kinetics for both adsorbents.

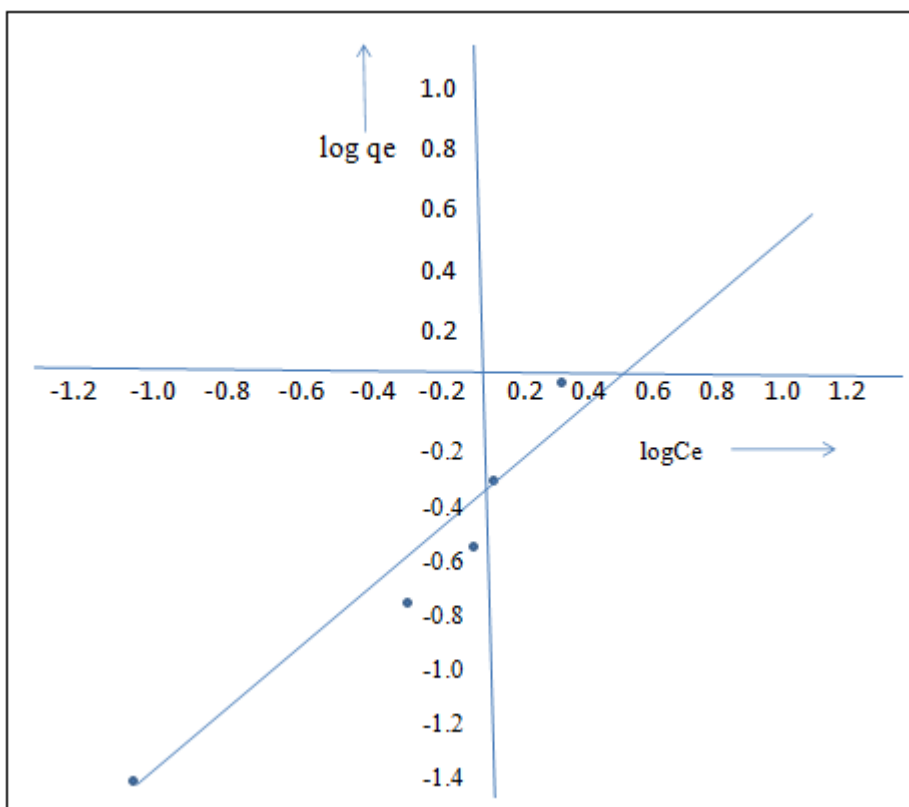


Figure 5: Plot of log Ce vs log qe for various concentration of Ni (II) using China clay

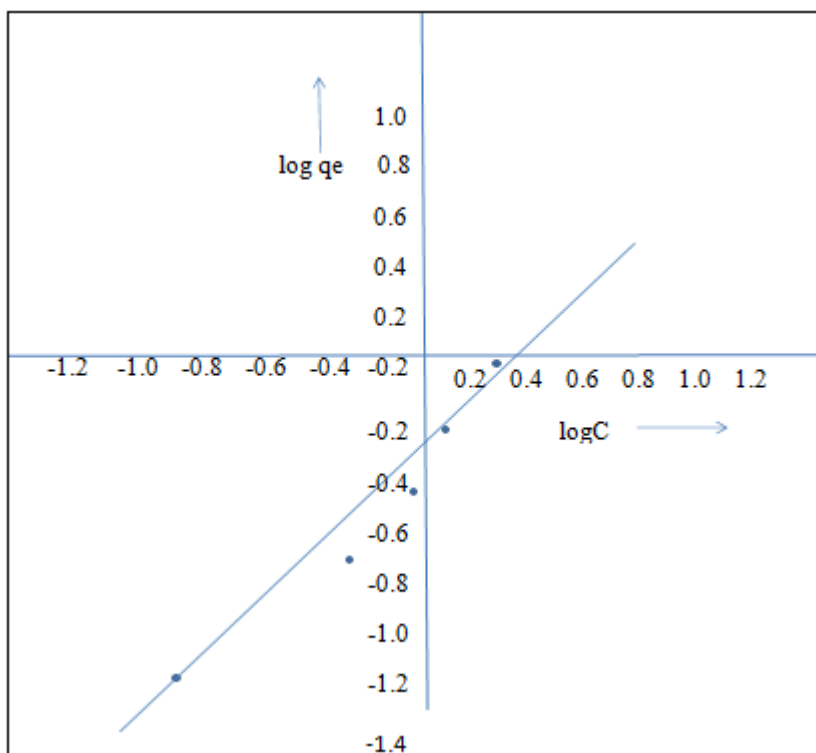


Figure 5: Plot of log Ce vs log qe for various concentration of Ni (II) using Fly ash.

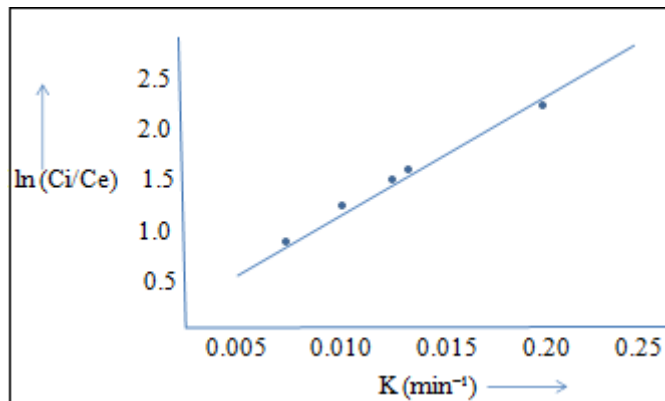


Figure 7: Plot of K vs $\ln(C_i/C_e)$ for various Ni (II) concentrations using China clay.

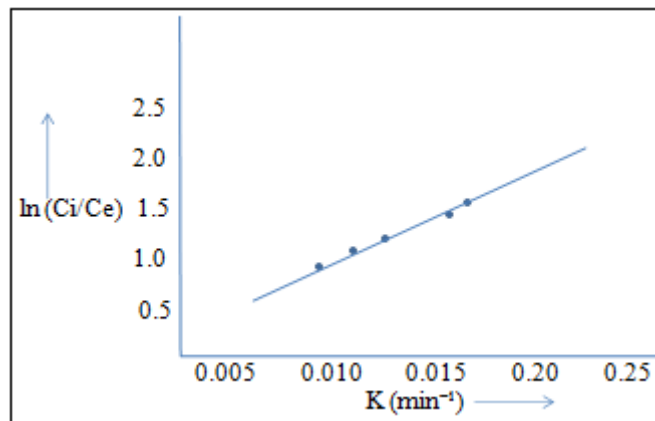


Figure 8: Plot of K vs $\ln(C_i/C_e)$ for various Ni (II) concentrations using Fly ash.

4. Conclusion

The maximum contact time and pH of solution for the removal of Ni (II) from both adsorbents was 120 minutes and 7.0 respectively. It was found that the higher the concentration of metal ions lower the efficiency of adsorbents.

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