

Nickel Removal by Activated Sludge: Sorption Isotherms and Kinetics

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Abstract

Presence of nickel in wastewater adversely affects man and environment. The higher concentration of nickel causes poisoning effect like headache, dizziness, nausea, dry cough, vomiting, chest pain, rapid respiration, cyanosis and extreme weakness. Activated sludge has biological adsorptive properties. Dry activated sludge has been proved to be effective biosorbent. Present research is aimed at studying use of wet activated sludge for nickel removal. Also optimum values for sorbent dose, contact time and initial concentration are reported. The behaviour of activated sludge with respect to nickel removal was as expected. With initial increase in adsorbent dosage, rise in nickel removal was observed. There after it was followed by constant removal and then slight drop. For contact time, the nickel removal increased rapidly initially and then it became gradual. The initial nickel concentration had positive effect on nickel removal, but the percentage removal drops. Considering concentration profile of treated effluent at various initial concentrations, 1000 mg/l was considered as optimum concentration.

Keywords - Kinetics, isotherm, solute uptake, dosage, adsorption capacity, analysis.

I. INTRODUCTION

Nickel is used in catalyst, electroplating, batteries, petrochemical industries. It is one of the major pollutants in the effluent which is discharged from these industries. The acceptable limit of nickel in drinking water is 0.01 mg/liter and the industrial discharge limit in wastewater is 2 mg/liter. Presence of nickel in wastewater adversely affects man and environment. The higher concentration of nickel causes poisoning effect like headache, dizziness, nausea, dry cough, vomiting, chest pain, rapid respiration, cyanosis and extreme weakness. Nickel can be removed by adsorption, ion exchange, membrane separation, chemical precipitation and biological methods. Biological methods include activated sludge process and trickling filter process. Activated sludge process is effective and environment friendly. Its serves the purpose of treating waste by using waste thereby minimizes the solid waste problem. Various investigators have studied activated sludge process for removal of Nickel. They have studied the effect of affecting parameters and isotherm-kinetic aspects of nickel uptake.

A. Overview of Activated Sludge Process

The objective of biological treatment of sewage is to coagulate and remove the nonsettable colloidal solids and to stabilize the organic matter with the help of micro-organisms (bacteria). For domestic sewage the major objective is to reduce the organic content and in many cases, the nutrients, such as nitrogen and phosphorus. For agricultural return sewage, the objective is to remove the nutrients, specifically nitrogen and phosphorous which are capable of stimulating the growth of aquatic plants. For industrial sewage, the objective is to remove or to reduce the concentration of organic and inorganic compounds. The activated sludge process for sewage treatment is based on providing intimate contact between the sewage and activated sludge. The activated sludge is the sludge which is obtained by settling sewage in presence of abundant oxygen so as to be enriched with aerobic micro-organisms. Thus activated sludge is biologically active and it contains a large number of aerobic bacteria and other micro-organisms which have an unusual property to oxidize the organic matter. The main advantage of activated sludge process is that it offers secondary treatment and an effluent of high quality with a minimum land area requirement. However, in this process a rather close degree of control is necessary in its operation to ensure that (i) an ample supply of oxygen is present (ii) there is intimate and continuous mixing of the sewage and the activated sludge (iii) the ratio of the volume of activated sludge added to the volume of the sewage being treated is kept practically constant [1]. Activated sludge has tendency to accumulate heavy metals. The industries like petrochemical industries, refinery plant, paper mills and chemical industries are sources of nickel in wastewater. These heavy metals disrupt the wastewater treatment plants performance by affecting microorganisms and synthetic reaction due to their toxicity. Consequently, the concentration of these compounds exceeds the maximum contamination level (MCL) in the effluent of wastewater treatment plants and causes many health and environmental problems. It is proven fact that microorganisms have ability to degrade heavy metal compounds. Biological activated sludge is widely used for removing heavy metals from industrial wastewaters. Bioreactors with fixed activated sludge beds are one of suitable method in this subject [2].

B. Literature Survey

Moving Bed Biofilm Bioreactor for heavy metal removal from wastewater was used by Alasl and Beiki [3]. Chemical oxygen demand (COD) and nickel removal of 85 percent and 33 percent nickel was obtained by them. An investigation on influence of anoxic selectors on heavy metal removal by activated sludge was carried out by Niec and Cha [4]. They compared the metal binding characteristics of an anoxic selector activated sludge system with a conventional activated sludge system. Their studies revealed that the selector sludge had significantly higher sorption capacity than the control sludge. Dhokpande et.al. found that activated sludge has been used for the heavy metal treatment efficiently by many researchers[5]. Maximum removal efficiency of 95 percent has been reported. According to the studies, the removal efficiency can be increased by techniques such as immobilization and use of anoxic selectors. Similar review was carried out by Gunatilake [6]. The review reiterated that activated sludge process is one of the efficient and effective methods for nickel removal. Anaerobic sludge was used for nickel sorption by Colussi et. al. They also studied the effect of removal of Nickel on methane production [7]. Biosorption of Ni (II) on industrial anaerobic sludge at 308.1 K and 7.5 pH in a batch reactor was observed by them. Also, they observed that the 10.25 mg of Ni was removed per gram of total suspended solids (TSS). Nickel uptake followed Freundlich isotherm. Their results showed that methane production drops rapidly with low metal concentration. Percentage nickel removal was observed to be 98.3 percent. Hashim studied nickel removal by Dried Water Hyacinth (*Eichhornia Crassipes*)[8]. Parameters like biosorbent dosage, contact time, pH and temperature were optimized in the research. They prepared synthetic solution of nickel in the form of 10 g/L of NiSO₄.6H₂O. Optimum adsorbent dose, contact time, pH and temperature were observed to be 3 g/l, 50 minutes, 6 and 35 °C respectively. Abdolmaleki et. al prepared conductive polypyrrole (PPV) for nickel removal from aqueous solution [9]. They carried out comparative studies on various adsorbents like anthracite, activated carbon and purolite with conductive electro active polypyrrole composite. The study indicated that the removal percentage decreased with increasing concentration of adsorbent. Also it was observed that alkaline nature of the solution favours metal removal.

II. EXPERIMENTAL PROCEDURE

A. Preparation of Synthetic Effluent:

1000 ml stock solution was prepared by adding 4.47gm of nickel sulphate in distilled water. The total volume was made up to 1000 ml. The stock solution corresponds to 1000 mg/liter of nickel. Standard nickel solutions were prepared by appropriate dilution of stock solution. The stock

solutions of different concentration ranges from 5 to 60 mg/liter were prepared.

B. Collection and Treatment of Activated sludge:

Activated sludge was collected from nearby sewage treatment plant in Airoli, Navi Mumbai. Sludge was concentrated by removing supernatant after allowing to settle for 10 hours.

C. Analysis:

UV spectrophotometric method was used for analysis.

D. Batch Studies for ASP:

Batch experiments were carried out for studying the effect of parameters namely adsorbent doses, contact time, pH and initial metal ion concentration. Initially sludge was collected from nearby sewage treatment plant and allowed to settle for 10 hours. It was filtered and used for batch studies.

III. RESULTS AND DISCUSSION

A. Effect of Sludge Dosages on Nickel Removal

Fig.1 indicates that with increase in sludge dosages, initially rapid decrease in nickel removal was observed which becomes slower latter on. When dosages are increased beyond 15 grams, dense slurry is formed. Due to highly dense slurry, the nickel may not come in contact with all available sorbent material and sites. As shown in fig. 2, the rate of nickel removal increases from 18.6 to 48.1 for increase in adsorbent dosages of 5 grams to 15 grams. For each 5 grams increase in dosages approximately 15 percent rise was observed. For further increase in adsorbent dosages only 6 percent rise was observed for 5 grams increase in dosages each. As shown in fig.3, the incremental removal upto 15 grams adsorbent dosages was observed from 80.6 to 43.15 that is around 37.45 percentage incremental removal.

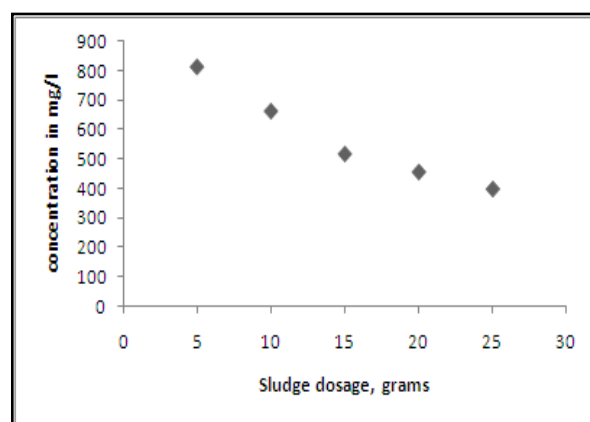


Fig.1: Effect of Sludge Dosages on Nickel Concentration

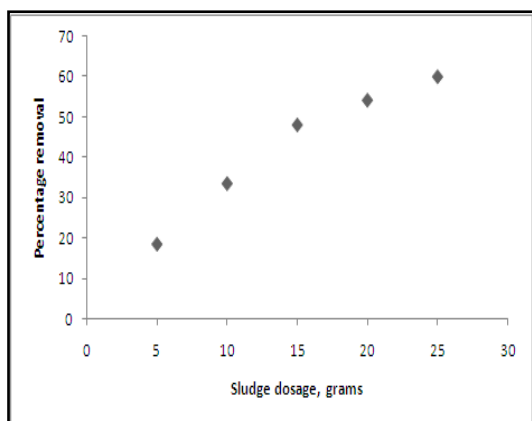


Fig.2: Effect of Sludge Dosages on Percentage Nickel Removal

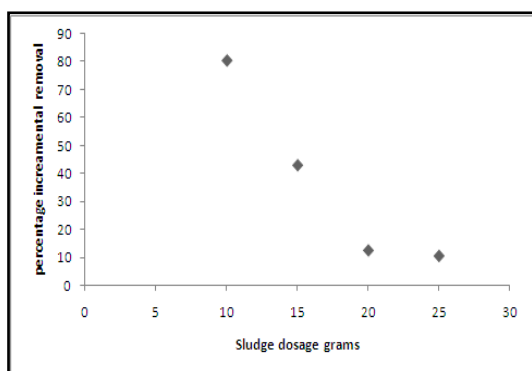


Fig.3: Effect of Sludge Dosages on Incremental Percentage Nickel Removal

B. Effect of Contact Time on Nickel Removal

Sufficient contact time should be provided for nickel to get adsorbed or biosorbed on the sorbent material. To determine optimum contact time required for nickel removal, batch studies were carried out with optimum amount of sorbent dosage (15 grams) as obtained above. The samples were collected after 4 hours intervals, filtered and analysed for nickel removal. Optimum contact time was observed to be 8 hours, as almost 76 percent removal was obtained. Also for, initial increase in the contact time from 4 to 8 hours, 21 percent increase in removal percent was observed. After 4 hours, incremental removal drops drastically. Fig. 4, 5 and 6 indicate the final nickel concentration, percent nickel removal and incremental nickel removal for the batch experiments. The results discussed here are on expected lines as with time the sorbent material gets saturated with the nickel. After 8-10 hours some of the nickel biosorbed on the sorbent may detach or get desorbed.

C. Effect of Initial Concentration on Nickel Removal

The nickel removal is expected to increase with the initial concentration, as driving force is more. The batch experiments were conducted to examine the optimum concentration of synthetic effluent with varying nickel concentration. It was observed as shown in fig.7, the optimum initial concentration was 1000 mg/l. More concentrated solution than this may

yield inferior results. For 500 mg/l initial concentration, 81 percent removal was obtained. Considering this, 1000 mg/l seems to be optimum initial concentration as shown in fig. 7. The results of incremental increase in percentage removal are plotted in fig. 8. For 100 percent increase in initial concentration from 500 to 1000 mg/l, only 3.5 percent loss in incremental removal was estimated.

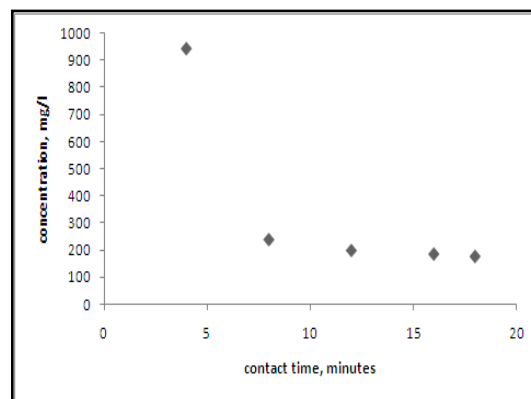


Fig.4: Effect of Contact Time on Nickel Concentration

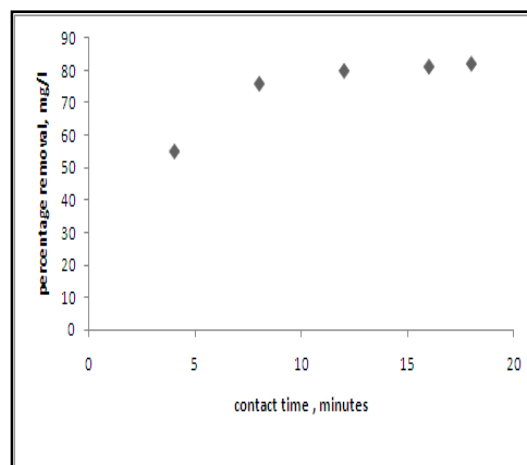


Fig.5: Effect of Contact Time on Percentage Nickel Removal

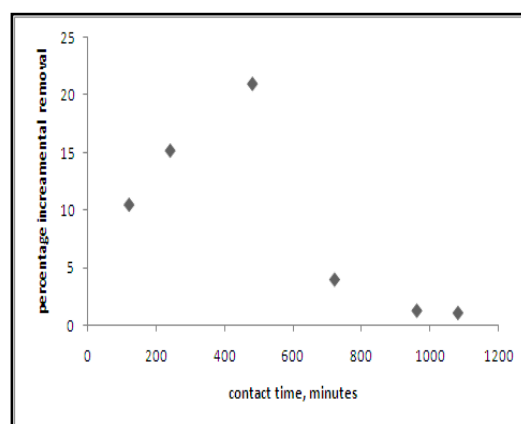


Fig.6: Effect of Contact Time on Incremental Percentage Nickel Removal

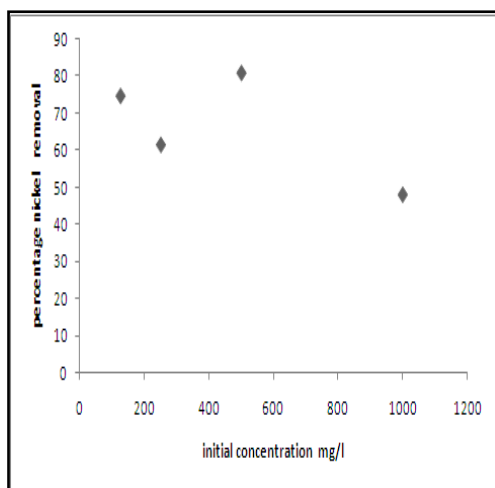


Fig.7: Effect of Initial Concentration on Percentage Nickel Removal

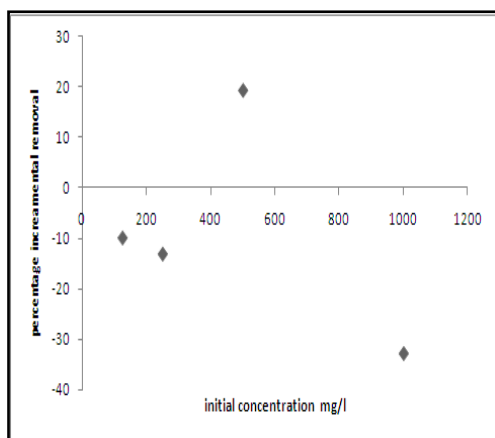


Fig.8: Effect of Initial Concentration on Incremental Percentage Nickel Removal

IV. ISOTHERM AND KINETICS

A. Isotherm

The Langmuir isotherm equation predicting monolayer physical adsorption is described as

$$q_e = \frac{q_0 b C^*}{1 + b C^*}$$

Where q_e is adsorbent loading (X/M), q_0 , maximum adsorption capacity. The plot of $\ln 1/X/M$ versus $\ln 1/C^*$ was plotted to fit the data in Langmuir equation [10].

Freundlich isotherm is given by the empirical equation:

$$\frac{x}{m} = K C^{*1/n}$$

$$\ln \frac{X}{M} = \ln k + \frac{1}{n} \ln C^*$$

X is the amount of adsorbate adsorbed and m is the amount of adsorbent. X/M is the adsorbent loading, C^* is the equilibrium concentration of nickel, k and n are constants. From fig. 9 and 10, the equilibrium data follows both the isotherms reasonably well with R^2 more than 0.9. The values of q_0 and b in the Langmuir equation were calculated.

These values were estimated to be 8 and 1.125×10^{-3} respectively. Values of K and n in Freundlich equation were estimated as 0.07615 and 1.712 respectively. The phenomenon of nickel removal is predicted to be physico-chemical one.

B. Kinetics

First order equation for sorption kinetics is written as

$$\ln (q_e - q_t) = \ln q_e - k_1 t$$

where q_e is the mass of metal ion adsorbed at equilibrium (mg/g), q_t is the mass of metal adsorbed at time t (mg/g), k_1 is the first order reaction rate constant (11). The Nickel uptake follows both first and second order kinetics with R^2 values more than 0.96 for all sorbent materials.

Second order equation for sorption kinetics is expressed as

$$\frac{t}{q_t} = \frac{1}{k_2} \frac{1}{q_e^2} + \frac{t}{q_e}$$

where k_2 is the second order reaction rate constant [12]. First and second order kinetic equations were tested for batch experimental data. As shown in fig.11, first order equation indicates poor fit for the equilibrium data. As shown in fig.12, second order kinetics describes the nickel sorption kinetics with R^2 value 0.979. The value of first order rate constant k_1 was found to be 0.002. The maximum sorption capacity, q_e was estimated to be 5.72. The second order rate constant was found to be 8.059×10^{-4} . The maximum sorption capacity, q_e by second order kinetic equation was found to be 6.711.

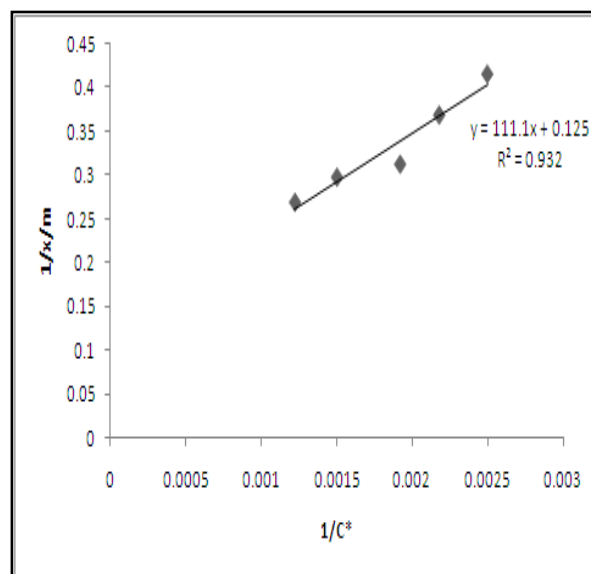


Fig. 9: Langmuir Isotherm Nickel Removal by Activated Sludge

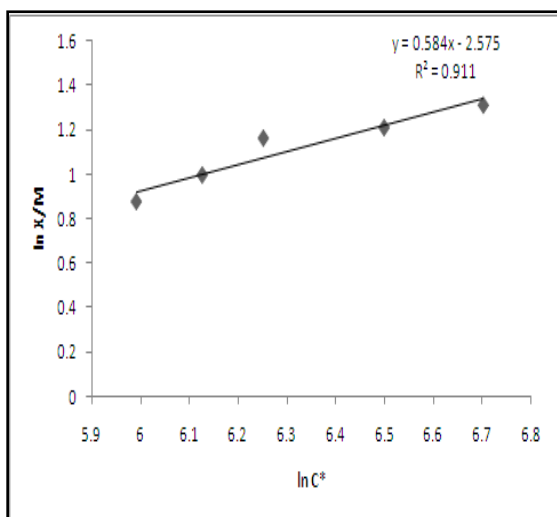


Fig.:10: Freundlich Isotherm Nickel Removal by Activated Sludge

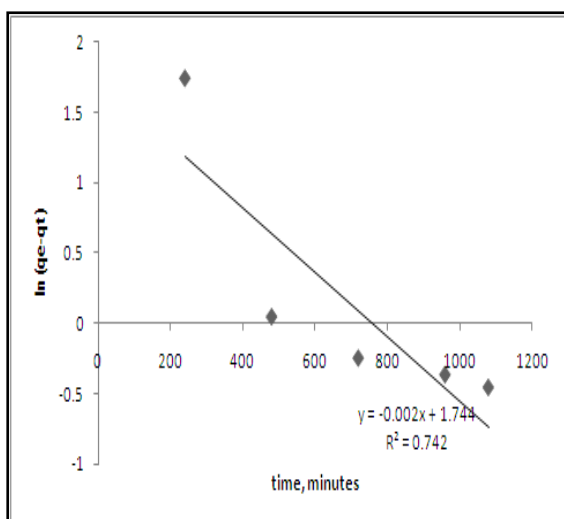


Fig.11: First Order Kinetics for Nickel Removal by Activated Sludge

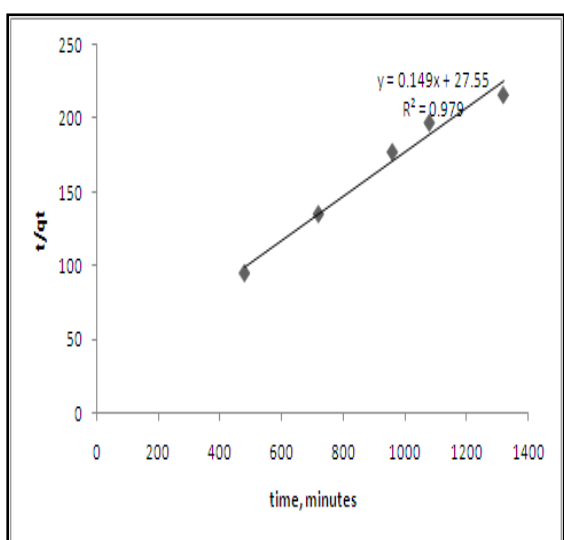


Fig.12: Second Order Kinetics for Nickel Removal by Activated Sludge

V. CONCLUSIONS

Activated sludge was used for nickel removal to study its potential to accumulate nickel. Maximum 82.2 percent nickel removal was obtained in the batch experimentation. It is established fact that dry activated sludge is very effective biosorbent. The present study explores use of wet activated sludge for nickel removal. In the present investigation, optimum values for sorbent dose, contact time and initial concentration were estimated. With initial increase in adsorbent dosage, rise in nickel removal was observed. It was then followed by constant removal and then slight drop. With respect to time, the nickel removal increased rapidly initially and then it became gradual. It was also observed that the initial nickel concentration had positive effect on nickel removal, but the percentage removal drops. Optimum values of sludge dosage, contact time and initial concentration were observed to be 15 grams, 8 hours and 1000 mg/l respectively.

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