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A Comparative Study: Adsorption Behavior of Different Nickel (II) Salts on to Alkaline Soil

Deepak Hada[1], Shweta Saxena[2]

[1]Department of Chemistry, University of Kota, Rajasthan, India
Email: *deepakhada1989[at]gmail.com*

[2]Department of Chemistry, Maa Bharti P. G. College Kota, Rajasthan, India
Email: *shwetasaxena1911[at]gmail.com*

Abstract: ***Ni(II) is one of many heavy metals that are present in the environment. The impact of heavy metals on the soil environment is determined by the soil's ability to immobilize these pollutants. From the viewpoint of soil stabilization, it is essential to look at how heavy metals and soil interact. A range of experiments were used in this study to investigate the adsorption behavior of different Ni(II) compounds [$NiCl_2$, $NiSO_4$ and $Ni(NH_4)_2(SO4)_2$] in alkaline soil. Soil is used as an adsorbent for Ni(II) removal from aqueous solutions. The experimental results were tested in a batch mode to analyze adsorption characteristics like P^H, amount of adsorbent and initial concentration of metal ions. The change in Ni (II) concentration due to adsorption was determined by the dimethylglyoxime spectrophotometric method. Maximum nickel adsorption occurred at an initial metal ion concentration of 4 mg/L, an amount of soil of 6 mg/50 ml, and pH of 10. The equilibrium time was 14 minutes. Under ideal conditions, the absorption spectrum of the Ni(II)-DMG complex was scanned with a visible spectrophotometer ((λ= 445 nm). This study aims to quantify whether the adsorption of Ni on soil is important for evaluating the data on nickel functioning in farm soil. The results indicated that alkaline soil of a farm site can be used as an effective and low-cost adsorbent to remove nickel ions from aqueous solutions.***

Keywords: Ni(II), adsorption, agriculture Soil, batch experiment, Visible spectrophotometer

1. Introduction

Heavy metal soil pollution presents significant risks to both human and ecological health. Because soil is the fundamental source for the manufacturing of human food and because there is a greater awareness of soil contamination from several sources, the environmental consequences related to the increased discharge of heavy metals into topsoil have given cause for significant concern in recent years [1]. A significant modern environmental concern is the control of nickel and other pollutants in soil and water. Surface water and soil naturally contain nickel, but some activities, such as industrialization, urbanization, usage of chemical fertilizers, pesticides and organic manures enhance the nickel concentration. Due to its toxicity toward humans, plants, and food, Nickel is classified as an environmental pollutant during the past decades [2][3].Nickel's natural composition in soil can vary widely from extremely low proportions (5 mg/kg), which designate it as a trace element, to excessively high concentrations (5000 mg/kg), which are deposited on ultra-basic igneous rocks [4]. Ni concentrations in agricultural soils range from 3-1000 mg kg-1 (WHO, 2000). Nickel concentrations in soil typically vary from 2-750 mg kg-1 [5]. The U.S. Environmental Protection Agency (EPA) has set a nickel acceptable limit for groundwater of 0.015 mg/l [6].Inthe surroundings, nickel usually exists in the divalentform,where it can be found in a variety of organic and inorganic forms. In soil Nickel may be present soluble compounds, such as chlorides, nitrates and sulfates.The mobility of soluble Ni compounds tends to be higher than that of insoluble Ni compounds, and the concentration of Ni in plants and other soil organisms is often closelyassociated with the soluble forms in soil. Therefore, Soluble Ni compounds
are a major concern when setting soil screening levels [7].Ni Cl_2,$Ni(NO_3)_2$, $NiSO_4$, $NiCO_3$, $Ni(OH)_2$, $Ni(CH_3COO)_2$ and NiO are the nickel salts with the major potential significance [8].The release of Ni effluent without the appropriate treatment results in Ni pollution. Soil, industrial wastes and effluents Ni removal leads to the requirement of efficient and cost-effective methods instantly [9]. According to reports in the literature, Nickel metal can be removed from wastewater using a variety of standard processes, such as membrane filtration, coagulation, reverse osmosis, adsorption, ion exchange, and precipitation. Particularly when the waste stream contains metal at relatively low concentrations (1–100 mg/l) dissolved in large amounts, these approaches may be ineffective or hugely expensive [10].Adsorption, however, can be regarded as one of the most widely used techniques for removing nickel metal from effluents because of its affordability, accessibility, biodegradability, ease of design, and high removal effectiveness [11]. Many researchers have investigated the suitability of using low-cost alternative approaches such as Pearl millet husk, date pits, calcined brick powder, saw dust, doum seed coat, agriculture waste, red mud, maize cob, fly ash, crude oil residue, glacial till soil, peel of banana etc. as activated carbon precursors for the removal of metal ion from soil, industrial discharges and agricultural runoff [12] [13] [14] [15] [16] [17]. Nickel was considered as an adsorbate for diverse industrial procedures that adopted its compounds.The Hadoti region in Rajasthan (India) is the focus of my research. According to related literature and studies, not a lot of research has taken place on the adsorption of Ni in this environment. As a consequence, we have designated the work for investigation. The purpose of this study was to determine the adsorption of Nickel salts onto alkaline soil. The goal of the present research was to analyze soil's capability for removing excess Ni (II) ions from aqueous solutions. The studies were carried out in a batch mode, and Ni adsorption was analyzed

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in relation to pH, initial metal ion concentration, and soil amount.

2. Experimental

2.1 Chemicals

A.1.1 Preparation of Ni^{+} solutions - Standard solutions of nickel salts (1000 mg/L) were made by saturating a specified amount of anhydrous $NiCl_2$ (3.95 g), $NiSO_4$ (4.5 g), and $NiSO_4(NH_4)_2.SO_4$ (6.73 g) in one liter of deionized water. The end concentration of Ni^{2+} is 1000 ppm, from which the standard solutions are further diluted with distilled water as per the needs of the study to prepare solutions having various concentrations of Ni^{2+} ions (4 mg/L–10 mg/L).

A.1.2 DMG solution (1%): One gram of dimethylglyoxime is saturated in 100 cm^3 of 95% ethanol to form it.

A.1.3 Saturated Bromine water: It is formed by carefully adding liquid bromine to filtered water in a bottle with a cork. The red-colored bromine is readily soluble in water. Bromine is continuously added up to a limited quantity that is kept confidential.

Using solutions of 1N NaOH or 1N HCl, the samples' P^H was changed.

2.2 Soil Sample (adsorbent)

The soil sample used in this research, which included a wide variety of organic matter, pH, and clay compositions, was taken from a farm field in the Teerath District of Kota, Rajasthan (India). Soil has a texture that ranges from clay loam to clay, is slightly to less penetrable, and creaks during the dry season. The collected topsoil is air dried for nearly three weeks. The soil was sieved to get various particle size distributions (100–300) using a British standard sieve after drying.

2.3 Equipments

All spectral and absorbance assessments for the quantitative estimation and comparative research of nickel salts were executed on a visible-spectrophotometer (Systronics-166, Ahmedabad, India) with 1 cm^3 matched glass quartz cuvette. The P^H of the samples was evaluated using a P^H meter (Systronics-335, Ahmedabad) with a cumulative glass electrode. A magnetic stirrer was used to perform the shaking. A graduated pipette is used to correctly estimate and transfer a liquid's volume from one container to another.

2.4 Principle of Spectrophotometric determination of Ni-DMG

When we mix Dimethylglyoxime with an alkaline solution of Nickel in presence of oxidizing agent such as bromine forms a red color complex, the red complex of Ni-DMG contains Nickel in higher oxidation state (III) and also (IV). The complex absorbs at 445 nm. The intensity of color varies with time and hence it is necessary to measure the absorbance after a fixed time within 10 minutes of mixing. Cobalt (II), gold (III) and dichromate ions interface under the experimental conditions.

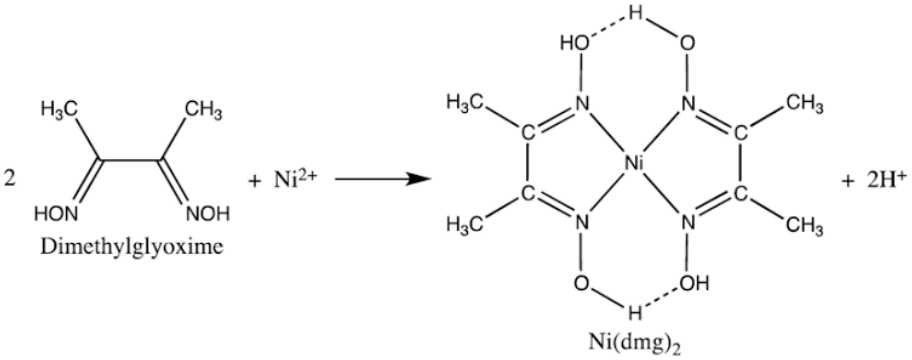

Figure 1: Reaction of Ni with DMG form Ni-DMG complex

2.5 Nickel (II) Batch Adsorption tests

Adsorption tests were done in the laboratory in an incubated shaker by adjusting the characteristics that influence the adsorption of Ni (II) onto soil. The effects of P^H, initial concentration, and adsorbent dose were examined by taking 100 ml of various nickel (II) salt solutions in 250 ml flasks and at room temperature. 2 g of soil (adsorbent)was added to 100 ml of aqueous solutions of various initial concentrations of Ni (II) (4 ppm, 6 ppm, 8 ppm, and 10 ppm) in each flask. Adsorption equilibrium was attained after the required period of time, and the adsorbate solutions were removed and filtered to separate the adsorbent. A magnetic stirrer was used to stir the flask at a speed of 120 rpm for 2–20 minutes. Following adsorption, the solution was filtered using Whatman filter paper. After that, a previously calibrated visible spectrophotometer at 445 nm was used to evaluate the concentration of the solution [18].Complex with a reddish undertone emerged. The amounts of Ni II that were adsorbed into soil solids at various times were estimated using a mass balance.

$$q = \frac{C_{init} - C_e X\, V}{w}$$

Where q is the adsorption capacity (mg g^{-1}), C_e is the equilibrium concentration of the metal ions in ppm, V is the volume of metal ions in the solution in dm^3, W is the mass

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of adsorbent added in gramsandC_0=initial concentration of Ni (II) equilibrium concentration of the metal ions in ppm

The removal efficiency (%) of the amount of soil can be calculated by using the following formula.

$$Efficiency\ (\%) = \frac{C_{init} - C_t X\ 100}{C_{init}}$$

3. Results and Discussion

A. **Effect of initial concentration of Nickel (II)**

The initial concentration of metal cations acts as a significant motive force to mitigate all mass transfer resistances of metal ions between the liquid and solid phases [19].The adsorption of Ni2+ ions onto soil adsorbent (2g) was tested by agitating 50 ml of different concentrations of Ni(II) salts solution at different initial Ni^{2+} ion concentrations ranging from 4 ppm to 10 ppm at pH 7, and the room temperature was maintained. The maximum and minimum removal efficiency for $NiSO_4$, $NiCl_2$and $NiSO_4(NH_4)_2SO_4$ were found to be 61% - 42%, 58%-42.33% and 56%-32% for 4 ppm to 10 ppm respectively. The results are illustrated graphically in figure (2) which shows that the percentage removal of Ni on natural soil decreases as the initial Ni (II) concentration increases. Metal ion removal was decreased as metal ion concentration increased and the ratio of active surface to ion concentration diminished. More active sites are present at low initial metal ion concentrations. But as the concentrations increase, more ions are vying for the biomass's available binding sites [20].The adsorption capacities of Nickel rapidly increase for the first 14 minutes or so of the reaction until maintaining practically constant. The initial metal ion concentration of these salts decreased in the following order.

$$NiSO_4 > NiCl_2 > NiSO_4(NH_4)_2SO_4$$

$NiSO_4$ has a higher adsorption capacity than $NiCl_2$ and $NiSO_4(NH_4)_2SO_4$. Due to the greater valence of sulfate ions and the ability for persistent electrostatic interaction even after some components of the soil surface have been adsorbed in monomolecular compounds, soil has a higher capacity to adsorb $NiSO_4$[21].

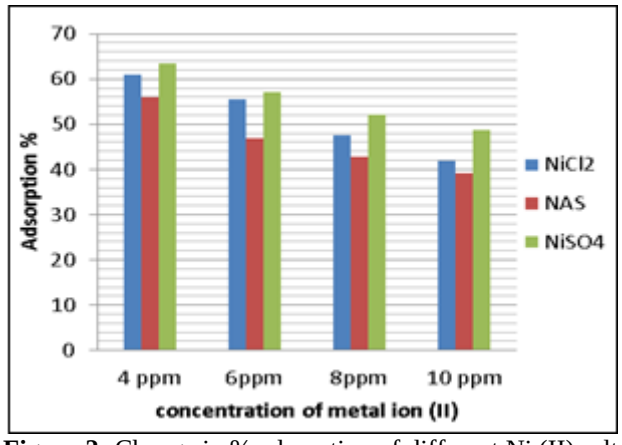

Figure 2: Change in % adsorption of different Ni (II) salt with different initial Ni (II) Concentration; adsorbent dosage=2 gm.; P^H=7; temp=30^0

B. Effect of Amount of soil

Adsorbent dose is a significant factor that affects the adsorption behavior of nickel by changing the adsorbent's capacity. For the purpose of examining how soil content affects adsorption, 250 ml flasks containing between 2 and 6 g of soil and 50 ml of various salts of Ni (II) solutions with 4 mg/L concentrations were used.Initial Nickel concentration was constant for each of these experiments. It is equilibrated in a magnetic stirrer for 20 minutes. The presence of nickel concentration in that filtered solution was detected using a visible spectrophotometer at 445 nm.The results obtained are graphically represented in Figure (3).It is observed that when the adsorbent dosage was increased from 2 g to 6 g, the percentage of Ni ion removal increased from 48.75% to 70.12%, 42% to 62.75%, and 39.25% to 56% for $NiSO_4$, $NiCl_2$, and $NiSO_4(NH_4)_2SO_4$, respectively. The phenomenon of increase in percentage removal of Ni (II) with increase in adsorbent dose may be explained as at a fixed initial concentration of adsorbate the increase in the adsorbent amount provides a larger surface area or adsorptive sites. There are two possible explanations for this:

- At increasing adsorbent amounts, there is relatively less adsorption because a large adsorbent amount effectively reduces the un-saturation of the adsorption sites and, thus, the number of such sites per unit mass decreases.
- Higher adsorbent concentrations lead to particle aggregation, which decreases total surface area and elongates diffusion lanes, both of which tend to reduce the amount of adsorbate per unit mass[22][23].

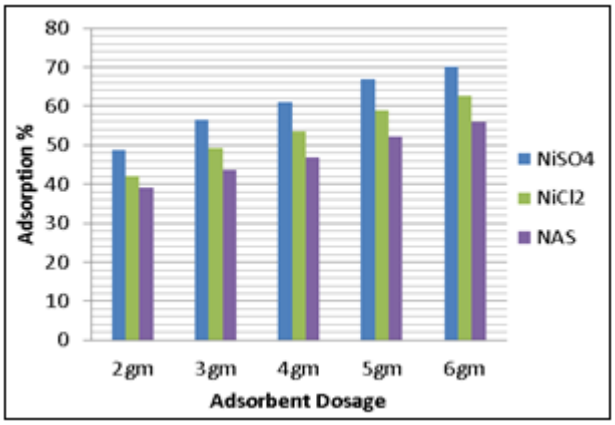

Figure 3: Change in %adsorption of Ni (II) with different amount of Soil; Ni concentration =4 ppm; P^H =7; Temp. = 30^0

C. Effect of P^H

The initial pH value of the solution is a fundamental controlling factor that influences adsorption behavior because it can affect on both the content of the solution and the properties of the adsorbent.The pH can have an impact on the adsorbent's surface anddegreeof ionisation.To examine the effects of pH, experiments were conducted at different pH, ranging from 2 to 10. By addingthe necessary amount of hydrochloric acid (HCl) and NaOH solution, the medium's acidic and alkaline pH were remained constant. While doing the experiment, the temperature and other variables, such as the adsorbent's particle size, were assumed constant. The results are shown in Figure (4),For $NiSO_4$, $NiCl_2$, and $NiSO_4(NH_4)_2SO_4$, the maximum

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concentration of Ni adsorbed on soil was found at pH 10 in each case. This result can be explained by the fact that the surface adsorbents' net total negative charges increased, magnifying electrostatic repulsion during the adsorption process. Consequently, as pH increased, a larger number of total negative groups became accessible for the adsorption of metal ions, reducing the competition between proton and metal ions. An increase in the concentration of Ni^{2+} and $NiOH^{+}$ entities in soil due to the precipitation of hydroxide and the production of hydroxyl species, $Ni(OH)_2$ was observed as a precipitate at pH 10[24].At higher pH values, greater than six, excessive OH- ions in the aqueous solution forms hydroxyl complexes of nickel, $Ni(OH)_2$[25][26].

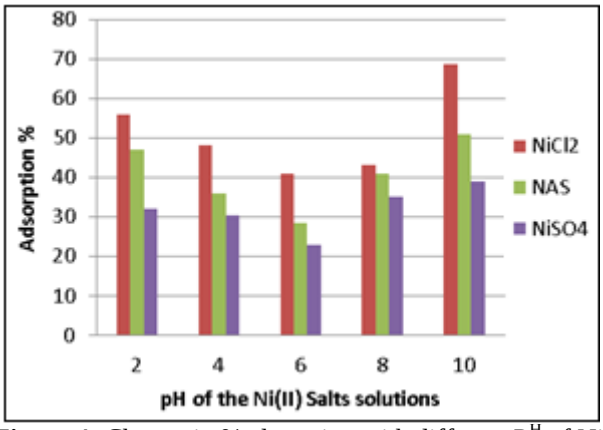

Figure 4: Change in %adsorption with different P^H of Ni (II) saltsolutions, concentration =4ppm; adsorbent dosage=2 gm.; P^H=7; temp=30^0

4. Conclusion

Adsorption reactions in soils are the procedures by which the components of solutions bind to the surfaces of soil particles and tend to gratify the surface forces of attraction. Using soil as an adsorbent, batch adsorption experiments were done in order to remove Ni(II) compounds from aqueous solutions. The adsorption characteristics have been examined at different P^H values, initial metal ion concentrations and adsorbent dosages. The obtained results can be summarized as follows:

1) Removal efficiency decreased with increasing concentration of Ni ions. Because at higher concentration, the binding sites were almost completely covered. The percentage removal of nickel decreased for $NiCl_2$ (61%- 42%), $NiSO_4$(58%-42.33%)and $NiSO_4$ $(NH_4)_2SO_4$ (56%-32%) respectively. when the initial concentration of metal solution varied from 4 mg /L to 10 mg/l.
2) Increase in mass of adsorbent leads to increase in Ni (II) adsorption due to increase in number of adsorption sites. Maximum uptake of Ni (II) obtained at adsorbent dose of 6gm for $NiSO_4$ (70.12%), $NiCl_2$ (62.75 %) and $NiSO_4$ $(NH_4)_2$ SO_4(56%) respectively.
3) High P^H alkaline soils favored a positive impact on the adsorption of nickel. Maximum adsorption was recorded at P^H 10. On this $P^H$$Ni(OH)_2$ were present as precipitate.

5. Future Scope

My research work will provide a database for pollution control area to determine the level of soil pollution with respect to nickel metal in Hadoti region of Rajasthan.

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Author Profile

Deepak Hada is Research Scholar, Maa Bharti PG College, Department of Chemistry, University of Kota, Rajasthan, India. Her research interests include Adsorption study of Nickel Salts in Hadoti region.

Dr. Shweta Saxena, principal of Maa Bharti PG College, Department of Chemistry, University of Kota, Rajasthan, India. Her research interests include Adsorption, Desorption, Studies of heavy metals, Fluroide, Phosphate

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