

Thermodynamic Study on the Adsorptive Removal of Cr(Vi) and Ni(II) Metal Ions Using Schiff Base as Adsorbent.

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Abstract

In this work, the efficiency of a Schiff base derived from ethylenediamine and benzaldehyde in the removal of Cr(VI) and Ni(II) ions from their aqueous solution in batch mode was investigated. The FT-IR spectra of the Schiff base before and after adsorption showed bands at 1640 cm⁻¹ and 1644 cm⁻¹ which indicate the formation of C=N functional group and coordination of the metal ions respectively. The Schiff base was found to be insoluble in water. SEM results of the Schiff base before and after adsorption revealed different morphology. Adsorption parameters were studied at equilibrium time of 80 min and 60 min for Cr(VI) and Ni(II) respectively. The optimum pH value for the adsorption of Cr(VI) and Ni(II) was 4 and 8 respectively. The thermodynamic parameters such as change in Gibbs free energy (ΔG), enthalpy (ΔH) and entropy (ΔS) were calculated at different temperatures. The values of Gibbs free energy were found to be negative, which that the adsorption process was spontaneous and feasible. The heat for adsorption of Cr(VI) and Ni(II) ions were 80928 J/mol and 47248 J/mol respectively, and this indicates the removal of Cr(VI) and Ni(II) is through chemisorption and endothermic. Furthermore, entropy values 277 J/molK⁻¹ for Cr and 168 J/molK⁻¹ revealed the spontaneity of the process..

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1.Introduction

Heavy metals are non-biodegradable pollutants and they are very difficult to eliminate naturally from the environment. Almost all heavy metal elements are highly toxic when their concentration exceeds their permissible limit in the ecosystem. Many industries such as electroplating, pigments, metallurgical processes, mining and leather industries release various concentrations of heavy metals. Metal ions such as cadmium, chromium, copper, lead, zinc, manganese, nickel and iron are commonly detected in both natural and industrial effluents [1]. Chromium and its compounds are toxic metals introduced into natural water from a variety of industrial wastewater. The major sources are from textile dyeing, leather tanning, electroplating and metal finishing industries which cause severe environmental and public health problems. The hexavalent form of chromium is considered to be a group "A" human carcinogen because of its mutagenic and carcinogenic properties. The permissible limit of chromium for drinking water is 0.1 mg/L (as total chromium) in environmental protection agency (EPA) Standard [2]. Nickel can enter body *via* inhalation, ingestion and dermal absorption, but the route by which nickel enters cells is determined by its chemical form. Contact with nickel compounds can cause a variety of adverse effects on human health, such as nickel allergy in the form of contact dermatitis, lung fibrosis, cardiovascular and kidney diseases and cancer of the respiratory tract. Like many environmental agents, the toxic effect of nickel is related to the way it gets into an organism [3]. The methods of heavy metal removal include; chemical precipitation, electro dialysis, coagulation/flocculation, ultrafiltration, reverse osmosis in which these methods have some drawback by creating a secondary pollutant and adsorption an effective methods for the removal of heavy metals from waste effluent due to its sludge free clean operation and completely removed metal ions, even from the diluted solution [4]. Resin of [5-((E)-1-(ethylimino) ethyl)-4, 7-dimethoxy benzofuran-6-ol] Schiff base (EEDB) was synthesized and successfully applied it for the removal of Cu (II) ions from aqueous solution [5]. Research conducted on Cellulose being the most abundant, renewable and natural green raw material that has the potential application in adsorption of heavy metal ions [6]. New chelating material was synthesized by modifying the activated silica gel with 4-hydroxy benzyldehyde [7]. Synthesis of novel Schiff-base/SBA-15 nano adsorbent was reported by the reaction of salicylaldehyde and (3-aminopropyl) trimethoxysilane in methanol and subsequent grafting with SBA-15 [8]. This work is aimed at utilizing Schiff base derived from ethylenediamine and benzaldehyde in removing harmful metal ions from their aqueous solutions.

2.Materials and Methods

All chemicals used in this work were of analytical grade, and they include; Benzaldehyde (99%), Ethylenediamine (98%), Ethanol (99%), Sodium hydroxide (NaOH) (99% Sigma Aldrich), Calcium Chloride (CaCl_2) (98% Sigma Aldrich), Nickel Chloride hexa hydrate $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (98% Sigma Aldrich), potassium permanganate $\text{K}_2\text{Cr}_2\text{O}_7$ (99.9% Sigma Aldrich) and Hydrochloric Acid (HCl).

2.1 Preparation of Schiff base

A mixture of 3.3 cm³ ethylenediamine (0.05 mol, 3.0 g) and 10.1 cm³ Benzaldehyde (0.1 mol, 10.6 g) in the ratio 1:2 solution that was dissolved in 50 cm³ ethanol, then followed by addition of 2 drops of NaOH (0.1 M) and then refluxed for 4 hours. Yellow crystalline solid appeared upon cooling which was filtered and then dried in a desiccator containing anhydrous calcium chloride (CaCl_2) [9].

2.2.FT-IR Analysis of the synthesized Schiff base

FT-IR spectra of the Schiff base before and after adsorption were determined using FTIR-Cary 630 from Agilent technologies was used and the spectra were recorded in the wavelength interval 4000 to 750 cm⁻¹.

2.3. Solubility Test

The solubility of synthesized Schiff base in DMF, DMSO, benzene, acetone, CCl_4 , CHCl_3 , distilled water, methanol and ethanol was tested by adding 0.1 g of freshly synthesized Schiff base in 10 cm^3 of each of the selected solvents. [10].

2.4. Scanning Electron Microscopy (SEM)

SEM was further carried out in order to investigate the surface morphology of the Schiff base before and after adsorption. The samples were analyzed using the microscope operated at an accelerated voltage of 15 kV.

2.5. Batch adsorption process

The influence of adsorption parameters such as contact time, effect of temperature, effect of solution pH on the adsorptive removal of metal ions was investigated in batch mode. To prepare the stock solution 2.8290 g of $\text{K}_2\text{Cr}_2\text{O}_7$ (99% Merck) and 4.0489 g of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (98% Merck) were carefully and accurately weighed using analytical weighing balance. The weighed amounts were then dissolved in beakers containing some deionized water. After complete dissolution they were quantitatively transferred into 1.0 L Volumetric flasks to give 1000 mg/L of the metal salts solutions (stock solution). The residual concentration of the metal ions after adsorption were determined using Atomic Absorption Spectrophotometer at the corresponding λ_{max} of each metal ion 357.9 and 232.0 nm for Cr(VI) and Ni(II) respectively [11].

3. Results and Discussion

3.1. Synthesis of the Schiff base

The synthesis of the Schiff base was carried out using benzaldehyde and ethylenediamine under reflux for 4 hours. As observed Figure 1 the presence of $\text{C}=\text{N}$ Azomethine or imine group is an indication that Schiff base has been formed from the condensation reaction of ethylenediamine and benzaldehyde. The synthesized Schiff base is a bidentate ligand with two donor atoms.

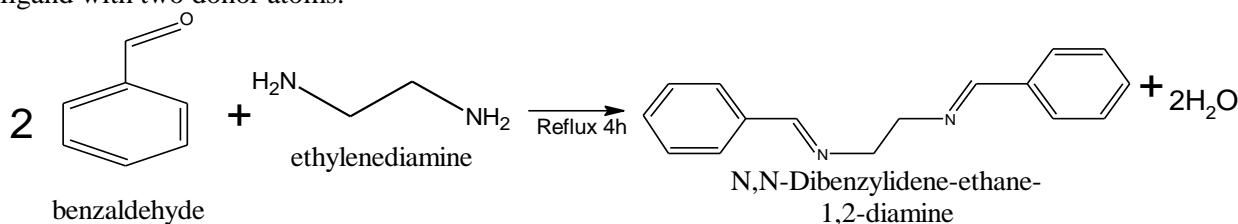


Figure 1: The Structure of N,N-Dibenzylidene-ethane-1,2-diamine Schiff base

3.2. Fourier Transform Infrared (FT-IR) Characterization

FT-IR spectroscopy was used to determine the main functional groups responsible for Schiff base formation and other important available functional groups. The synthesized Schiff base was characterized using FT-IR and the summary of the results is presented in Table 1. The FT-IR spectra of the synthesized Schiff base before and after adsorption were presented in Table 1. The peaks at 2847 and 1640 cm^{-1} were attributed to the C-H stretching (sp^3) and $\text{C}=\text{N}$ bonds, respectively. The presence of imine or azomethine group, $\text{C}=\text{N}$ confirmed that a Schiff base was formed from the reaction between benzaldehyde and ethylenediamine. The characteristic peaks found at 1376 and 2910 cm^{-1} were due to C-N stretching in the ethylenediamine and C-H bending (sp^2) in the benzaldehyde, peak found at 1532 was due to $\text{C}=\text{C}$ for aromatic ring of benzene. The observed shifts of the imine functional group from 1640 cm^{-1} to 1644 cm^{-1} after adsorption of Cr(VI) and Ni(II) ions were due to coordination of the metal ions to the Schiff base adsorbent.

Table 1: Summary of FT-IR results of Schiff base both before and after adsorption with Cr and Ni

| Peaks | Schiff baseν (cm ⁻¹) | | | | Functional Group Assignment |
|-------|----------------------------------|-----------------------|------------|--|--------------------------------|
| | Before Adsorption | After adsorption with | | | |
| | | Cr | Ni | | |
| 1 | 2847 | 2847 | 2847 | | C-H Stretching |
| 2 | 1640 | 1644 (+4) | 1644 (+4) | | Imine Functional group (C=N) |
| 3 | 1532 | 1581 (+49) | 1581 (+49) | | C=C (Aromatic ring of benzene) |
| 4 | 1376 | 1451 (+75) | 1451 (+75) | | C-N Stretching |
| 5 | | 754 | 754 | | M-N bond |
| 6 | 2910 | 2929 (+19) | 2933 (+23) | | C-H bending |

NB: Values in Parenthesis represent the change in the wavenumber (cm^{-1}) after the respective metal adsorption

3.3. Solubility Test

The solubility test was achieved by suspending 0.1 g of the Schiff base over 10 cm^3 of the chosen solvents at room temperature, and solubility was checked after 24 hours. The results was depicted in Table 2. It was found that the Schiff base is completely insoluble in distill water which give it a good potential to serve as adsorbent for adsorption process. However, it was found that is completely soluble in methanol, ethanol, DMF and DMSO and partially soluble in benzene and acetone. This may be likely due to the polarity nature of some solvents as polar solvents dissolve polar compounds while non-polar solvents dissolve non-polar compounds. This result is in consistent with the result obtained by [12].

Table 2: Solubility Test Result

| S/N | SOLVENTS | SOLUBILITY |
|-----|-----------------|------------------|
| 1 | DMF | Soluble |
| 2 | DMSO | Soluble |
| 3 | Benzene | Slightly Soluble |
| 4 | Acetone | Slightly Soluble |
| 5 | CCl_4 | Insoluble |
| 6 | CHCl_3 | Insoluble |
| 7 | Distill water | Insoluble |
| 8 | Methanol | Soluble |
| 9 | Ethanol | Soluble |

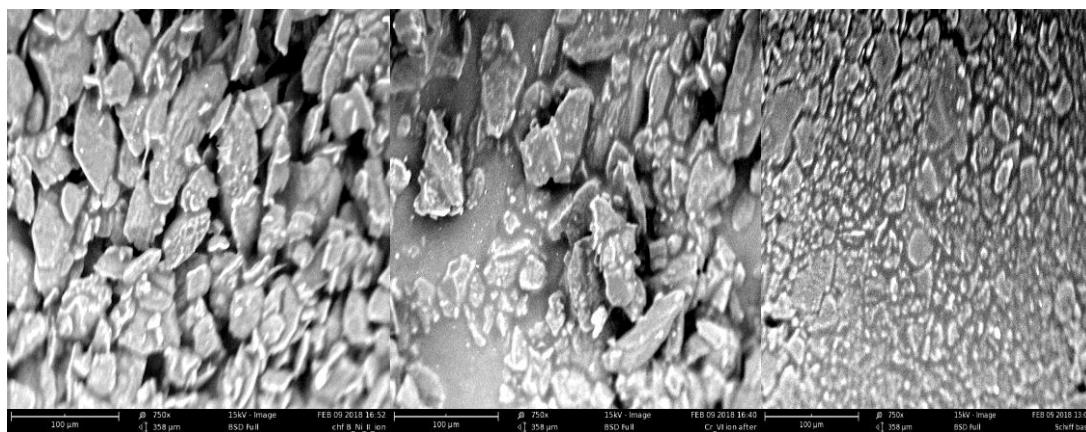


Figure 2:(a) SEM Image of Schiff Base , (b) SEM Image of Schiff Base after adsorption with Cr (VI), (c) SEM Image of Schiff Base after adsorption with Ni(II)

3.4. Scanning Electron Microscope (SEM)

Scanning Electron Microscopy give further insight into the morphology and size details of the Schiff base. The surface characteristics of the sample are obtained from the secondary electrons emitted from the sample surface. From the SEM images it could be observed that various shapes of Schiff base have been produced. The synthesized Schiff base shows a uniform and evenly distribution of particle surface. The surface of the Schiff base has changed drastically after adsorption which shows different morphology based on the nature of metal ion adsorbed. The larger and uneven distribution of the particle is a clear indication that the metal ions has attached itself or make bond with the active site in the Schiff base surface. SEM images of the Schiff base, Schiff base after adsorption of Cr and Schiff base after adsorption of Ni were presented in figure 2 a, b and c respectively.

3.5. Effect of Contact Time on adsorption of Ni(II) ion

The result of adsorption of Ni(II) ion with increasing contact time is presented in Fig.3. The increase in contact time at 300rpm stirring rate leads to increase in percentage removal of the metal ions. The adsorption process is a fast process, so about 68.87% of the metal ion removal took place within the first 60 min, this may be attributed to the high affinity and interaction between the adsorbent (Schiff base) and the metal ion due to the availability of more active site on the Schiff base. Thus, the optimum time for Ni(II) ion removal is 60 min. This is in line with the result obtained by [13] in the adsorptive removal of Cu(II) and Ni(II) from single-metal, binary-metal and industrial wastewater systems by surfactant modified alumina. Their result revealed that during the initial 2 min of contact, a rapid uptake took place and finally the equilibrium was reached after 80 min (94.6%) and 60 min (87.5%) for Cu(II) and Ni(II), respectively.

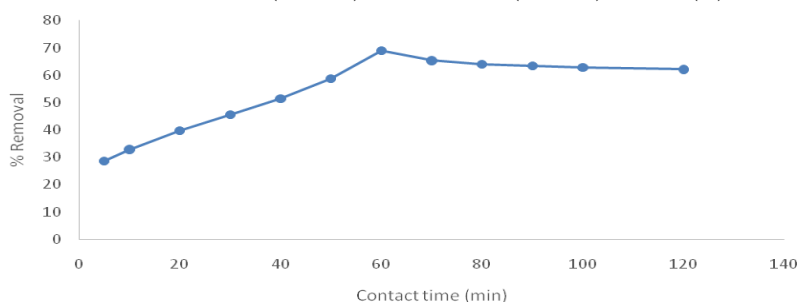


Figure 3: Effect of Contact Time on the % Removal of Ni(II) ion.

3.6. Effect of Contact Time on the Removal of Cr(VI) ion.

Figure 4, revealed the result obtained from the study of effect of contact time on the removal of Cr(VI). Maximum percentage removal was observed at 80 minutes with 72.75%. After 80 min, percentage removal decrease due to exhaustion of the active sites of the adsorbent. The equilibrium time obtained in this adsorption process is nearly closer when compared to the result obtained by [14], on his research for heavy metals removal from aqueous solutions using *Xanthium Pensylvanicum*. His result revealed that most of the maximum percent removal for Pb^{2+} , Cu^{2+} , Zn^{2+} , Cd^{2+} , Ni^{2+} , Co^{2+} and Fe^{3+} were attained after about 90 minute of shaking time. The difference in percentage removal of Cr(VI) and Ni(II) ions may be attributed to the difference in their ionic sizes. The ionic sizes of Cr and Ni are 0.52Å and 0.69Å respectively. The smaller the ionic size the greater its affinity to reactive sites, thus Cr(VI) with highest percentage removal among the metal ions may be due to its smaller size. The percentage removal trend observed was $\text{Cr} > \text{Ni}$ this trend of the adsorption is due to the fact that metal ion with smaller ionic radius diffuse faster in aqueous systems and compete better for exchange site than for those with larger sizes. According to [15] in his study the kinetics and effect of pH on removal of manganese, cadmium and lead from aqueous solution by maize cobs, he reported that the differential adsorption of Mn^{2+} , Cd^{2+} , and Pb^{2+} ions may be ascribed to the difference in their ionic sizes. The ionic sizes of Mn^{2+} , Cd^{2+} , and Pb^{2+} are 0.67, 0.97, and 1.20 respectively. So, the adsorption capacities increases from $\text{Mn}^{2+} > \text{Cd}^{2+} > \text{Pb}^{2+}$.

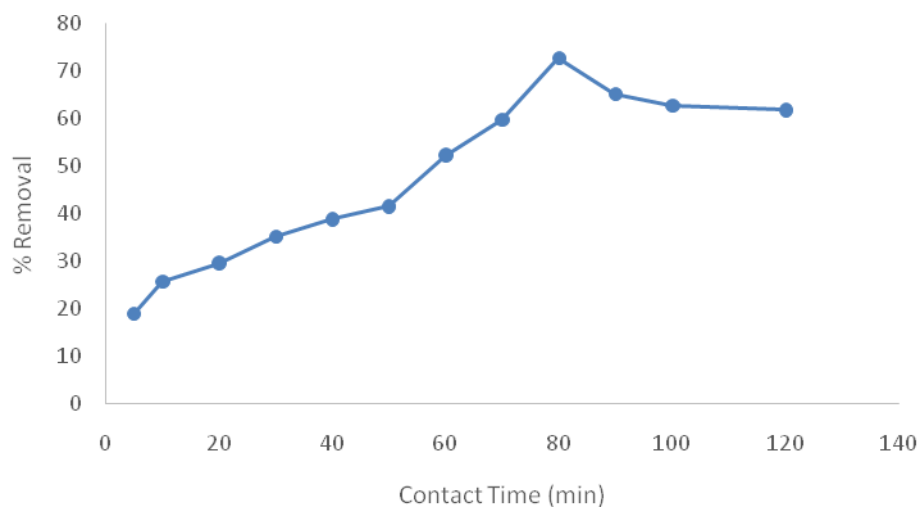


Figure 4: Effect of Contact Time on Cr(VI) ion Removal

3.7. Effect of Temperature and Adsorption Thermodynamic

In adsorption process, temperature is an important parameter due to the effect it imposed in the process. In the present paper, different temperatures (303K, 313K, 323K and 333K) have been chosen in order to investigate their effects in adsorption of metal ions. An increase in percentage removal was observed in all the metal ions as the temperature is increased with maximum percentage removal of 98.57 and 96.90% for Cr(VI) and Ni(II) respectively. This is because of increase surface activity suggesting that adsorption of the metal ions by the Schiff base was an endothermic process. The results were presented in Figure 5. These results are in agreement with the result obtained by [16]. They reported that adsorption of metal ions (Pb^{2+} and Cd^{2+}) by *C. bicolor* biomass increase with increase in temperature which is typical for the biosorption of most metal ions from their solution. The equilibrium concentration was obtained at 50 mg/L for Pb^{2+} and 70 mg/L to Cd^{2+} as temperature increased above 50°C.

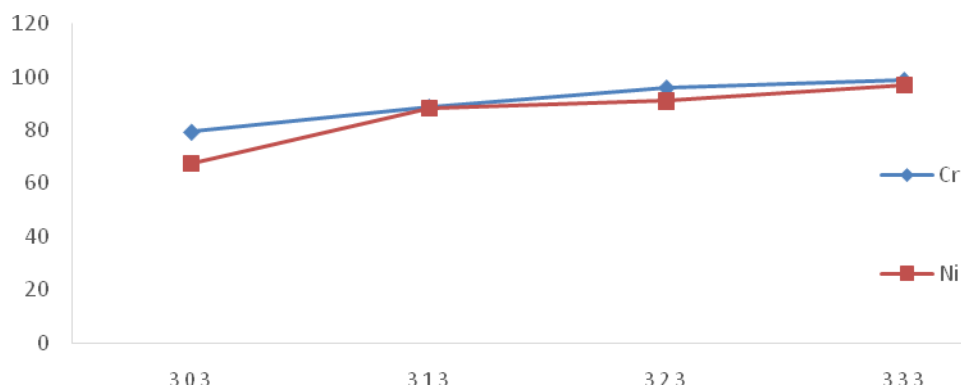


Figure 5: Effect of Temperature on Adsorption of Cr(VI), Ni(II) and Cu(II) ions

3.8. Adsorption Thermodynamic

Thermodynamic parameters are essential for the interpretation of the nature and characteristics of adsorption process concerning their physicochemical attributes. Gibbs free energy, adsorption enthalpy, and entropy hold fundamental knowledge about the character of adsorption. Gibbs free energy change (ΔG), provides the information of whether the adsorption process is spontaneous or not, meaning if it is necessary to give an external support to the system in order to start the adsorption. Adsorption free enthalpy (ΔH) change gives the knowledge of the thermal character of the adsorption, providing whether the adsorption of metal ions on adsorbent is endothermic or exothermic. While, adsorption free entropy change (ΔS) is an indicator of magnitude concerning the disorder at adsorbate/adsorbent interphase [17]. If $\Delta G < 0$ (negative): it indicates that the adsorption occurs spontaneously without the need for an external energy. If $\Delta G > 0$ (positive), it means the adsorption does not take place spontaneously and the reaction mechanism needs a supportive force, mostly the heat energy. Usually, it is favorable for ΔG to be spontaneous (negative value) for ideal adsorption mechanism. These parameters can be calculated using the following relations;

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad (1)$$

$$\Delta G^0 = -RT \ln K_d \quad (2)$$

$$\text{Where } K_d = \frac{C_{ads}}{C_e} \quad (3)$$

$$\ln K_d = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \quad (4)$$

Where k is equilibrium constant, T absolute temperature in Kelvin, and R is universal gas constant (8.314 J/mol/K). The values of ΔH and ΔS are obtained from the slope and intercept of plot $\ln k$ versus $1/T$ (Van't Hoff's equation) for the adsorption of the metal ions onto Schiff base as adsorbent at different temperatures. Table 3 shows the calculated thermodynamic parameters for the adsorption of Cr(VI) and Ni(II) onto the Schiff base. It can be seen that for all the metal ions ΔG values are negative indicating the feasibility and spontaneity of the adsorption process. However, an increase in the values was observed from -3072 to -11389 J/mol for Cr(VI) and -3781 to -8834 J/mol for Ni(II) as the temperature increase from 303K to 333K. The ΔH values of the adsorption process are 80928 J/mol for Cr(VI) and 47248 J/mol for Ni(II). The positive values is an indication that the adsorption process of all the metal ions is endothermic in character and occurred through chemisorption. Derived enthalpies indicated that charge transfer and ligand-exchange interactions may likely play a role in the adsorption mechanism. In addition, the values of ΔS were found to be 277 J/mol/K for Cr(VI) and 168 J/mol/K for Ni(II). This further proved that the adsorption process is spontaneous. This result is consistent with the result obtained by [18].

Table 3: Thermodynamic parameters for the adsorption of Cr and Ni onto Schiff base

| Metal ions | $\Delta G = \Delta H - T\Delta S$ (J/mol) | | | | ΔH (J/mol) | ΔS (J/mol/K) |
|------------|---|-------|-------|--------|--------------------|----------------------|
| | 303K | 313K | 323K | 333K | | |
| Cr | -3072 | -5844 | -8616 | -11389 | 80928 | 277 |
| Ni | -3781 | -5465 | -7150 | -8834 | 47248 | 168 |

Optimum Conditions: 200 mg/l, 0.4 g for Ni and Cu, 0.5 g for Cr, 300 rpm, 333 K.

3.9 Effect of Solution pH

The effect of solution pH has great influence in adsorption process; so therefore, the pH of metal solution is an important parameter governing metal ion adsorption. This is because the pH of the metal solution affects the solubility of metal ion and surface charge of the adsorbent. In this study the pH was varied from 2 to 12. Figure 6 shown the effect of solution pH of the adsorption process. Cr(VI) ion has a maximum percentage removal of 95.70% at pH 4, while a decrease in percentage removal at higher pH. This is due to the fact that at lower pH there is an excessive protonation of the adsorbent active sites, at this range Cr(VI) ions change to $\text{Cr}_2\text{O}_7^{2-}$ and an electrostatic force between oxyanions and cation increase the percentage removal, as such, the optimum pH for Cr(VI) ion adsorption is pH 4. This result is closer to the result obtained by [19], they reported that the removal of Chromium was maximum at pH value of 3 with a removal of 73%. In the case for Ni(II) ions, maximum percentage removal of 89.29% was achieved at pH 8. This is because at low pH, the removal of these metal ions was low due to the protonation of adsorbent surface which give rise to positively charge surface thereby creating an electrostatic repulsion between the positively charge adsorbent surface and the metal ions which subsequently compete with the H^+ present in the solution for the active sites of adsorption. Therefore, the optimum pH for removal of Ni(II) ion was observed at pH 8. This result is in accordance with the result obtained by [20] reported an optimum pH for Ni(II) of pH 8.

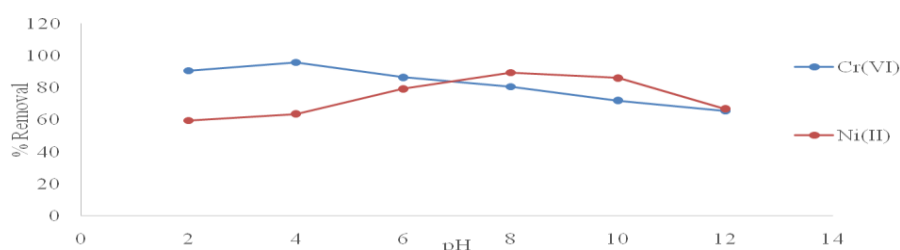


Figure 6: Effect of pH on the removal of Cr(VI) and Ni(II) ions.

4. Conclusion

This study revealed that the synthesized Schiff base derived from ethylenediamine and Benz aldehyde was successfully utilized as adsorbent for the removal of Cr (VI) and Ni(II) ions from their aqueous solutions in batch mode with high efficiency. The process was found to be pH dependent, endothermic, feasible and spontaneous.

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