



## Removal of Cr(VI), Cu(II), Pb(II) and Ni(II) from Aqueous Solutions by Adsorption on Alumina

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### Abstract

The extent of removal of heavy metal ions (Chromium, copper, lead and nickel) by adsorption on alumina has been investigated. Adsorption experiments were performed in batch technique from synthetic solutions using alumina as adsorbent. Several experimental parameters that affect the extent of adsorption of the metal ions of interest have been investigated such as adsorbent dosage, concentration of the adsorbate, contact time, temperature and pH of the system under study. The equilibrium nature of the adsorption of the metal ions at different concentrations has been followed by Freundlich and Langmuir adsorption isotherms. This work proposes a cost-effective method for the efficient removal of Cr(VI), Cu(II), Pb(II) and Ni(II) from aqueous solutions. The conditions required for effective removal have been optimized.

**Keywords:** Adsorption, alumina, heavy metal ions, adsorption isotherms.

### Introduction

Adsorption is a surface process that occurs when a solute is selectively retained on the surface of an adsorbent forming a thin layer of the adsorbate<sup>1</sup>. Thus adsorption finds its use in the removal of dissolved substances from water with careful choice of adsorbent and adsorbate<sup>2</sup>. It involves selective retention of the adsorbate to the adsorption sites of the adsorbent<sup>3</sup>. Disposal of industrial wastes with an appreciable concentration of heavy metal ions is a persistent environmental issue<sup>4</sup>. The metals such as Aluminium, Cadmium, Zinc, Chromium, Nickel, Copper, Mercury and Lead are considered to be prominent in industrial waste streams whose removal requires keen attention<sup>5,6</sup>. The conventional methods in practice for the removal of heavy metal ions from waste waters include precipitation by chemical methods, ion exchange and biosorption<sup>7</sup>. Although these methods are expensive they are also associated with several limitations such as the generation of sludge, low percentage retention of metal ions, energy consumption and low selectivity which makes the process less suitable for small scale industries. Thus adsorption is proposed as an economical and effective method for the retention of heavy metal ions from aqueous industrial wastes. Adsorption is considered as an effective and economical method for the removal of metal ions from waste waters<sup>8,9</sup>. Low cost adsorbents<sup>10</sup> such as nut wastes, peat moss<sup>11</sup>, waste wool, silica gel<sup>12</sup>, tree barks, activated carbon<sup>13,14</sup>, saw dust<sup>15</sup>, amla dust, etc. have been established as efficient adsorbents for the same purpose.

This work describes the removal of heavy metal ions such as chromium, nickel, lead and copper from synthetic solutions by using adsorption on alumina. Alumina (Al<sub>2</sub>O<sub>3</sub>) is a fine white powder which resembles common salt. When an adsorbent

which is resistant to attrition and which retains more of its adsorptive capacity at elevated temperatures than silica gel is required, activated alumina may be used.

The aim of the present study is i. to optimize the conditions required for the effective removal of heavy metal ions from solution by means of batch adsorption experiments. ii. to study the capacity of adsorption by Freundlich and Langmuir equilibrium isotherm models.

### Material and Methods

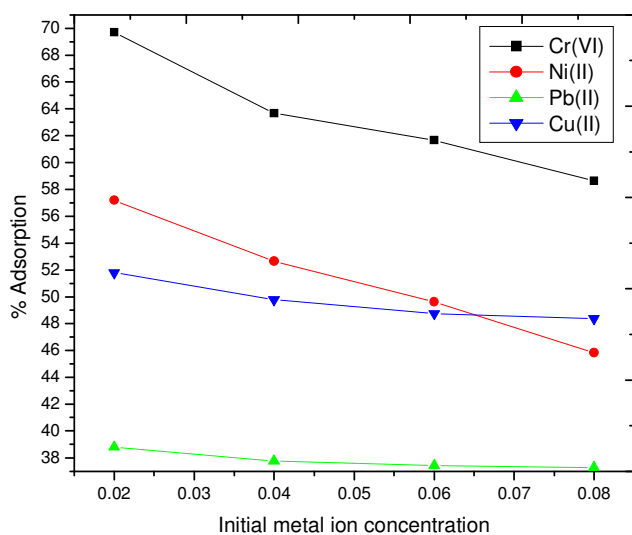
**Materials:** AR grade potassium dichromate (K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>), nickel ammonium sulphate (NAS), lead nitrate (Pb(NO<sub>3</sub>)<sub>2</sub>) and copper sulphate (CuSO<sub>4</sub>) of assay 99.0% manufactured by fischer chemicals, Chennai were used for preparing synthetic solutions of heavy metal ions in the required concentration. Alumina (Al<sub>2</sub>O<sub>3</sub>) of 99.9% purity manufactured by Loba Chemie Pvt Ltd., Mumbai was used as the adsorbent for the study. Alumina was activated by heating at 500°C for 12 hours before being used.

**Batch Adsorption experiments:** A definite volume of heavy metal ion stock solution with a known initial concentration was stirred with a definite amount of activated alumina for the stipulated time at a fixed temperature in a mechanical shaker. The unadsorbed heavy metal ions which remained in solution were filtered and the amount of heavy metal ions was estimated after attainment of equilibrium. The extent of retention of the different metal ions by alumina was studied by varying several parameters such as the initial concentration of adsorbate (0.02, 0.04, 0.06 and 0.08 N), adsorbent dosages (0.5 – 2.0g), solution temperature (30°C - 70°C), pH (3 – 7) and contact time (20–70 minutes). Freundlich and Langmuir isotherms were also studied

for varying concentrations of the different metal ions at constant temperature.

## Results and Discussion

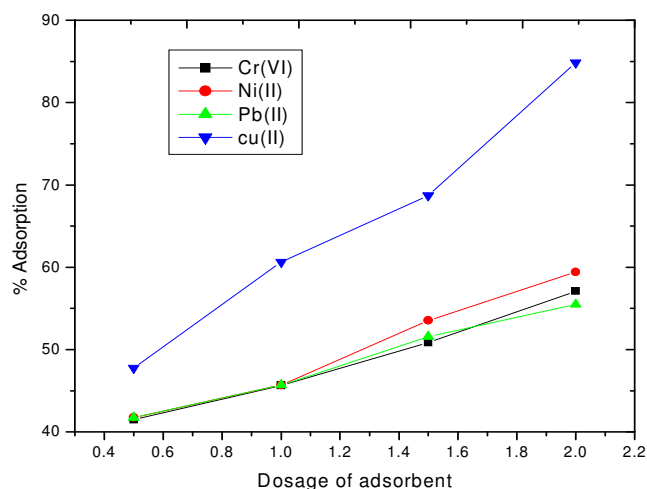
**Effect of initial heavy metal ion concentration:** Figure 1 illustrates the effect of initial heavy metal ion concentration on adsorption and retention of metal ions by alumina. The pH, adsorbent dosage, temperature and contact time were kept constant. A decrease in % adsorption is observed with increase in concentration of the heavy metal ions. On increase in heavy metal ion concentration, the available adsorption sites are already occupied and consequent adsorption is not as efficient as in the beginning, which explains the observed decrease. This suggests that further dilution will enhance the extent of retention of metal ions from solution.



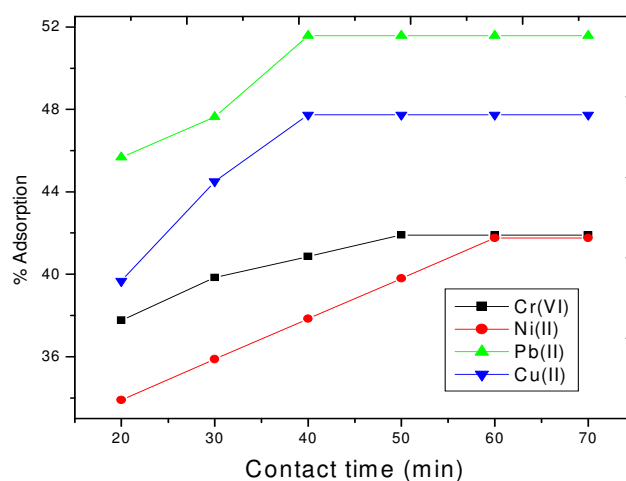
**Figure-1**  
Effect of initial metal ion concentration

**Effect of adsorbent dosage:** The variation in % removal of heavy metal ions with increase in adsorbent dosage is presented in figure 2. An increase in % removal of Cr(VI), Ni(II), Pb(II) and Cu(II) ions has been observed on increasing the dosage of the adsorbent. The number of sites available for adsorption increases with increase in surface area of the adsorbent. This facilitates an increase in the retention percentage of the metal ions with an increase in the dosage of the adsorbent.

**Effect of Contact time:** The effect of contact time between the adsorbent and the adsorbate on the % of adsorption is plotted in figure 3. On increasing the contact time between the alumina and heavy metal ions (i.e. Cr(VI), Ni(II), Pb(II) and Cu(II)) an increase in the retention percentages of all elements has been observed. The percentage removal of heavy metal ions remains constant after attainment of equilibrium. As a result, the time taken for attainment of equilibrium has been optimized as 40 min for Pb(II) and Cu(II), 50 min for Cr(VI), 60 min for Ni(II).



**Figure-2**  
Effect of adsorbent dosage



**Figure-3**  
Effect of contact time

**Effect of pH:** The extent of retention of the metal ions on the surface of the adsorbent is strongly dependent on the pH of the system under study. pH affects the availability of adsorption sites on the adsorbent and also the solubility of the metal ions in solution. The study was carried out by varying the pH from 3 to 7 by adding suitable buffer solutions. Figure 4 shows the variation in % removal of heavy metal ions with pH. An increase in % adsorption is observed at initial pH, more markedly than the increase at higher pH. The change in the retention percentage of the heavy metals on alumina is attributed to the binding of the metal ions in their hydrated state with alumina. The extent of removal of metal ions is minimum at lower pH values which are attributed to the competition between hydrogen and metal ions for retention in the available sites of alumina. By increasing the initial pH, a higher % of adsorption is observed since the competition is minimum.

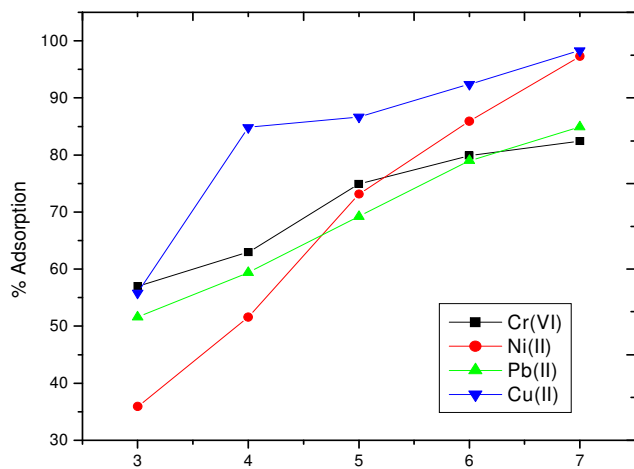


Figure 4  
Effect of pH

**Effect of temperature:** Figure 5 represents the change in extent of adsorption with respect to temperature. A linear increase in % adsorption is observed which indicates an endothermic process. The retention of metal ions increases with increasing temperature, which may be attributed to the activation of alumina at increased temperatures<sup>11</sup>. This suggests the monolayer coverage of the surface of alumina by the metal ions which may be followed by other extra layers of molecules which may be physically adsorbed<sup>16</sup>.

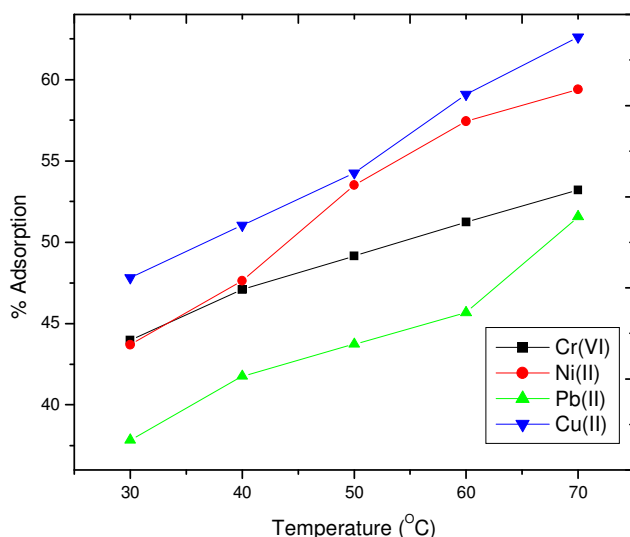


Figure-5  
Effect of temperature

**Freundlich and Langmuir adsorption isotherms:** The fitness of the adsorption behavior of the different metal ions on alumina has been tested with different adsorption isotherms which further explain the heterogeneity of alumina. Freundlich

isotherm is a common isotherm which is used for the determination of the parameters of adsorption<sup>17</sup>.

$$\log q_e = \log K_f + \frac{1}{n} \log c_e$$

Where  $K_f$  is the adsorption coefficient and  $n$  represents the order of adsorption. The isotherm represents a straight line equation which shows that a plot of  $\log q_e$  versus  $\log C_e$  gives a straight line with slope  $(1/n)$  and an intercept of  $\log K_f$ . Langmuir isotherm also plays a vital role to determine different parameters. The relationship between the equilibrium concentration of the adsorbate in the solid phase ( $q_e$  mg/g) and the equilibrium concentration in the aqueous phase ( $C_e$  mg/l)<sup>18</sup> has been established by the isotherm equation which is written as

$$\log q_e = \frac{1}{b} + \frac{1}{ab} c_e$$

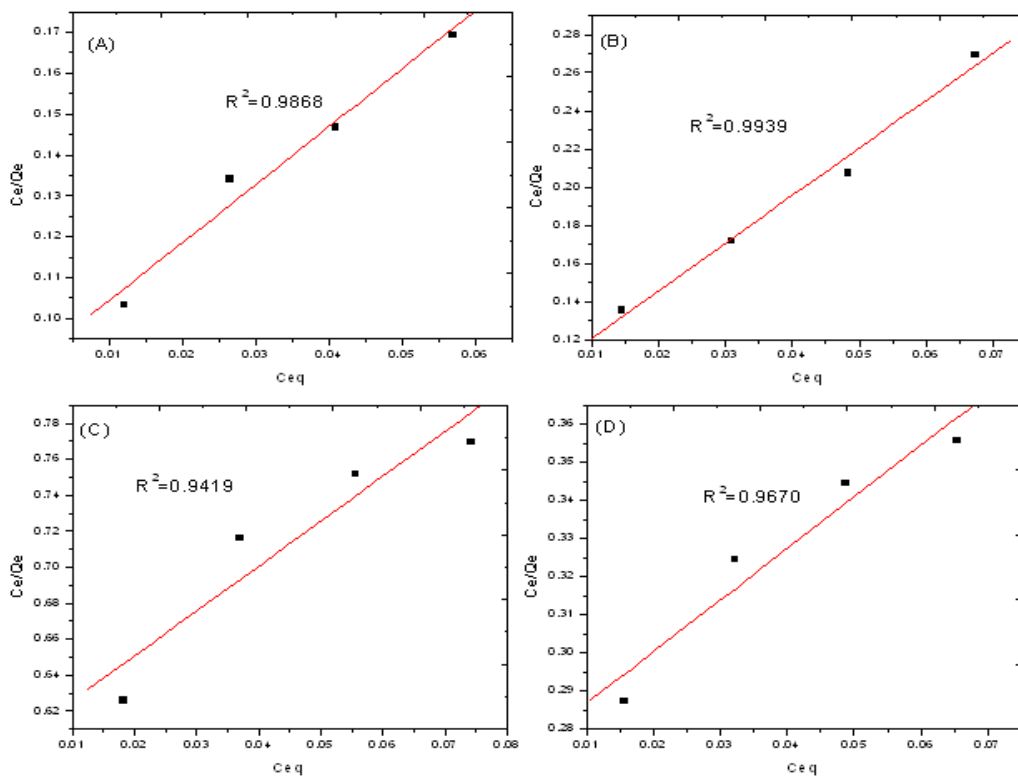
where  $q_e$  is the mass of heavy metal adsorbed per gram adsorbent,  $C_e$  is the equilibrium heavy metal solution concentration in mg/litre,  $a$  is the Langmuir constant and  $b$  is the monolayer coverage mg of heavy metal/g of adsorbent. A plot of  $C_e/q_e$  versus  $C_e$  should indicate a straight line of slope  $(1/b)$  and an intercept of  $(1/ab)$ .

**Langmuir Isotherm:** Figure 6 illustrates the linear plot of Langmuir equation of Cr(VI), Ni(II), Pb(II) and Cu(II) metal ions at varying concentrations using 0.5g alumina and at room temperature. Straight line plots are obtained on plotting  $C_e/q_e$  against  $C_e$ , and the Langmuir constants have been evaluated. Linear plots are observed for all metal ions which shows that the retention of Cr(VI), Ni(II), Pb(II) and Cu(II) metal ions on alumina follows Langmuir adsorption isotherm. Good correlation coefficients have been observed which suggest that a monolayer adsorption of metal ions occurs at the surface of alumina.

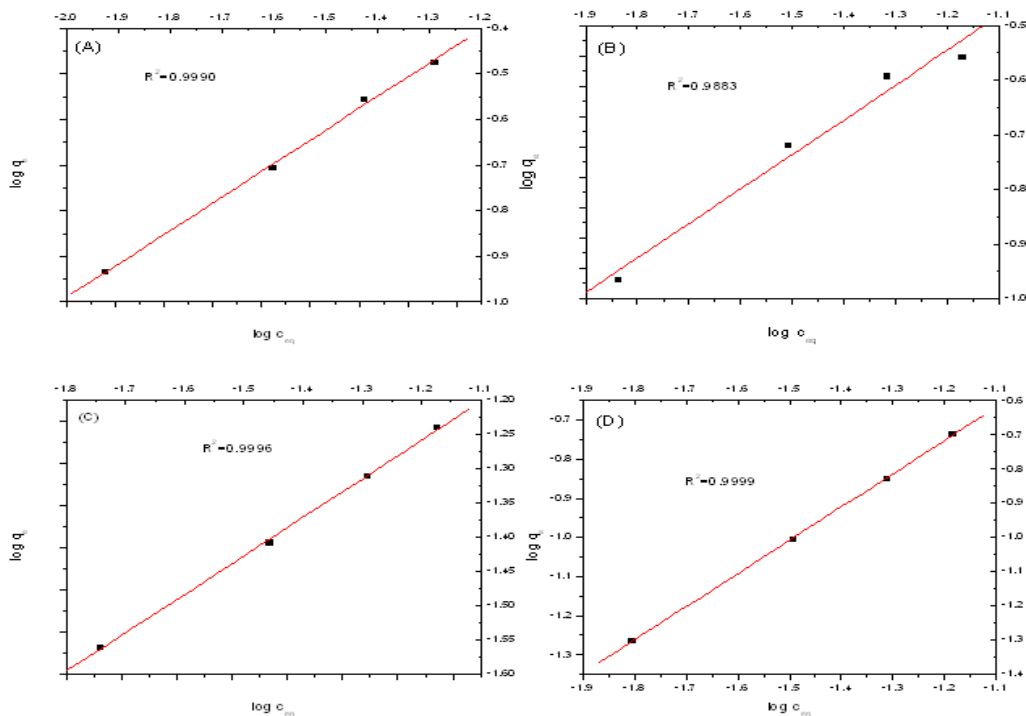
**Freundlich Isotherm:** Figure 7 shows the Freundlich plots of Cr(VI), Ni(II), Pb(II) and Cu(II) ions at different concentrations using 0.5g alumina and at room temperature. Straight line plots have been obtained on plotting  $\log C_e$  and  $\log q_e$  and the values of the constants have been calculated and tabulated in table-1. Linear plots show that adsorption follows Freundlich adsorption isotherm.

Table-1  
Freundlich constants for adsorption of Cr(VI), Ni(II), Pb(II) and Cu(II) on alumina

Metal ion	$K_f$	$n$
Cr(VI)	2.82	1.41
Ni(II)	2.30	1.70
Pb(II)	2.10	1.20
Cu(II)	2.30	1.20



**Figure-6**  
 Langmuir adsorption isotherm for adsorption of (A)Cr(VI), (B)Ni(II), (C)Pb(II) and (D) Cu(II) on alumina



**Figure-7**  
 Freundlich adsorption isotherm for adsorption of (A)Cr(VI), (B)Ni(II), (C)Pb(II) and (D) Cu(II) on alumina

## Conclusion

The retention of Cr(VI), Ni(II), Pb(II) and Cu(II) onto activated alumina has been carried out. Batch adsorption experiments were used for analyzing the effects of the following variables: such as concentration, adsorbent dosage, pH, temperature and contact time. The % of adsorption increases on changing the pH of the medium from acidic towards neutral. The time taken for attainment of equilibrium for all the metal ions has been established. The removal yield increases with increasing the adsorbent dosage and decreases with increase initial metal ion concentration. The effective removal of the heavy metal ions is mainly dependent on the ratio of adsorbent dosage to the concentration of metal ions, which is of course a compromise between cost effectiveness of the process and the desired retention percentage. The mathematical description for the adsorption behavior fit well to Langmuir and Freundlich isotherm models with good correlation coefficients.

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