

Based on the performed experimental results, a comparison of the sorptive ability among the chosen adsorbent materials to trap Ni(II), Co(II) and Cr(VI) ions is analyzed in this chapter. In addition, preferential order of adsorption of the metal ions by the adsorbents is also evaluated.

8.1 Comparison of Sorption Ability of Treated Adsorbents

The enhanced sorption capacity of TTCNS over that of TAINS is explained from the results obtained from different isothermal constants (Table 8.1). The sorption capacity values calculated for Langmuir (q_m), Freundlich (K_F) and DKR isotherm (q_s) models exhibit higher range for TTCNS as depicted in table 8.1. TTCNS is observed to be a more promising adsorbent than TAINS because of its higher intraparticle diffusion rate constant (K_i) and higher degree of randomness (ΔS). This statement can be further supported with the enhanced surface area and higher porosity values of TTCNS as evident from the table 3.1. Also the desorption efficiency of TTCNS is greater than TAINS for Ni(II) and Co(II) system being substantiated by the data from table 8.2.

Comparison efficiency of the treated materials can also be justified from the tabulated results (Tables 4.25, 6.19) of the collected effluents' analysis. The percentage removal of Cr(VI) was 57% for TTCNS and 47% for TAINS at a dosage of 450 mg for both the sorbents.

Table 8.1 Comparison of isothermal and thermodynamic constant values

Constants	TTCNS			TAINS		
	Ni(II)	Co(II)	Cr(VI)	Ni(II)	Co(II)	Cr(VI)
q_m (mg/g)	62.50	50.0	18.6	63.29	31.15	10.6
K_F (mg/g)	47.02	37.35	33.00	54.26	27.46	26.48
q_s (mg/g)	62.46	60.6	14.04	58.10	39.8	10.95
ΔH° (kJ/mol)	16.40	5.4	39.89	23.15	6.34	14.05
ΔS° (kJ/mol K)	136.34	18.77	36.54	81.36	21.68	47.76

Table 8.2 reveals a higher adsorption capacity, desorbing ability and regeneration capability of TTCNS in terms of desorbing medium, which establishes itself as an excellent adsorbent.

Table 8.2 Effect of desorbing medium

Metal ions	TTCNS		TAINS	
	Percentage of desorption	Desorbing medium	Percentage of desorption	Desorbing medium
Ni(II)	90.12	0.75 M HCl	83.20	0.40 M HCl
Co(II)	81.14	0.75 M HCl	72.45	0.40 M HCl

8.2 Comparison of Sorption Ability of Modified Adsorbents

The data shown in tables 7.1 & 7.2 of chapter VII, is indicative of the enhancement in the amount adsorbed is [i.e] 140.35 mg/g for MTCNS onto Ni(II)] at a chosen concentration, when compared to MAINS, wherein only 43.84 mg/g was the amount adsorbed under the same experimental conditions. Similar results have been recorded for removal of Co(II) and Cr(VI) with both the modified sorbents. Thus the results are illustrative that the phosphate modification was found to be more suitable for *Terminalia*

catappa nut shell as it possessed better sorption ability, compared to *Azadirachta indica* nut shell.

8.3 Preferential Order of Adsorption of Metal ions

Among the three metal ions studied, Ni(II) was adsorbed preferentially by the employed adsorbents. The order of preferential adsorption is found to be in the order of Ni(II) > Co(II) > Cr(VI) in terms of isothermal and thermodynamic constants.

The preferential order of adsorption of metal ions and the relative abilities of the solute- ion species to compete for surface sites of adsorbents are governed by intrinsic factors such as valence, ionic radius, pH, and the solution activities. Because the pH of the solution was kept constant and both Ni and Co are divalent cations, the selectivity depends entirely on the hydrated radii of the ions. Smaller the size of the ion, greater is the degree of hydration. Smaller the hydrated ionic radius, the greater is its efficiency to activate groups of the adsorbent. Thus for ions of similar charge, [Ni(II) and Co(II)] the ionic radius or hydrated ionic radius determines the order of preference of adsorption. With a radius of 4.04 and hydrated ionic radius of 0.690, Ni(II) is smaller in size than Co(II), whose radius and hydrate ionic radius are 4.23 and 0.745 respectively²⁹⁵. Thus Ni(II) is more effective in reacting with the sorbent particles because of its smaller size.

The above discussion is in accordance with the findings of Anoop Krishnan et al.,²⁶² wherein they state that the energy required in the dehydration of metal ions plays an important role in determining the selectivity series.

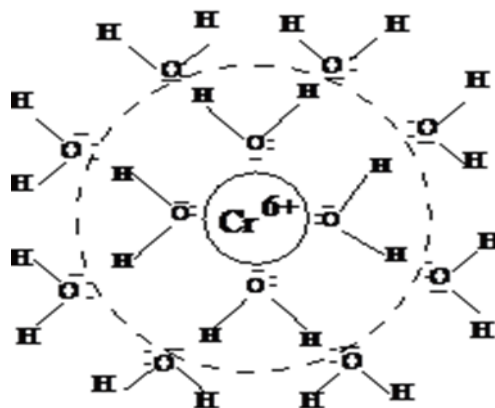
The factor which plays key role in explaining the sorption order is covalent index²⁹⁶. The covalent index of metal ions can be calculated from the equation (28), taking into account electro negativity (X) and ionic radius (r) of the metal ions. The value 0.85 in equation (28) represents an appropriate constant assumed to reflect the radius of oxygen and

nitrogen donor atoms. A high value of the covalent index exhibits the high degree of binding capacity of metal ions to the functional groups of the adsorbent.

$$\text{Covalent index} = X_m^2(r+0.85) \quad \dots (28)$$

The covalent index was found to be 5.709, 5.619 and 3.661 for Ni(II), Co(II) and Cr(VI) respectively thus supporting the preferential order of adsorption.

Cr(VI), the least sorbed, can be explained by its solvation property. The solvation property of Cr(VI) is more than that of Ni(II) and Co(II) due to its lower ionic radius (0.58 \AA) and greater charge (+6), resulting in higher hydration. Cr(VI) can bind with more water molecules and retards itself from being trapped by the adsorbents. The less solvation of Ni(II) and Co(II) ions result in greater sorption by the sorbents. Primary and secondary hydrated spheres of Cr(VI) ion is illustrated in the following figure.



Primary and secondary hydrated spheres of Cr(VI) ions

The stability constants of the Cr(VI) ions with encircling water molecules increase with ionization energies of the metallic species i.e., 8744.9 kJ/mol is the ionization energy of chromium in +6 oxidation state and 1753, 1648 kJ/mol are the ionization energy of nickel and cobalt in +2 oxidation state²⁹⁷. The more stable solvated Cr(VI) ions in aqueous medium with very high ionization energy compared to the other metal ions prevents them from getting sorbed easily by the adsorbent.