Adsorption and Desorption Performance of *Acacia nilotica* for the Removal of Cobalt(II) by Column and Batch Mode Study from Aqueous Phase and its Suitability in Real Waste Water

P. Thilagavathy[1], **T. Santhi**[2]

[1]Department of Chemistry, Professional Group of Institutions, Palladam - 641 662, India

[2]Department of Chemistry, Karpagam University, Coimbatore-641 021, India

Abstract: ***This study on the removal of cobalt ions from aqueous solutions by Acacia nilotica was conducted in batch and column method. The operating variables studied were contact time, initial solution pH, initial metal concentration, temperature and adsorbent dosage. Kinetics and isotherm models were validated to understand the mechanism of adsorption of Co(II) ion by Acacia nilotica. Thermodynamic properties such as ΔG°, ΔH° and ΔS° were determined for the cobalt adsorption. Further, the adsorption of cobalt ion was confirmed through instrumental analyses such as SEM. In column studies, the decrease of the flow rate resulted in the increase of the removal efficiency. The desorption and recyling ability of adsorbent was found to be good. We conclude that such modified Acacia nilotica can be used for the efficient removal of Co (II) ions from aqueous and industrial wastewater.***

Keywords: Adsorption-Desorption, Batch-column, Isotherm, Kinetics, Thermodynamics**.**

1. Introduction

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The rapid growth of industrial activities during the last few decades is one of the major reasons for pollution of water, air and soil. According to the World Health Organization [1], the metals of most immediate concern are lead, cadmium, copper, cobalt, aluminium, chromium, manganese, iron, nickel, zinc and mercury. Cobalt is a hard, ferromagnetic, lustrous, and brittle element widely used in many industries. The radioactive isotopes of cobalt are not present in the natural environment, but they are released as effluent from many industries such as nuclear power plants, the mining, metallurgical, electroplating, paints, pigments, and electronic industries [2]. The presence of cobalt in the environment leads to many human health problems such as vomiting, nausea, vision problems, heart diseases, thyroid damage, sterility, hair loss, bleeding, diarrhea, low blood pressure, bone defects, and even death [3]. Various treatment techniques including adsorption, precipitation, ion exchange and reverse osmosis have been employed to eliminate or reduce the toxic ion concentrations in wastewaters. Adsorption on solid surfaces is the most common one and efforts are being made continuously to develop new, low cost and efficient adsorbents for removal of heavy metals. Low cost adsorbent materials used by various investigators include saw dust, slurry, biomass and cellulose, peat, chitin, orange waste, rice husk, wheat bran, orange peel, banana pith, banana peel, apple pumice, wheat straw, sawdust, coir pith, sugarcane bagasse, tea leaves, rice husk, bamboo, ginger waste, pineapple leaves, tamarind fruit shell, fly ash, bottom ash, bagasse fly ash, Epicarp of Ricinus communis, Cucumis sativus, etc. has been tested (as such or after some minor treatment) for their efficacy as adsorbent for removal of heavy metals from aqueous media [4-13]. *Acacia nilotica* is a species of *Acacia*, native Africa and the Indian sub continent, which is widely found in abandoned areas of the Tirupur district. Its potential for the removal of Co(II) ion has been studied. Recently we have reported that ZAN exhibited appreciable capacity for removing Chromium ions from water [14]. The aim of the paper is to investigate the potential of eco friendly *Acacia nilotica* leaves as an agricultural waste for the removal of cobalt(II) ions from water. There are two main objectives of this study: the first is to compare the adsorption capacity of zinc chloride activated leaves of *Acacia nilotica*(ZAN) in batch and column studies; the second is to investigate the effect of the presence of one metal ion on the adsorption of the other metal ion in binary and ternary mixtures and then the results were compared with a single system. We investigate the recovery of the used adsorbent for its reuse is of great importance for environmental and economical reasons. i.e., adsorbents will be recovered by the desorption method by using a proper desorption agent like HCl and NaOH by batch mode study etc.

2. Methods and Materials

2.1 Preparation of adsorbent

The leaves of *Acacia nilotica* used in this work were collected locally (Palladam, India). It was twice washed with distilled water and subsequently with deionized water to remove the soluble impurities. It was then shade dried and powdered which is named as AN.

2.2 Adsorbate

All chemical reagents were of analytical degree and were used without further purifications. An aqueous stock solution (1000mg/L) of Co (II) ions was prepared using Cobalt sulphate (from Aldrich) salt. The working solutions were obtained by diluting the stock solution with double distilled water 50-200 mg/L. pH of the solution was adjusted using 0.5N HCl and 0.5N NaOH. Fresh dilutions were used for each study.

2.3 Experimental procedure

Batch adsorption experiments were conducted at room temperature by agitating 0.2 g of adsorbent(ZAN) with 50 mL of metal ion solution of desired concentration in 250 ml stoppered conical flask using a rotating shaker at a speed of 160 rpm for 120min. The effect of solution pH on the equilibrium uptake of Co(II), was investigated under similar experimental conditions between pH 1 - 10. The pH was adjusted using 0.5N HCl or 0.5N NaOH solutions. All pH measurements were performed with a digital pH meter (Elico Model L1120). Equilibrium studies for single metal system were conducted by agitating 50 mL of Co(II) solution with 0.2 g of adsorbent at different initial metal ion concentration (50-200 mg/L) upto equilibrium time. After equilibrium, the solution was analyzed for remaining metal ion concentration. UV-Visible spectrophotometer was used for the detection technique. For kinetic studies, the initial metal concentration was 50 mg/L. The sorption time was varied between 0 and 120 min. At predetermined times (i.e. at 5, 10, 15, 20 to 120 min), the samples were withdrawn and were analyzed for the residual metal ion concentration spectrophotometrically (SHIMADZU UV-2450), 1 cm glass cell, against a blank solution. All the experiments were carried out in duplicate. The effect of competitive adsorption of Co(II) with Cr(VI) and Cu(II) on PAN was also investigated. A 50 ml solution in which Cu(II) and Cr(VI) coexisted was agitated with 0.2g of AN in which 25 mL of 50mg/L concentration of working metal and 25mL of Cr^{6+} and Cu^{2+} of various concentrations (10, 20, 30, 40, and 50 mg/L) were taken in the conical flask. The percentage removal and the amount of equilibrium uptake of metal (q_e) were calculated using the following equations, Removal percentage =

$$C_o - C_{e/}\, C_o \times 100 \qquad (1)$$

$$q_e = (C_o - C_e)V/W \qquad (2)$$

where C_0 is the initial metal ion concentration (mg/L), C is the final metal ion concentration (mg/L), q_e is the adsorption capacity (mg/g), W is the weight of the adsorbent in gm, and V is the volume of the metal ion solution (L).

3. Results and Discussion

3.1 Characterization of ZAN Scanning electron microscope

The SEM image (Fig. 1a) shows a highly porous morphology of the raw biomaterial with pores of more or less different shapes and sizes. This figure also reveals the existence of variety of cavities on the external surface. These may contribute to the relatively high surface area of the biomaterial. Such biomaterial refined with zinc chloride, and further playing the role of biomass in the adsorption process (Fig. 1b), exhibits somewhat changed morphology with extended surface arrangement regarding the repetition of structures, the subsistence of pores of comparable shapes and sizes, and the smallest openings becoming more available for reactants. One of the reasons for this change may be the removal of the alkaline and alkaline earth metals during refinement, which could contribute to the changes in morphology. Dimensions of the smallest pores are comparable in both samples, suggesting that the refinement procedure has its main impact on the uniformity of the biomass structure. The authors suggest that the mentioned pores represent active sites of the adsorption process [15]. In the procedures investigated here, the effect of metal binding to the biomass surface caused some changes in the surface morphology in the case when refined biomass was used (Fig. 2c) where Co(II) adsorption was clearly seen.

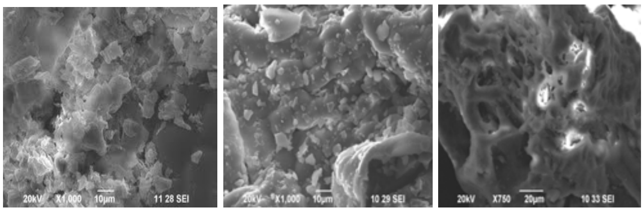

Figure1:a.SEM image of ZAN, **b.**ZAN without Co(II), **c.**SEM image of ZAN with Co(II)

3.2 Effects of pH

The extractability of the cations from the solution phase is pH dependent. The effectiveness of the process can be expressed by the percentage adsorption of Co(II) versus pH plot for the cations involved, as represented in Fig. 2. From the corresponding data for each metal, an increase in pH was followed by an increase in adsorption, reaching the maximum capacity at pH 4.5. For higher pH values it was observed a slightly decrease of adsorption for Co(II) and this diminution was more remarkable. The metal ion could be suffering hydrolysis, starting at pH higher than 5, forming $Co(OH)^+$ species, which promotes a diminution of the adsorption capacity, because the diminution of the formal charge of the metallic ion. Besides that, at pH around 7.0, a slight decomposition of the natural adsorbent could takes place.

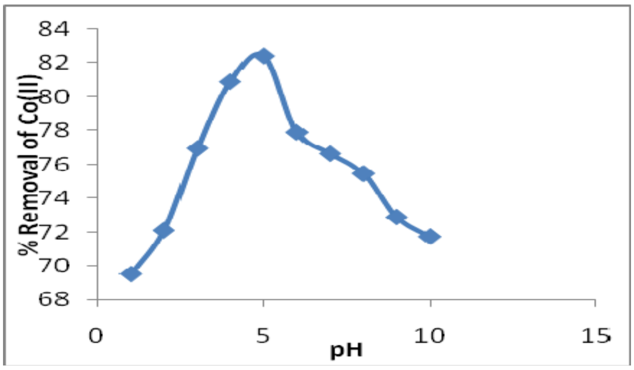

Figure 3: Effect of contact time and initial concentrations onto ZAN

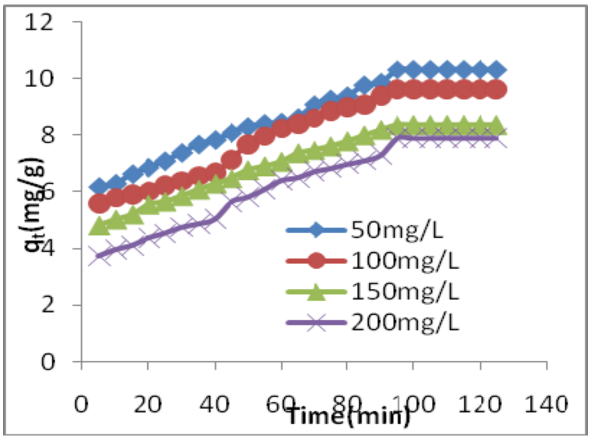

Figure 2: Effect of pH onto ZAN

3.3 Effect of contact time and initial concentration

Two of the most important parameters, which define an adsorbent, and evaluation of adsorption process are adsorption time and adsorption capacity. Adsorbent time is particularly important in defining the efficiency of adsorption and it helps to determine the effluent flow rate through a column for optimum removal of particular contaminants. Adsorption capacity determines the maximum amount of metal ions that can be removed per weight of adsorbent. The experimental results demonstrate the effect of initial Co(II) concentration (50–250mgL^{-1}) with time is shown in Fig. 3 for the adsorption of Co(II) onto ZAN. The results show that the adsorption of Co(II) increases very rapidly up to about 95min occurred by surface reaction and slowly reaches a constant value beyond which no more of the metal is removed from solution. A quasi stationary state was obtained within 2h of shaking time and is independent of initial concentration. For practical consideration 2h time was presumed to represent the equilibrium time for the adsorption of metal ions. When the initial Co(II) concentration increases from 25 to 150mg/L, the adsorption density increases from 12.4mg/g to56.5mg/g, but then percentage removal efficiency decreases from 99% to 75%. The result showed that the removal of Co(II) is concentration dependent. At higher initial concentrations the available adsorption sites of adsorption became fewer and hence the percentage removal of Co(II) depends upon the initial concentration. For fixed adsorbent dose the total available adsorption sites are limited thereby adsorbing almost the same amount of the adsorbate, thus results in a decrease in percentage removal of the adsorbate corresponding to an increase in initial sorbate concentration. It can alsobe concluded that higher removal at low concentrations important in terms of industrial application.

3.4 Effect of temperature on the uptake of cobalt

To investigate the effect of temperature on ZAN, experiments were carried out with five different concentrations of 50, 100, 150 and 200 mg/L at four temperatures (283, 293, 313 and 323 K). As shown in (Fig.4), adsorption capacity of the adsorbents increased with the growing temperature. The highest capacity was observed on ZAN at 323K (55.67 mg/g). This is because, the deprotonation reaction was easy at high temperature, which made more positive groups (amino and carboxyl groups) available for metal removal and the increasing temperature likely influenced the internal structure of the adsorbent and simplified the ion distribution in the adsorbent's interspaces structure [18].

3.5 Effect of adsorbent dose on adsorption

The adsorbent dosage is an important parameter because this determines the capacity of a adsorbent for a given initial concentration. The adsorption efficiency for Co(II) ions as a function of adsorbent dosage was investigated. The percentage of the metal adsorption steeply increases with the adsorbent loading up to 1g (Fig. 5). This result can be explained by the fact that the adsorption sites remain unsaturated during the adsorption reaction whereas the number of sites available for adsorption site increases by increasing the adsorbent dose.

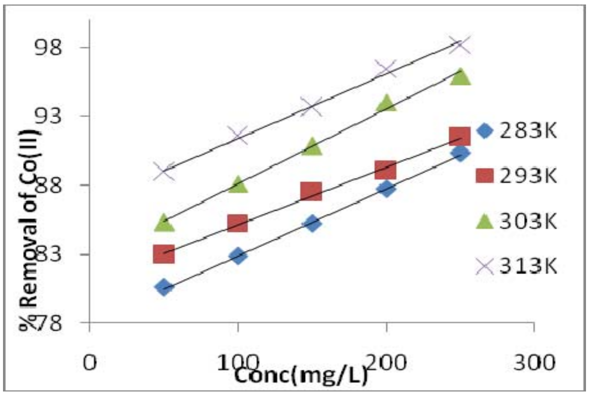

Figure 4: Effect of Temperature

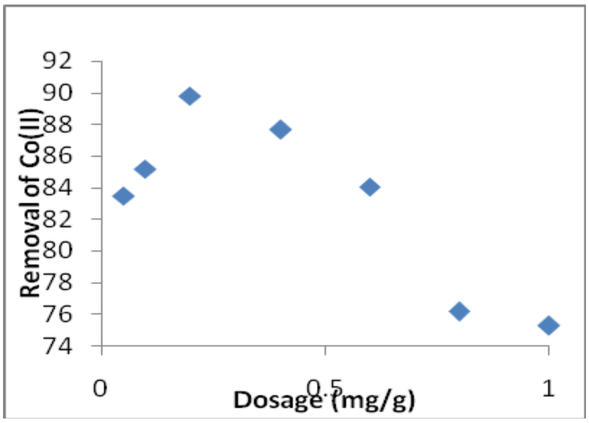

Figure 5: Effect of Dosage

3.6 Equilibrium Studies

In order to optimize the design of a sorption system for the removal of metals from effluents, it is important to establish the most appropriate correlation for the equilibrium curves. Four isotherm equations have been tested in the present study: Langmuir, Freundlich, Temkin, Dubinin-Radushkevich, Harkin-Jura and Frenkel-Halsey-Hill isotherms [18-22, 10]. These plots were used to calculate the isotherm parameters given in Table. 1. It has been observed from Langmuir isotherm that the maximum sorption capacity(q_m) was found to be 50.7614mg/g for Co(II) ions(Table 1). Freundlich equilibrium constants were determined from the plot of log qe versus log C_e, Fig. 6. It is found that from the correlation coefficient (0.9953) the adsorption of cobalt onto ZAN was correlated well with the

Freundlich equation and Frenkel-Halsey-Hill followed by Langmuir, Temkin, Harkin-Jura and Dubinin-Radushkevich equations under the concentration range studied.

3.7 Adsorption kinetics

Information on the kinetics of pollutant uptake is required for selecting optimum operating conditions for full scale batch process. In order to clarify the adsorption kinetics of heavy metal ions, experimental data are mostly tested for the pseudo-first-order and pseudo-second-order and Elovich equation and intra-particle diffusion model are also applied to examine the adsorption kinetics of Co(II) ion uptake by ZAN [23-25]. In Table 3, different kinetic models used in this study and their calculated results are given.

S. No	*Isotherms*	*Formula used*	*Parameters and values*
1	Langmuir	$C_e/q_e = 1/K_a q_m + (1/q_m \times C_e)$, $R_L = 1/1+K_L C_o$	q_m(mg/g) – 50.7614, b(L/mg) - 0.0244, R_L- 0.4505 and R^2 - 0.9625
2	Freundlich	$\text{Log } q_e = \log K_F + 1/n \log C_e$	n-1.9069, K_f (mg/g) – 1.9692 and R^2– 0.9953
3	Temkin	$q_e = \beta \ln\alpha + \beta \ln C_e$	α (L/mg) – 4.8328, β(mg/L) - 0.0885, b - 20715.9 and R^2 - 0.9598 b - 28183 and R^2 - 0.9625
4	Dubinin-Radushkevich	$\ln q_e = \ln q_d – K\varepsilon^2$	q_d (mg/g)-169.87, K (×10^{-5} molKJ^{-2})1.285, E – (KJ/mol) -0.6238 and R^2 – 0.9290
5	Harkin-Jura	$1/qe^2 = (B_2/A) – (1/A)\log C_e$	A – 109.2, B- 1.915 and R^2 - 0.883
6	Frenkel-Halsey-Hill	$\ln q_e = 1/n \ln K – 1/n \ln C_e$	1/n-2.283, K-1.898 and R^2 – 0.995

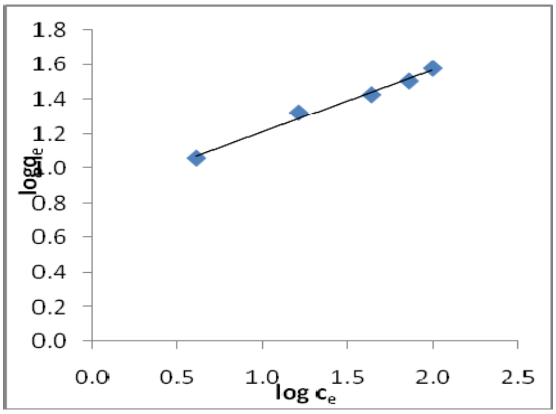

Figure 6: Freundlich Isotherm for Co(II) onto ZAN

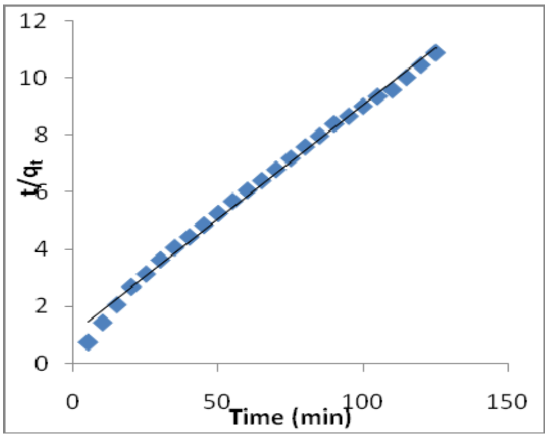

Figure 7: Pseudo second-order kinetic plot

Table 2: Kinetic Parameter for the Adsorption of Co(II) onto ZAN[29-32]

S.No	*Kinetic model*	*Formula used*	*Parameters and values*
1	Pseudo-first order	$dq_e/dt = K_1(q_e\text{-}q_t)$	K_1 – 0.0152, q_e – 3.7299 and R^2 - 0.5954
2	Pseudo-second order	$t/qt = 1/K_2 q_e^2 + 1/q_e\,(t)$	K_2 - 0.010,q_e – 11.4025 and R^2 - 0.9872
3	Elovich	$dq_t/dt = B_E \exp(-A_E q_t)$	A_E - 1.7848,B_E – 2.9903 and R^2 - 0.9012
4	Intra-particle diffusion	$q_t = K_d t^{1/2} + C$	K_d – 2.0281, C – 7.9511 and R^2 - 0.9775

The correlation coefficient for pseudo-second-order kinetic model obtained was greater(0.9872) than for pseudo first-order model(Fig 7). In addition, the experimental q_e(exp) 10.3034 mg/g values also agreed well with the calculated q_e value of 11.4025 mg/g (Table 2). Both factors suggest that the adsorption of Cobalt ions followed the pseudo second-order kinetic model, indicating that the rate limiting step was a chemical adsorption process between metal ions and clove adsorbent through the exchange of electrons between the particles involves.

4. Thermodynamic studies

To determine whether the process is spontaneous, both energy and entropy factors were considered. The thermodynamic parameters were calculated by the following equation where b is the adsorption equilibrium constant. ΔS°, ΔH° and ΔG° are the changes of entropy (J/K/mol), enthalpy (kJ/mol) and Gibbs energy (kJ/mol). T (K) is the temperature. R (J/mol/K) is the gas constant. The negative values for the Gibbs free energy change ΔG°(-22.31, -23.91, -24.66, -25.81 kJ/mol) confirmed the process of the adsorption was spontaneous in nature and the degree of the reaction spontaneity increased with the rising temperature. The absolute value of ΔG° increased probably related to the ascending number of the active sites which are available for adsorption process and the decrease of the boundary layer surrounding the adsorbent [26].

The positive value of ΔH° (8.23kJ/mol) indicated that the adsorption process is endothermic. The positive value of ΔS° (67.63 J/K/mol/) reflects the growth of randomness at the solid/solution interface and a good affinity of Co(II) towards ZAN. This is due to the structural changes of adsorbate and adsorbent during the adsorption, which made the increase in the disorderness of the solid/solution system [27].

5. Results of fixed bed experiments

5.1 Effect of flow rate

Experiments were performed with flow rates of 1-5(mL/min) whereas the thickness of the adsorbent was 3 mm. As depicted in Fig. 8, it was observed that the lower the flow rate the higher the copper removal. This is due to the more contact time when the flow rate is low.

5.2 Effect of bed thickness

The removal of Co(II) by *Acacia nilotica* fixed bed composite of different thickness at a constant flow rate of 1 (mL/min). As shown in Fig. 9, by increasing the thickness of the fixed bed layer, the uptake of chromium ions increases. Increasing the fixed bed layer leads to increase of the available interaction sites of the composite that provided more sites for adsorption of chromium ions with a thicker layer and the efficiency is increased by allowing sufficient time for the adsorbate to diffuse into the adsorbent. When the thickness of the layer of the composite was increased from 0.5 mm to 3 mm, the percentage removal was increased from 55% to77%. Comparing with its efficiency in batch mode, the prepared adsorbent displayed the main advantage of separation convenience when a fixed bed column was used. This is because the chromium anions are forced to interact with the active adsorbing sites on the large surface-area composite during the penetration.

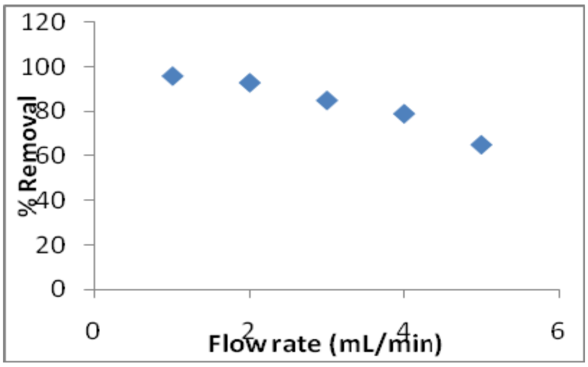

Figure 8: The effect of flow rate (ml/min) on amount of Co(II) adsorbed on ZAN.

6. Competitive adsorption of Binary(BMS) and ternary metals(TMS) onto ZAN

Adsorption of binary and ternary metal ions onto ZAN was examined. In the BMS system, working metal ion Co(II) was used as the main metal, the initial concentration of which was remained unaltered while the other two metal ion (Cu^{2+}& Cr^{6+}) concentrations are varied from 10 to 50 mg /L to determine the maximum adsorption.

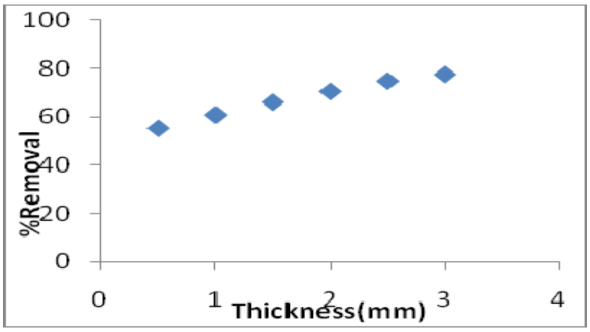

Figure 9: The effect of layer thickness on the amount of Co(II) adsorbed on ZAN.

The proposed binary mixtures were in the following combinations: Co^{2+}/Cu^{2+} & Co^{2+}/Cr^{6+}, whereas a grouping of $Co^{2+}/Cu^{2+}/Cr^{6+}$ was taken as ternary aqueous phase. It can be seen from the Fig. 10 there is a considerable reduction in metal sequestering ability of the adsorbents in binary and tertiary metal system in comparison with single metal system(i.e.,% Removal of Co(II) onto SMS is 82%). In case of binary metal system the ZAN exhibit the highest decline of 19% in adsorption efficiency for Co^{2+}/Cr^{6+} (63%) than Co^{2+}/Cu^{2+} (69%) compared to 82% percentage removal of Co(II) in SMS. From the (Fig.10) it was observed that there is a reduction of 67% metal uptake efficiency of ZAN in TMS in contrast to metal confiscating potential in SMS. Adsorption in multi-component systems is complicated because of the fact that solute–surface interactions are involved. The second metal ion present in the water solution competes with the single metal (Co(II)) ion adsorption. The results in binary and ternary systems clearly indicate that the combined action of multiple ions was antagonistic. Thus, the metal removal efficiency was greater in the single component system in comparison with multiple component one. It is probably due to the absence of competitive processes between metal and adsorbent in single component system [14]. The most likely reason for the antagonistic effect is the competition for adsorption sites on the cell surfaces and /or the screening effect by the competing metal ions. Results of present research showed that Co(II) adsorption is affected by Cr(VI) followed by Cu(II).

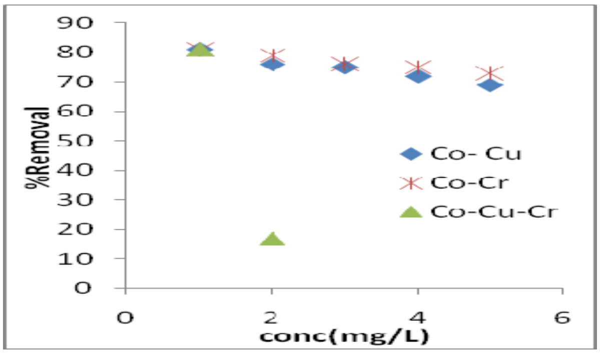

Figure 10: Adsorption of co(II) in binary and ternary metal system onto ZAN

7. Desorption and Reusability tests

In order to repeatedly use the adsorbent and to recover the Co(II) ions, the adsorption tests were conducted with various concentrations of HCl or NaOH aqueous solutions. The results are summarized in Table 4 which shows that the recovery percentage is 89% using a HCl or NaOH solution. The results indicate that the adsorbed Co(II) ions ZAN can be recovered by treating it with a HCl or NaOH solution, and a greater recovery rate can be obtained when a HCl solution is used. Moreover, almost 89% of the Co(II) ions can be recovered when a 2.0 mol/L HCl solution is used. Readsorption tests were also carried out to evaluate the practical utility of ZAN. After 10 replications of adsorption and desorption, almost no loss of adsorption capacity is observed. Only 8% of the adsorption capacity decreases after 10 cycles.

Table 4: Recovery Rate of Co(II) Ions on Adsorbent

Solution	*Conc (mol/L)*	*Recovery Rate (%)*	*Solution*	*Conc (mol/L)*	*Recovery Rate (%)*
HCl	0.5	71.4	NaOH	0.5	58
HCl	1.0	78.7	NaOH	1.0	69.8
HCl	2.0	89	NaOH	2.0	72

8. Suitability of ZAN onto Real Industrial Waste Water

The industrial waste water was collected locally from a metal finishing industry in Vangepallayam (India). The adsorption technique was carried out in the real waste water onto ZAN, in order to remove the toxic metal from water. The effect of pH, adsorption dosage and desorption were investigated. In this study, Initial pH values were adjusted in the range of 1 to 10 before addition of the adsorbent. Fig.11 shows that the adsorption was highly pH dependent. The uptake was maximum at the acidic pH and the maximum uptake was obtained at pH 5 (52%) and then decreased gradually. The optimum pH value (pH 5) was adjusted for further experiments.

The effect of changing adsorbent dosage on the adsorption rate of real industrial waste water was studied by varying the concentration of the sorbent from 0.4g to 1g while keeping the other experimental conditions constant. The percentage removal versus adsorbent dosage is shown in Fig. 10. An increase in the percentage of adsorption with increasing adsorbent dosage was observed. Desorption studies help to elucidate one mechanism of adsorption and recovery of the adsorbate and adsorbent. The maximum desorption of ZAN from real industrial waste water is shown in Fig.11. It suggests that the recovery of metal from the adsorbent was possible and it make the process more feasible.

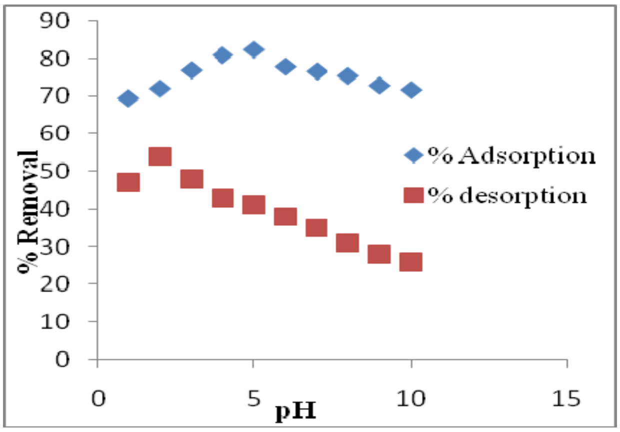

Figure 11: Percentage of adsorption and desorption

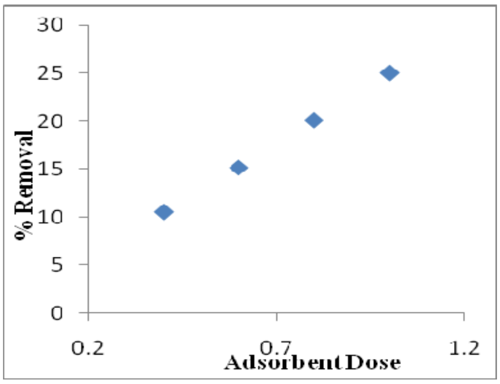

Figure 12: Effect of sorbent dose on the adsorption of real industrial waste water onto ZAN

9. Conclusion

Hydroxyl and carboxylic groups on surface of adsorbent have high affinity for heavy metal ions. In this study the heavy metal, namely, co (II)) was selected for removal from aqueous solutions using adsorption technique. Batch experiments were conducted to study the impacts of pH, adsorbent dose and initial metal ion concentrations. Maximum adsorption was recorded at pH 5.0 for Co(II). An increase in the adsorbent dosage gave increased adsorptions for Co(II), whereas the adsorption decreased with increase of initial metal ion concentrations. Additionally, a competitive mechanism seems to be dominant during adsorption in binary systems. In column studies the decrease of the flow rate resulted in the increase of the removal efficiency. The adsorption of Co(II) ions on *Acacia nilotica* follow Freundlich adsorption isotherms. Thermodynamic constants were also evaluated using equilibrium constants changing with temperature. The negative value of ΔG for Co(II) ions indicated the spontaneity of the process. The positive value of ΔH showed the endothermic nature of Co(II) sorption. Regeneration of spent adsorbent has become a cost effective and sound environmental option. Desorption and regeneration can be done to recover valuable metal from spent adsorbent. Hydroxyl and carboxylic groups present in Acacia nilotica make them amenable to easy desorption and regeneration with acidic and basic solution. Heavy metal removal with the above adsorbent appears to be technically feasible, user-friendly, eco-friendly and economical process and with high efficacy.

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Author Profile

P. Thilagavathy received M.Sc., M.Phil., degree in chemistry from Bharathiyar University in 2009 and 2011 respectively. Now pursuing Ph.D in Karpagam University.