



Biosorption of COBALT (II) by *Acacia nilotica* from single and multicomponent systems of Aqueous solution: Equilibrium, isotherm, kinetic and thermodynamic studies

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Abstract

The applicability of *Acacia nilotica* as adsorbent for the effective removal of Co(II) from aqueous solutions was investigated. Batch experiments were performed to study the effects of various parameters such as pH, initial concentration, biosorbent dose and contact time was studied for adsorption of Co(II) ion. Kinetics and isotherm models were validated to understand the mechanism of adsorption of Co(II) ion by AN. 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 and FTIR. Maximum adsorption was observed at the pH range of 5 with an initial concentration of 50 mg/L of the adsorbate. The percentage adsorptions were found to be 81%. Results indicated that adsorption process obeys Freundlich isotherm model other than other models. The pseudo-first order and pseudo-second order kinetic equations were used to model the adsorption kinetics, with the pseudo second order giving a better fit, as seen from the correlation coefficient (R^2) which is 0.9897 for pseudo-second order model. The applicability of the Elovich equation and intra particle diffusion model to the sorption kinetics were also investigated. negative enthalpy confirmed that the process was exothermic. The desorption and recycling ability of Co(II) and AN are found to be good. This work therefore shows that *Acacia nilotica* leaf could be used to remove Co(II) ions from aqueous solutions.

Key words: Cobalt (II), Biosorption, Isotherms, Kinetics, Thermodynamics, Desorption.

1. Introduction

Heavy metal pollution is spreading throughout the world with the expansion of industrial activities. The industrial use of metals increases their concentrations in air, water and soil. The metal ions do not undergo biodegradation and many of them are soluble in aqueous solutions, therefore become more available for living systems and accumulate in the environment (Laws 2000; Gupta *et al.*, 2002). Trace metals are widely spread in environment and may enter the food chain from the environment. It is well recognized that the presence of heavy metals in the environment can be detrimental to a variety of living species, including man. Unlike organic pollutants, metals are non-biodegradable hence removal of heavy metal ions becomes essential. Cobalt (II) compounds are essential in many industries. Their applications in nuclear power plants, metallurgy, mining, pigments, paints and electronic are only few examples where the presence of cobalt in waste waters represents a major environmental problem (Babel and Krniavan 2003). Cobalt as a pollutant has many toxic effects such as imparting neurotoxicological disorders, genotoxicity, carcinogenicity, cardiomyopathy and bronchial asthma. The tolerance limit for Co (II) in potable water has been fixed as 0.05 mg L⁻¹. A number of physico-chemical technologies compared with the traditional wastewater treatment technologies like coagulation, biodegradation, electroflocculation, membrane filtration, ion-exchange, precipitation, ozonation, etc., are available, these methods often involve high capital and operational costs and may also be associated with the generation of secondary wastes, which present treatment problems. This has resulted a need for innovative treatment technologies for trace metal removal. Adsorption has received global attention due its simplicity and flexibility of design, high selectivity and efficiency, low operating cost and high quality-treated effluent. In recent years, adsorption has been extensively studied by researchers worldwide as an efficient and economically sustainable technology for the treatment of waste water (Gupta and Suhas 2009; Gupta and Rastogi 2009). Use of low cost adsorbents offers a potential alternative to existing methods for removal of metals from solutions (Harshala Parab *et al.*, 2006). 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 pomace, 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, etc. has been tested (as such or after some minor treatment) for their efficacy as adsorbent for removal of metals from aqueous media (Al-Degs *et al.*, 2006, Missana and Garcia *et al.*, 2007; Gupta and Suhas 2009; Gupta *et al.*, 2005, 2008; Kurniawan *et al.*, 2006). For the present work adsorptive properties of one such low cost adsorbent *Acacia nilotica*, have been evaluated for Co(II), *Acacia nilotica* is a species of *Acacia*, native Africa and the Indian sub continent. The main objective of this study was to investigate the equilibrium and kinetic parameters of the adsorbent. In addition, parameters that influence adsorption, such as initial copper concentration, agitation time, pH, isotherm and kinetic studies were investigated.

2. Materials and Methods

2.1. 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. After preparation the solution was standardized (Dean 1995), for to determine the exact concentration of metal ion. 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. Batch adsorption study

Batch adsorption experiments were conducted at room temperature by agitating 0.2 g of adsorbent(AN) 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 with rubeanic acid (SHIMADZU UV-2450) $\lambda_{max}= 450$ nm, 1 cm glass cell, against a blank solution (Flaska. and Barnard 1976). All the experiments were carried out in duplicate. The effect of competitive adsorption of Co(II) with Cr(VI) and Cu(II) on AN 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 amount of equilibrium uptake of metal (q_e) and the percentage removal were calculated using the following equations,

$$q_e = \frac{(C_o - C_e)V}{W} \quad (1)$$

$$\text{Removal percentage} = \frac{(C_o - C_e)}{C_o} \times 100 \quad (2)$$

where C_o and C_e are the initial and final equilibrium concentrations, V is the Volume(L) of the solution and W is the weight (g) of the adsorbent.

3. Results and Discussion

3.1. Characterization of AN

Determination of Zero Point Charge (pH_{zpc}) was done to investigate the surface charge of both adsorbent. For the determination of pH_{zpc} , 0.2g of the sample suspension was prepared in 50mL of $NaNO_3$ electrolyte of concentration approximately 10^{-2} M. Aliquots of suspension were adjusted to various pH values with dil. NaOH and HNO_3 . After 60 min for equilibrium, initial pH was measured. Then 0.1g of $NaNO_3$ was added to each aliquot to bring the final electrolytic concentration to about 0.45 M. after an additional of 60 min of agitation, final pH was measured. The results were plotted with initial pH (final pH- initial pH) against final pH. The pH at which it is equal to zero is zero point charge (pH_{zpc}).The surface morphology was studied using scanning electron microscopy (SEM) (Fig. 1a & 1b).

An SEM (Jeol jsm-6390) image of AN before Co(II) loading at a magnification of 1000X shows that the surface of material was porous, and Fig.1b shows the Co(II) loaded sites at magnification of 2000X. It is clear from the SEM image that the external surface of the sample was rough and contained abundant porous structures of different size and shapes. The inner cavities in porous structures provide new structures for the accommodation of Co(II) ions.

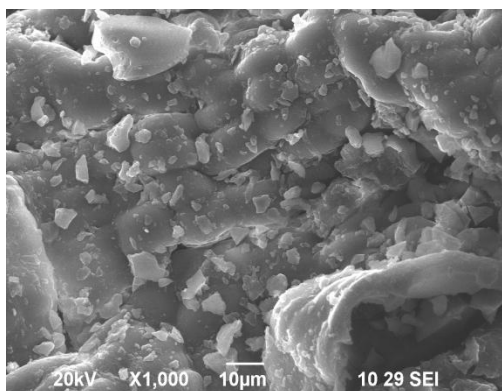


Fig. 1a. SEM image of AN before Co(II) loading

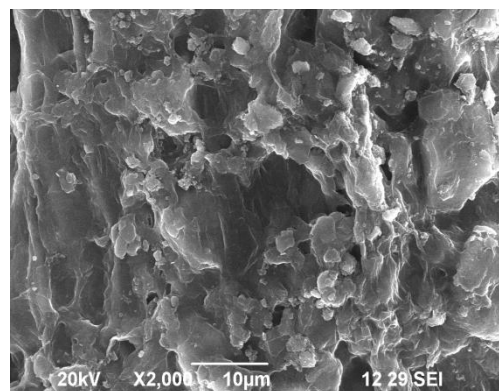


Fig. 1b. AN after Co(II) loading

Fourier transform infrared spectroscopy (FTIR) of dried *Acacia nilotica* leaves after and before adsorption was carried out to know if any changes have taken place on metal-binding sites on the biomaterial (Fig. 2a and 2b). As the constituents of biomaterials are mainly carbohydrates, proteins, and phenolic compounds comprising of functional groups as carboxyl, hydroxyl, and amine groups. These functional groups may act as sorption sites for the binding of metal ions. The spectra of *Acacia nilotica* leaves before and after the adsorption of Co(II) showed the presence of three fundamental constituents/three visible changes in biotic material. In the adsorbed sample spectrum, the band at 3,424 and 1,735 cm^{-1} are due to hydroxyl and acetyl groups in hemicelluloses as well as overtones of Co–O stretch (Dhara Shukla *et al.*). The bands from 1,238 to 1,656 cm^{-1} , specially the one at 1,656 cm^{-1} , are representative for lignin, while the one at 1,033 cm^{-1} is due to carbohydrates (C–O bonds in alcohols). The band centered at the 2,900- cm^{-1} region (aliphatic C–H stretching), which is progressively resolved in two separate bands (2,850 and 2,900 cm^{-1}) after the Co(II) adsorption. The appearance of a new peak at 3,784 cm^{-1} in the adsorbed AN sample is due to the OH group interacting with Co(II) ion. The spectra showed a wide band with two maximum peaks at 3420 and 3566 cm^{-1} . This band can be assigned to the O–H stretching mode of hydroxyl groups and adsorbed water. Moreover, this broad peak band in the range of 3200–3650 cm^{-1} is attributed to the hydrogen-bonded OH group of alcohols and phenols. In the 1050–1200 cm^{-1} regions, peak at 1072 might be related to the carbon–oxygen dingle bonds displayed stretching in acids, phenols, ethers, and esters (Puziy *et al.*, 2003). In the region 500–900 cm^{-1} , there is a peak at 607 cm^{-1} which is assigned to C–H out-of-plane bending in benzene derivative. The peak at 1456 cm^{-1} appeared due to C=C stretch in aromatic rings (Guo *et al.*, 1999). The peaks at 1600–1700 cm^{-1} are due to the double bond C=O stretching vibrations with aromatic carbons (Arriagada *et al.*, 1997 and Chiang *et al.*, 2002). The band at 2343 cm^{-1} is ascribed to the carboncarbon triple bond vibrations in alkyne group (Yang *et al.*, 2003).

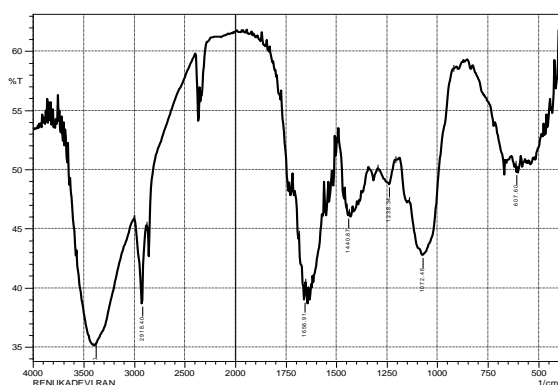


Fig. 2a FTIR of AN before Co(II) loading

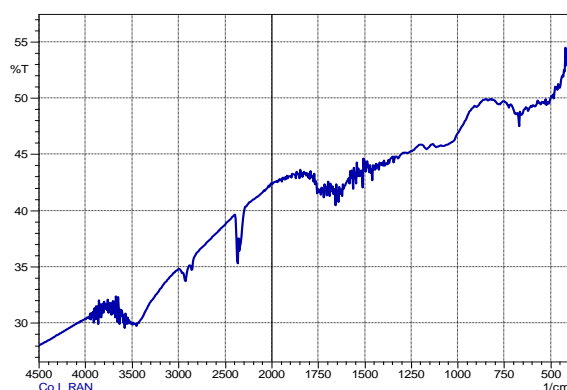


Fig. 2b FTIR of AN after Co(II) loading

3. 2. Effect of initial solution pH

The initial solution pH is an important parameter in the adsorption process of metal ions from aqueous solutions, which affect both the dissociation degree of functional groups from adsorbent surface and the speciation and solubility of metal ions (Ma and Tobin 2004). It is clear that the AN was effective for the removal of Co(II) over the pH range 1–10. The adsorption of the metalcation on adsorbent depends on the nature of the adsorbent surface and species distribution of the metalcation. As can be seen from Fig. 3, the adsorption efficiency gradually increased with the increase of initial solution pH. This behaviour is mainly determined by the ionic state of functional groups from adsorbent surface involved in adsorption process. Thus at lower pH, most of functional groups are un-dissociated and the obtained values of removal percent are lower. The increasing of initial solution pH determined the increasing of functional groups dissociation degree, and thus the Co(II) ions can be more easily bonded. In consequence, the adsorption efficiency increases. Because the maximum efficiency of cobalt (II) removal is obtained at initial solution pH = 5, this was considered as optimum value, and was used in all further experiments. For AN, the adsorption at pH above 6 shows a decreasing trend because of the formation of hydroxyl complexes of cobalt, $\text{Co}(\text{OH})_2$ (Periasamy *et al.*, 1991).

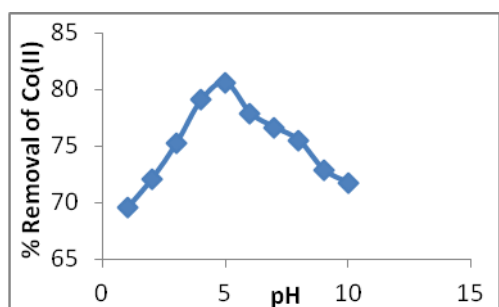


Fig. 3 Effect of pH onto AN

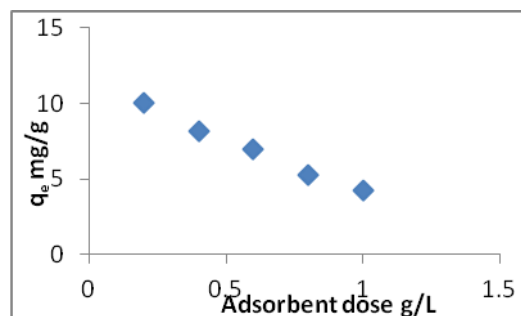


Fig. 4 Effect of Adsorbent dose

3. 3. Effect of Adsorbent dose

Fig. 4 presents the effect of adsorbent dose for cobalt (II) adsorption on AN. It can be observed that varying the adsorbent dose from 0.2 to 1 g/L, keeping initial Cobalt concentration (50mg/L), room temperature and contact time (2 h) constant, the q_e values decrease from 9.36 to 4.23 mg/g for AN. Therefore 0.2 g/L was considered sufficient for

quantitative removal of Co(II) from aqueous solutions, and was selected as the optimum value for the adsorption experiments. The results showed that with increasing the adsorbent dose, the adsorption% of Co (II) was increased. The increase in the adsorption percentage with AN doses can be explained by the increase in the adsorbent surface area and the availability of more adsorption sites (Garg *et al.*, 2004).

3.4. Effect of initial cobalt (II) concentration

The Co(II) removal AN was studied as a function of its initial concentration under optimized conditions, initial solution pH and amount of adsorbent. The amount of Co(II) retained on weight unit of adsorbent (q_e , mg/g) (Fig. 5) increase with the increasing of initial metal ion concentration from aqueous solution. At the same time, the percent of Co(II) removal (%) (Fig. 5) sharply decrease with the increasing of the initial concentration. This opposite trend is determined by the fact that at higher concentrations, the most superficial groups are already occupied and in consequence, the diffusion of Co(II) ions to the un-reacted functional groups is inhibited. A good retention of Co(II) take place at initial metal ion concentration lower than 95 mg/L when the residual concentration is lower than the permissible limit for cobalt discharge. The increasing of initial Co(II) concentration over these values, determined a decrease of adsorption efficiency, and in consequence for its removal are necessary two or more adsorption steps. These experimental results suggest that the removal of Co(II) from aqueous solutions, by adsorption on AN occurs predominantly by ion exchange interactions, and the efficiency of adsorption process depends on the ionic state of superficial functional groups of adsorbent. Thus, in case of AN, most of functional groups are un-dissociated and the number of electrostatic interactions between these and the metal ion is low.

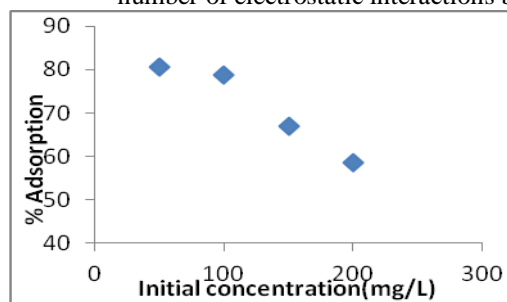


Fig. 5 Effect of initial Co(II) concentration

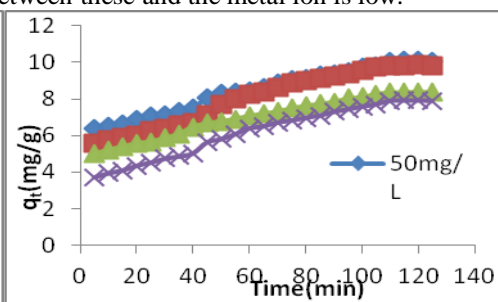


Fig. 6 Effect of contact time

3.5. Effect of contact time

The effect of contact time between adsorbent (AN) and Co(II) aqueous solutions with an initial concentration of 50 mg/L and pH = 5 is illustrated in Fig. 6. It can be seen that the Co(II) removal percent increase rapidly with the contact time up to 45 min for the AN. After this fast initial step, the rate of adsorption process becomes slower and the maximum removal is attained at 110 min. The low values of contact time necessarily for to reach the equilibrium sustains the hypothesis that the Co(II) adsorption on un-treated and treated peat moss occurs predominantly by electrostatic interactions.

3.6. Adsorption isotherms

The Langmuir, Freundlich models are often used to describe equilibrium adsorption isotherms Temkin and Dubinin-Radushkevich models are also applied to describe equilibrium sorption isotherms. In Table 1, different isotherm models used in this study are given. The calculated results of these isotherm models and their constants are given in Table.3

It has been observed from Langmuir isotherm that the maximum sorption capacity(q_m) was found to be 49.01mg/g (Table 3). Table 2 compares the q_m values from the current research with those obtained for other adsorbents for Co(II) in literature. It is found that the adsorption of cobalt onto AN was correlated well with the Freundlich equation followed by Dubinin-Radushkevich equations, Langmuir, and Temkin under the concentration range studied(Table 4). The correlation factors R^2 (0.9185, 0.9183, 0.8343 and 0.8442) for D-R, Langmuir, Freundlich, and Temkin models, respectively) confirm good agreement between both theoretical models and our experimental results. The R^2 values for the Freundlich model are closer to unity than those for the other isotherm models for Co(II) ($R^2 = 0.9185$). The Freundlich isotherm equation is therefore expected to best represent the equilibrium adsorption data. It is clear that the Freundlich isotherm is best fitted for the sorption of Co(II) ion onto AN. So, we conclude that the adsorption process may be a heterogeneous multilayer adsorption.

Table 1 Comparison of the maximum adsorption capacity of *Acacia nilotica* leaves with other adsorbent used in the literature.

S.No	Adsorbent	Q_m mg/g	Reference
1	Coir pith	12.82	Parab <i>et al.</i> , 2006
2	Kaolinite	0.919	Yavuz <i>et al.</i> , 2003
3	Montmorillonite-K	20.45	Assaad <i>et al.</i> , 2007
4	Magnetic chitosan nanoparticle	27.4	Chang <i>et al.</i> , 2006
5	Sterified coir pith	34.13	Assaad <i>et al.</i> , 2007
6	Chitosan	76.34	Assaad <i>et al.</i> , 2007
7	<i>Acacia nilotica</i> leaf	35.46	current study
8	Ceralite IRC-50	58.8	Dahiya <i>et al.</i> , 2008

Table 2 Different isotherm models used in this study

S.No	Isotherm	Formula	Parameters	Reference
[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, b, R_L and R^2	Langmuir, 1918 Eloussaief <i>et al.</i> , 2010
[2]	Freundlich	$\log q_e = \log K_f + 1/n \log C_e$	n, K_f and R^2	Freundlich <i>et al.</i> , 1906
[3]	Temkin	$q_e = \beta \ln \alpha + \beta \ln C_e$	α, β, b and R^2	Temkin, 1940
[4]	Dubinin-Radushkevich	$\ln q_e = \ln q_d - K \varepsilon^2$	q_d, K, E and R^2	Dubinin, 1960, Radushkevich, 1949

Table 3 Isotherm Constants for Co(II) Adsorption onto AN

Adsorbent	Isotherm model	Constants and Correlations	values
AN	Langmuir	Q_m (mg/g)	49.0186
		b (L/mg)	0.0204
		R^2	0.8343
		$1/n$	0.5398
	Freundlich	K_f (mg/g)	1.9692
		R^2	0.9185
		Q_m (mg/g)	161.16
		$K(\times 10^{-5} \text{ mol}^2 \text{ KJ}^{-2})$	1.1133
	Temkin	α (L/mg)	4.8328
		β (mg/L)	0.0743
		B	33569.3
		R^2	0.8442
	Dubinin-Radushkevich	E (KJ/mol)	0.6702
		R^2	0.9183

3.7. Adsorption kinetic study

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 Cu(II) and Co(II) ions uptake by AN. In Table 4, different isotherm models used in this study are given. The calculated results of these models and their constants are given in Table.5

Where t is the contact time of adsorption experiment (min); q_e (mg/g) and q_t (mg/g) are respectively the adsorption capacity at equilibrium and at any time t ; k_1 (1/min), k_2 (g/mg min), a (mg/g min), b (g/mg), k_{id} (mg/g min^{1/2}) are the rate constants for these models, respectively. The kinetic constants along with the correlation coefficients are listed in Table 5. The correlation coefficient for pseudo-second-order kinetic model obtained was greater(0.9897) than for pseudo first-order model. In addition, the experimental q_e (exp) 10.0996 mg/g values also agreed well with the calculated q_e (cal) value of 10.917 mg/g (Table 5). Both factors suggest that the adsorption of Cobalt ion 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. Similar conclusions were found by Ho as a result of an analysis of data from literature[34]. The adsorption process of Co(II) can be well fitted by use of the pseudo-second order rate constant for AN. The linear regression coefficient value R^2 (0.9897) obtained for pseudo-second-order kinetics was closer to unity than the R^2 value (0.6227) for first-order kinetics. This indicates that adsorption of cobalt ions by AN follows pseudo-second-order kinetics. In the intra particle diffusion model, the values of q_t were found to be linearly correlated with the values of $t^{1/2}$. The k_{dif} values were calculated by use of correlation analysis. $K_{dif} = 20.281$, $R^2 = 0.9786$) for AN. The R^2 values were closer to unity for cobalt onto AN. The adsorption of metal ions onto AN may be controlled via external film diffusion at earlier stages and later by the particle diffusion. This may confirm that the rate-limiting step is the intra particle diffusion process.

Table 4 Different kinetics models used in this study

S.No	Kinetics model	Formula	Parameters	Reference
[1]	Pseudo first-order	$dq_e/dt = K_1(q_e - q_t)$	K_1, q_e and R^2	Langergren, 1898
[2]	Pseudo second-order	$t/q_t = 1/K_2 q_e^2 + 1/q_e (t)$	K_2, q_e and R^2	Demirbas, 2004
[3]	Elovich equation	$dq_t/dt = B_E \exp(-A_E q_t)$	A_E, B_E and R^2	Chein, 1980
[4]	Intra-particle diffusion model	$q_t = K_{dif} t^{1/2} + C$	K_{dif}, C and R^2	Weber, 1963

Table 5 Kinetic Parameter for the Adsorption of Co(II) onto AN

Kinetic models	parameters	values
Pseudo-first order	$K_1(\text{min})$	0.0290
	$q_e(\text{mg/g})$	6.9151
	R^2	0.6227
Pseudo-second order	$K_2(\text{g/mg/min})$	0.010
	$q_e(\text{mg/g})$	10.917
	R^2	0.9897
Elovich	A_E	1.5936
	B_E	5.8467
	R^2	0.8878
Intra-particle diffusion	K_{dif}	20.281
	C	9.5718
	R^2	0.9786

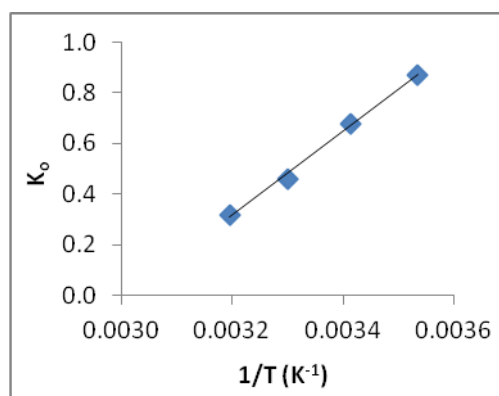
4. Thermodynamic Studies

Adsorption studies in the temperature range 283–313 K were conducted to determine thermodynamics constants such as Gibbs free energy change (ΔG°), enthalpy change (ΔH°) and entropy change (ΔS°) for the system and to ascertain the sorption mechanism. For this study, adsorbent dosage selected was 0.2 g and cobalt concentration was 50 mg/L with pH= 5 in a stoppered conical flask and allowed to equilibrate for 2 h at the different temperatures ranging from 283 to 323 K. The Gibbs free energy change, of the process is related to equilibrium constant by the equation (Ozcan *et al.*, 2006; Akcay 2004).

$$\Delta G^\circ = -RT \ln K_d \quad (3)$$

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

Where K_d is the distribution coefficient for the adsorption; ΔS° , ΔH° and ΔG° are the changes of entropy, enthalpy and the Gibbs energy; T (kelvin) is the temperature and R (8.314 J/mol/K) is the gas constant. The values of ΔH° and ΔS° were determined from the slopes and intercepts of the plots of $\ln K_d$ versus $1/T$ (Fig. 7). The negative ΔG° values, 0.519, 0.682, 0.965 and 1.329 kJ/mol for 283, 293, 313 and 323 K, respectively, increase with increase in temperature, indicating the feasibility and spontaneity of the adsorption process. The positive value of ΔH° (11.324 kJ/mol) confirmed the endothermic nature of the adsorption process, while the positive value of ΔS° (42.72 J/mol/K) revealed the increase in randomness at the solid–solution interface during the adsorption process (Zou *et al.*, 2006; Gupta *et al.*, 2002).

**Fig. 7** Plots of $\log K_d$ vs. $1/T$ for adsorption of Co(II) on AN

5. Competitive adsorption of Binary(BMS) and ternary metals(TMS) onto AN

Adsorption of binary and ternary metal ions onto AN 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. The proposed binary mixtures were in the following combinations: $\text{Co}^{2+}/\text{Cu}^{2+}$ & $\text{Co}^{2+}/\text{Cr}^{6+}$, whereas a grouping of $\text{Co}^{2+}/\text{Cu}^{2+}/\text{Cr}^{6+}$ was taken as ternary aqueous phase. The adsorption experiment was carried in the similar fashion as was performed for SMS. 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 81%). In case of binary metal system the AN exhibit the highest decline of 16% in adsorption efficiency for $\text{Co}^{2+}/\text{Cr}^{6+}$ than $\text{Co}^{2+}/\text{Cu}^{2+}$ 65% compared to 81% percentage removal of Co(II) in SMS. From the (Fig.12) it was observed that there is a reduction of 64% in metal uptake efficiency of AN in TMS in contrast to metal confiscating potential in SMS. The results are presented in Fig. 8.

It was observed that cobalt is preferentially adsorbed over copper and chromium. The results were likely due to high adsorption affinity of Co(II) onto AN. 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 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 (Kovacevic *et al.*, 2000). 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 (Sheng *et al.*, 2007). Results of present research showed that Co(II) adsorption is affected by Cr(VI) followed by Cu(II).

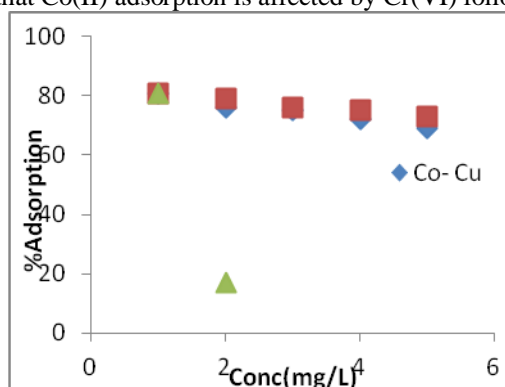


Fig. 8 Adsorption of Cr(VI) onto AN in binary and ternary metal system

6. Desorption and Regeneration Studies

In order to investigate biosorption on Co(II) ions from metal- loaded AN, the metal–loaded biosorbent was treated with HCl. Desorption studies were performed with different hydrochloric acids concentration. The recovery percentage is obtained from the following relation (Zhao, *et al.*, 1999 and Arica, *et al.*, 2003):

$$\text{Recovery (\%)} = \left(\frac{\text{Desorbed}}{\text{Adsorbed}} \right) \times 100 \quad (23)$$

that the “desorbed” is the concentration and/or the mass of metal ions after the desorption and the “adsorbed” is equal to $(C_o - C_e)$ and/or $(m_o - m_e)$ for each recovery process. m_o and m_e are the heavy metals mass in the aqueous solution, before and after the biosorption, respectively. Maximum elution of the loaded Co(II) 73% could be achieved by using 0.2N HCl. To keep the biosorption process cost down, our results indicate that AN biosorbent could be used repeatedly in Co(II) biosorption.

Table 6 Desorption data of Co(II) onto AN

Initial concentration Co(II) (mg/L)	Removal efficiency	Desorption ^a with HCl				
		0.05M ^b				
		0.1M ^b	0.2M ^b	0.3M ^b		
50	81	59	65	73	67	
100	79	54	50	67	54	
150	67	43	36	46	38	
200	59	35	31	42	33	

^aAll values are percent recovery of cobalt.

^bConcentration of HCl

7. Conclusions

In this investigation, AN is used for the removal of Co(II) ion from the aqueous solution by batch adsorption study. The influence of process parameters, such as effect of pH, effect of temperature, and contact time, was evaluated. The optimized conditions for the effective Co(II) adsorption were pH 5.0, initial concentration 50 mg/L and contact time 110 min. The second order rate kinetic model was followed as the best model, and the adsorption isotherm model was obeyed by the Freundlich equilibrium model. The thermodynamic properties of cobalt ion adsorption concluded that the process was spontaneous and favorable by the adsorption of AN. In the binary component system, the adsorption maximum of total adsorption was approximately constant, but the adsorbent had better affinity for single ion than multi metal ions. The used adsorbents could be regenerated using 0.1 mol/L HCl solutions. The adsorption of cobalt ion was confirmed through SEM and FTIR analyses. Hence the use of the leaf biomass of *Acacia nilotica* can be employed as good biosorbent for the removal of Co (II) from aqueous solutions.

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