Journal of Academia and Industrial Research (JAIR)
Volume 2, Issue 4 September 2013

ISSN: 2278-5213

RESEARCH ARTICLE

Effect of Solution parameters on the Adsorption of Cobalt (II) ions on Smectite from Cameroon: Equilibrium studies

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Abstract

Equilibrium studies were carried out on the adsorption of Co(II) ions from aqueous solution in the presence of four different electrolytes at three different ionic strengths; 0.05, 0.1 and 0.2 M. The efficiency of the adsorbent, smectite clay was studied for its adsorption of Co(II) ions. Factors such as initial concentration (C_o), ionic strength, ion pair formation (counter ions) were studied. It was observed that initial uptake of Co(II) ions in solution increased with increase in initial concentration. Also adsorption of Co(II) ions decreased with increase in ionic strength. The adsorption data were confronted by using both Langmuir and Freundlich classical adsorption isotherms. From the correlation coefficients, the experimental data fitted the Freundlich isotherm. Quantity of Co(II) ion adsorbed was greater from electrolytes with chloride as dominant anions and for those with sodium as dominant cations. The adsorption efficiency reached a maximum of 21.92 mg/g in the absence of electrolyte, 16.32, 9.92, 5.52 and 3.52 mg/g in the presence of NaCl, $CaCl_2$, $NaNO_3$ and $Ca(NO_3)_2$ electrolytes respectively.

Keywords: Equilibrium studies, cobalt (II) ions, smectite, ionic strength, adsorption, electrolytes, isotherms.

Introduction

Heavy metals can pose health hazards to man and aquatic lives if their concentrations exceed acceptable limits. Even concentrations below these limits are potentially toxic in the long run, because heavy metals are known to accumulate within biological systems and are non-biodegradable. Cobalt is used in the manufacture of many items from pigments of inks and paints to high performant magnets such that its impact on the environment cannot be neglected (Naimo, 1995; Malakootian *et al.,* 2008). Despite its numerous uses, ingestion of cobalt above certain limits is toxic and can cause health problems such as brain damage, respiratory problems, asthma, contact dermatitis. All these industrial and human activities have led to the pollution of surface and underground waters (Borgmann *et al.,* 2005).

In the eastern region of Cameroon, the mining of cobalt and other metals is being carried out by Geovic–Cameroon, SA, over an area of about 1250 square kilometers. This project known as the Nkoumane project started in 2010 and is expected to run for 25 years. The production will be about 5000 tons a year (GEOVIC mining corp., 2002). Pollution is expected to increase thereby posing a serious problem in the area. Steps have to be taken to put this situation under control. Decontamination of surface and underground water supplies is a major concern and conventional methods such as: chemical precipitation, membrane filtration (Reverse osmosis and electro dialysis), electrolytic processes, biosorption and adsorption can be used for the decontamination of effluents. The above techniques, with the exception of adsorption are expensive and also have disadvantages such as incomplete metal removal, high reagent, energy requirements and generation of toxic sludge or other waste products that require proper disposal (Harter and Naidu, 2001).

In this study, adsorption has been chosen because; it is cheaper, making use of low cost and local adsorbents. Research on the adsorption of Co(II) ions has been carried by many researchers (Borggaard, 1988; Nasr *et al.,* 1996; Eric *et al.,* 2002; Malakootian *et al.,* 2008; Kocaoba, 2008). However, these studies were not directed towards elucidating the effect of solution variables. On the other hand, others studied solution parameters that influence adsorption on cobalt and other metals of which ionic strength effect and ion pair formation were part (Mattigod *et al.,* 1979; Harter and Naidu, 2001; Li *et al.,* 2006). It should be noted that the quantity of metal adsorbed by a given adsorbent is a complex function of surface properties, environmental and solution parameters. In order to elucidate sorption processes, surface chemists have paid much attention to surface properties, but the potential influence of solution parameters cannot be ignored. Some of these solution parameters include: ionic strength, counter ions, pH, metal loading rate and organics (Harter and Naidu; 2001; Igwe and Abia, 2007; Ketcha *et al.,* 2007).

The goal of this study was to verify the factors that affect metal adsorption and to indicate the impact of these factors on adsorption and also to valorize local materials (smectite clays). These factors include; ionic strength and ion pairs. In this study, the adsorption of Co(II) ions onto a Cameroon smectite Clay with respect to the changing ionic strength (presence of calcium salts and sodium salts) and as influenced by ion pair formation with counter ions such as nitrate and chloride will be investigated.

Materials and methods

Adsorbent preparation: The adsorbent used here was smectite clay, which was obtained from Sabga in the North West region of Cameroon with geographical coordinates: latitude 6° N and longitude10°19 E (Tonle *et al.,* 2003). Smectite (Sa01) was sun dried, ground into fine powder by the use of a mortar and sieved using a sieve (Retsch) to get geometrical sizes of 80 µm, which by the use of a beaker was kept in an oven at 110°C for a period of 24 h, removed and cooled in a dessicator containing $CaCl_2$ (drying agent) for 30-60 min. These adsorbents were removed from the dessicator and the required mass 0.5 g, weighed and stored in an airtight plastic container for the experiment (Mattigod *et al.,* 1979; Harter and Naidu, 2001).

Batch adsorption study: Batch equilibrium experiments of the adsorption studies were conducted at ambient temperature in a 250 mL stoppered conical flask. First, the equilibrium or contact time was determined by placing 0.5 g of the adsorbent in the flask containing 20 mL solution of Co(II) ions of a given concentration (800-1000 ppm) at pH = 3. The suspension was stirred for an interval of time (30-240 min), using a magnetic stirrer. The contact time was 30 min. For the adsorption study, the same mass of adsorbent and volume of solution were used for each run, but this time concentration was varied from 800-1000 ppm and agitation was carried out for 30 min. After agitation, the suspensions were centrifuged to separate the solid and liquid phases. The supernatant was capped into test tubes and labelled (Ketcha *et al.,* 2011).

Variation of ionic strength: Solutions of Co(II) ions in the concentration range of 800-1000 ppm were prepared together with given electrolytes to give ionic strength values of 0.05, 0.1 and 0.2 M or simply 0.05, 0.1 and 0.2. Isotherms were plotted for each given ionic strengths. The ionic salts used here were NaCl, $CaCl_2$, $NaNO_3$ and $Ca(NO_3)_2$ and the effects of these ions on the adsorption of Co(II) ions in solution were studied (Mattigod *et al.,* 1979; Li *et al.,* 2007). The concentration of solute adsorbed at equilibrium is given as:

$$Qe = \frac{V(Co-Ce)}{m} \quad (1)$$

Where, Q_e is the adsorption capacity at equilibrium (mg/g), Co and Ce are initial and equilibrium concentrations (mg/L), V is volume of liquid phase (in L) and m mass of adsorbent (g).

The Langmuir isotherm: The Langmuir adsorption isotherm describes the relationship between the amount of gas adsorbed on a surface and the pressure of that gas. It is often used for adsorption of a solute from a liquid solution. It is often expressed as:

$$Q_e = \frac{Q_m K C_e}{1 + K C_e} \quad (2)$$

Where, Q_e is the adsorption capacity at the equilibrium (mg/g). C_e is the equilibrium concentration of adsorbate in solution (mg/L). Q_m is the maximum adsorption capacity corresponding to complete monolayer coverage. K is the Langmuir constant related to energy of the adsorption (L/mg).

The above equation can be rearranged to the following linear form:

$$\frac{C_e}{Q_e} = \frac{1}{Q_m K} + \frac{C_e}{Q_m} \quad (3)$$

The linear form can be used for linearization of experimental data by plotting C_e/Q_e against C_e. The Langmuir constants Q_m and K can be evaluated from the slope and intercept of the linear equation (Muhammad *et al.,* 2008).

Freundlich adsorption isotherm: Freundlich isotherm is the earliest known relationship describing the adsorption equation and is often expressed as: (Van Bladel *et al.,* 1993; Ayaz *et al.,* 2009).

$$Q_e = K_f C_e^{1/n} \quad (4)$$

Where, Q_e is the quantity of solute adsorbed at equilibrium (adsorption density: mg of adsorbate per g of adsorbent). C_e is the concentration of adsorbate at equilibrium (mg/L). K_f and n are the empirical constants dependent on several factors and n is greater than one.

This equation is conveniently used in linear form by taking the logarithm of both sides as:

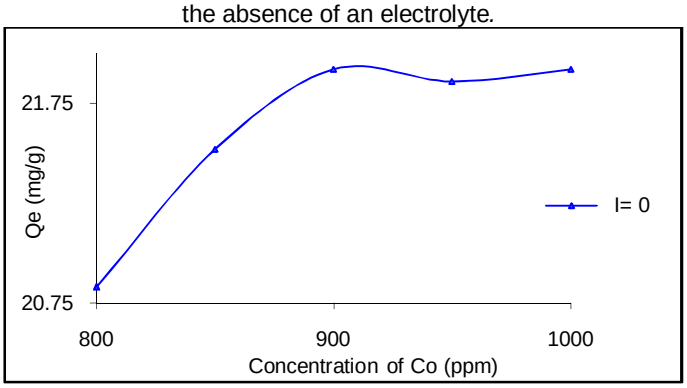
$$\ln Q_e = \ln K_f + \frac{1}{n} \ln C_e \quad (5)$$

A plot of $\ln Q_e$ against $\ln C_e$ yields a straight line. The constants can be determined from the slope and the intercept.

Results and discussion

Adsorption isotherm in the absence of an electrolyte (I=0): The quantity of Co(II) at equilibrium (Q_e) is plotted against initial concentration (Co), varying between 800-1000 ppm in the absence of an electrolyte (I=0) and is represented in Fig. 1. It is observed that the quantity of Co(II) adsorbed in the absence of an electrolyte is better (21.92 mg/g) than in solutions containing electrolytes, with highest value 16.92 mg/g at I=0.05 in NaCl. Many reasons accounted for this, especially competition for adsorption sites and interaction between ions in solution (Sanchez *et al.,* 1999; Krupka and Serne, 2002).

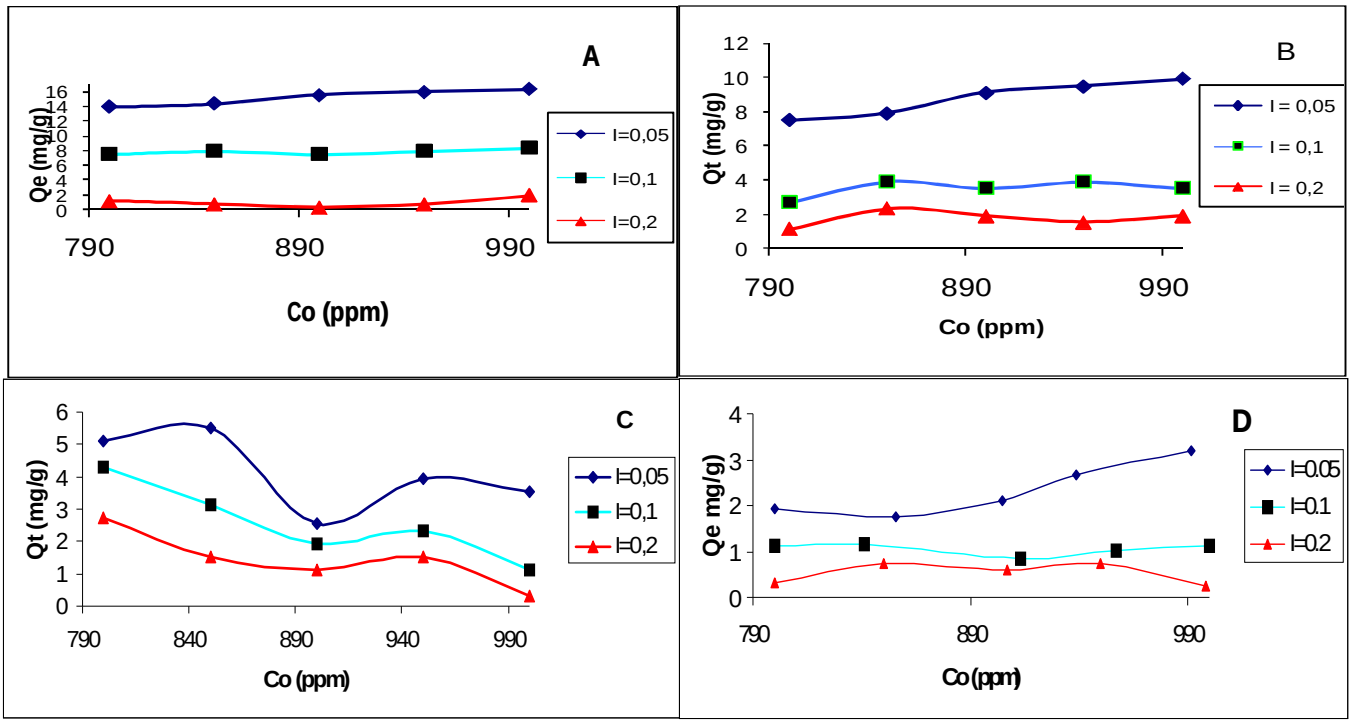
Fig. 1. Adsorption of Co(II) ions on smectite in the absence of an electrolyte.



Variation of ionic strength in different electrolytes: The quantity of Co(II) ions adsorbed at equilibrium (Q_e) is plotted against initial concentration (C_o) to obtain isotherms at different ionic strengths (I) is given in Fig. 2.

From Fig. 2, it is observed that quantity of Co(II) ions adsorbed from solution, decreases with increase in ionic strength. For example in NaCl electrolyte, (A) adsorption at an ionic strength of 0.2 is about ten times less than that at ionic strength of 0.05. This agrees with work encountered in the literature (Mattigod *et al.,* 1979; Harter and Naidu, 2001; Pathak and Choppin, 2009). Similar decreases in Co(II) adsorption with increasing ionic strength were observed in experiments with $CaCl_2$, $NaNO_3$ and $Ca(NO_3)_2$ as background electrolytes. This phenomenon can be attributed to: increasing Ca^{2+} or Na^+ concentration with increasing ionic strength and therefore increasing competition between these ions and Co^{2+} ions for adsorption sites on clay mineral and decreasing activity of Co(II) ions in solution due to increasing non-ideality of solution with ionic strength. This non-ideality is due to increasing electrostatic interaction and resulting formation of $CoNO_3^+$ and $CoCl^+$ ion pairs. Since adsorption of Co^{2+} is governed by its activity in solution, decreased activity in solution means decreased adsorption on smectite. Adsorption was better in electrolytes containing sodium ions (A, B) than those having calcium ions (C, D). This can be explained by the fact that Na^+ competes effectively with Co(II) for non-specific (outer sphere) adsorption sites especially at high ionic strengths and that Ca^{2+} can compete with Co (II) for inner sphere sites better than Na^+. Given the fact that smectite presents a larger internal than external surface (Masayuki *et al.,* 2002), less cobalt is adsorbed in Ca^{2+} than in Na^+ media (Tournassat *et al.,* 2009).

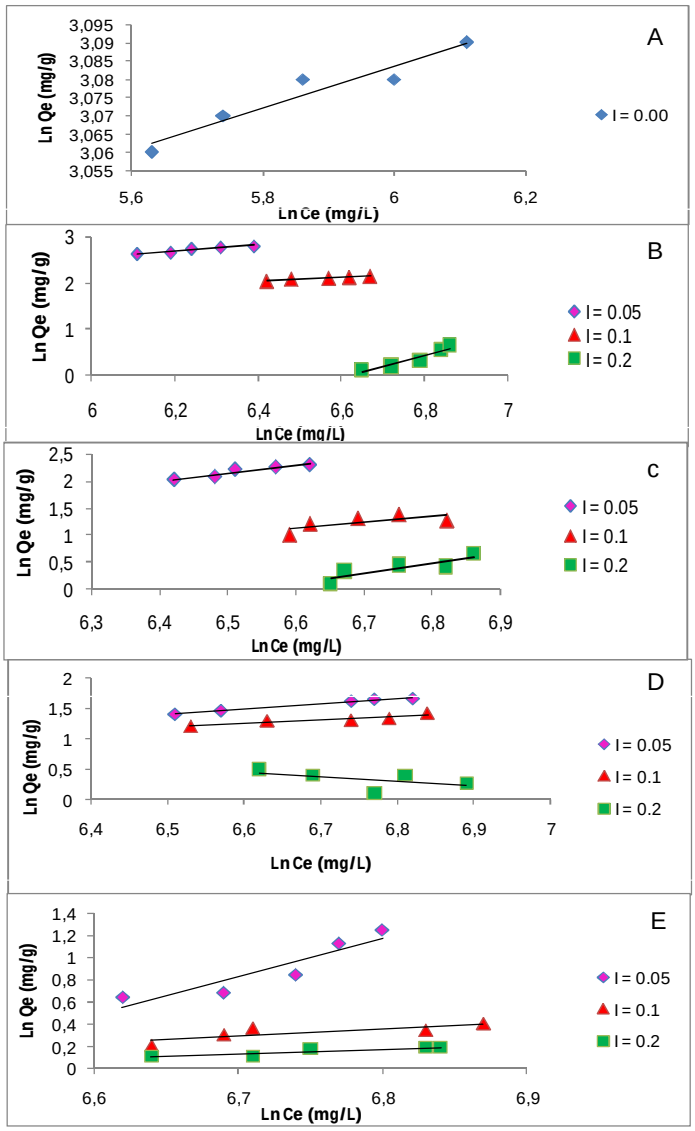
Fig. 2. Influence of ionic strength (I) on the adsorption of Co(II) ions on smectite, A: NaCl, B: $CaCl_2$, C: $NaNO_3$ and D: $Ca(NO_3)_2$.



This can also be attributed to the fact that Ca^{2+} having a smaller ionic radius and a larger hydration energy than Na^{+}, can effectively distort the interlayer spacing and hence better compete with Co(II) ions for adsorption sites (Krupka and Serne, 2002). Also Ca^{2+} ions which have the same valency as Co(II) ions can effectively compete with it for adsorption sites and hence reduce its adsorption. Other sorption studies done by other researchers have shown that adsorption of heavy metal cations is decreased in the presence of Ca^{2+} compared to Na^{+} (Chan-Ho *et al.,* 1996; Pathak and Choppin, 2009). Previous research has described Co(II) adsorption to be partly affected by ion exchange processes, where ions found in solution replace those that are lodged in the various sites (octahedral and tetrahedral) found in the smectite (Mermut and Lagaly, 2001; Wolters *et al.,* 2009). It is also observed that adsorption is better in chloride than in nitrate electrolytes. It should first be noted that the adsorption of metal ions in solution in the presence of different anions, will be a function of free metal activity, rather than total metal concentration in solution (Mattigod *et al.,* 1979). So it can be said that free Co(II) ions are more available in chloride than in nitrate media (Tamotsu *et al.,* 2001). This can be attributed to the fact that the counter ion that associates better with Co(II) ion will reduce the amount and mobility of free Co(II) ions in solution and hence its quantity adsorbed. From the isotherms in Fig. 2, it can be inferred that nitrate associates better with Co(II) than chloride and similar trends have been studied by Harter and Naidu (2001) and Usman *et al*. (2005) with other metals such as cadmium and lead. Another explanation can be that the anions might interact and modify the clay surface charge density through the formation of covalent bonds, hence affecting the amount of cobalt adsorbed (Strawn *et al.,* 2004; Pathak and Choppin, 2009). Reduction in metal adsorption, can therefore, be related to the nature of ion pairs involving the dominant anion in a system (Black and Waring, 1979; Payne *et al.,* 2009).

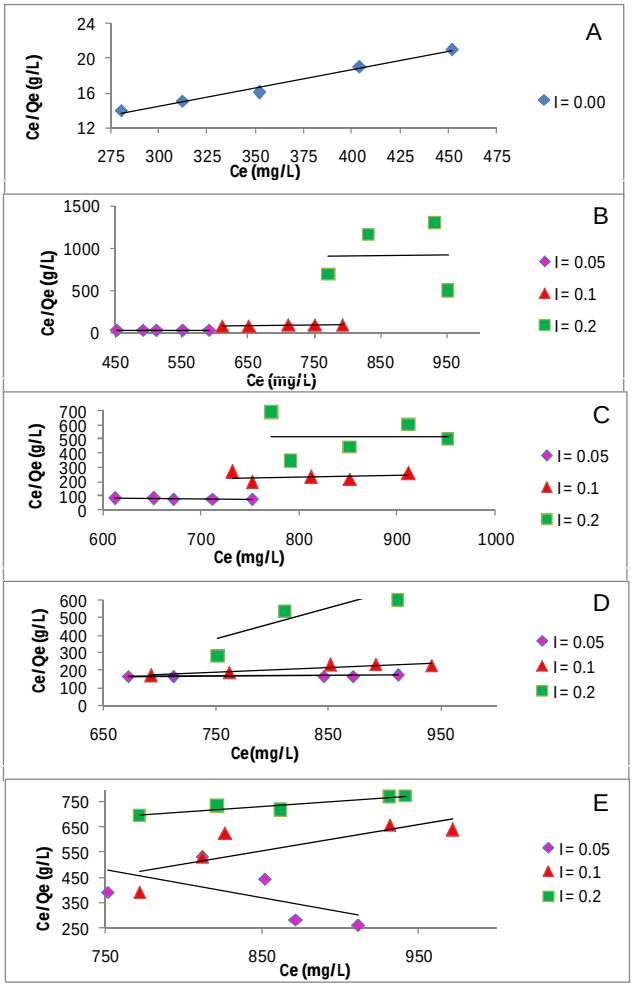
Graphical representations of the Freundlich and Langmuir linear models are given in Fig. 3 and 4 respectively**.** The adsorption data was also described using the linear forms of the Freundlich and Langmuir isotherms. The values of the equation constants are shown in Table 1. The Freundlich linear model generally presents greater R^2 values, describing adsorption better on smectite compared to the Langmuir model. This was especially observed for all low ionic strength solutions, except for $Ca(NO_3)_2$, whose R^2 = 0.847 at I = 0.05. The low value for $Ca(NO_3)_2$ might be due to its strong interference in the adsorption process. This linearity indicates that the number of sites for adsorption remains constant. It is confirmed from the R^2 values which is above 0.9 for I = 0.05 for NaCl, $CaCl_2$ and $NaNO_3$ solutions. The parameter 1/n is related to the degree of surface heterogeneity.

Fig. 3. Freundlich linear model: A (no electrolyte), B (NaCl), C ($CaCl_2$), D ($NaNO_3$) and E ($Ca(NO_3)_2$).



Values between 0 and 1 indicate a heterogeneous surface and values of 1/n greater than unity indicate a material with relatively homogeneous surface (Muhamed *et al.,* 2008). Sorption studies by Tella and Owalude (2007) indicate that values of 1/n less than unity or high values of Freundlich constant, showed favorable adsorption mechanism and high affinity of adsorbate for adsorbent. The value for 1/n in the absence of an electrolyte (0.056) shows that the surface is relatively heterogeneous, while values of 1/n in the presence of electrolytes are higher, indicating that adsorption was taking place on a relatively homogeneous surface. The heterogeneity might be due to the fact that the adsorbent presents many chemical groups on its surface that take part in the adsorption process (Li *et al.,* 2003; Wahba and Zaghoul, 2009).

Fig. 4. Langmuir linear models: A (no electrolyte), B (NaCl), C ($CaCl_2$), D ($NaNO_3$) and E ($Ca(NO_3)_2$).



On the other hand, the homogeneity might be as a result of additional adsorbate stacking on that already adsorbed on adsorbent (Schlegel *et al.,* 1999). When sorption data was plotted according to linear form of Langmuir adsorption isotherm as given in Table 1, R^2 values in Langmuir equations were non-significant in the case of all ionic strengths except at I = 0.

The fact that the Langmuir isotherm fits the experimental data very well in this case, may be due to the homogenous distribution of active sites on the adsorbent surfaces; since the Langmuir equation assumes that the surface is homogenous. Thus, the applicability of the Langmuir isotherm in the present system indicates the monolayer coverage of cobalt ions on the outer surface of the adsorbents (Muhammad *et al.,* 2008).

Conclusion

Equilibrium studies were determined for the adsorption of Co(II) ions from aqueous solutions onto smectite (Sa01) in the concentration range of 800-1000 ppm and the initial pH of 3.0 at 25°C and in electrolytes with ionic strengths of; 0.05, 0.1 and 0.2. A contact time of 30 min was enough for the system to reach equilibrium. From the isotherms obtained the quantity of Co(II) adsorbed from solution decreased with increased ionic strength, due to the interference of electrolytes during adsorption. Reduction of Co(II) ion adsorption can therefore be related to the nature of ion pairs involving the dominant anion in the system. Adsorption of Co(II) is reduced to a greater degree when nitrate is the dominant anion in solution instead of chloride. A similar trend is observed in solutions containing calcium ions instead of sodium ions. According to the R^2 values, adsorption of Co(II) ions onto Sa01 fitted the Freundlich model is better than the Langmuir model. These were observed mainly for low ionic strengths solutions; in sodium and calcium chloride and in sodium nitrate solutions.

The analysis of results clearly established that Sa01, is efficient in the adsorption of Co(II) ions from aqueous solution. It can be concluded that Sa01, can be used as natural low-cost alternative and abundant source for the removal of Co(II) ions, since it is economical, easily available and efficient. It is also practically feasible for developing countries and will be useful for the economic treatment of wastewaters containing cobalt metal.

Table 5. Values for Langmuir and Freundlich equation constants.

Linear model		Freundlich constants			Langmuir constants		
		R^2	1/n	k_f	R^2 values	Q_m	k
No electrolyte	I = 0.00	0.9230	0.056	15.53	0.9820	24.39	17.720
NaCl	I = 0.05	0.9140	0.619	0.22	0.7859	40.00	0.001
	I = 0.10	0.9510	0.404	0.57	0.8600	11.24	0.004
	I = 0.20	0.9020	2.478	0.01	0.7170	-0.959	-0.001
$CaCl_2$	I = 0.05	0.9010	1.429	0.0007	0.4520	-22.73	0.001
	I = 0.10	0.5020	1.061	0.0028	0.0280	14.08	0.0004
	I = 0.20	0.7690	1.877	0.009	0.0150	-31.55	-0.0006
$NaNO_3$	I = 0.05	0.9860	0.884	0.013	0.7440	45.45	0.0002
	I = 0.10	0.8650	0.587	0.030	0.8540	3.74	-0.021
	I = 0.02	0.5250	0.789	0.309	0.6660	0.56	-0.002
$Ca(NO_3)_2$	I = 0.05	0.8470	3.455	0.010	0.3470	-0.90	-0.001
	I = 0.10	0.6520	0.630	0.020	0.6240	0.98	-0.003
	I = 0.20	0.8680	0.500	0.060	0.8730	2.35	1.150

Acknowledgements

The authors thank all the members of the Research Group: 'Adsorption and Surface' of the Physical and Theoretical Chemistry Laboratory of the University of Yaoundé 1 for their remarks and suggestions.

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