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Study of Co (II) and Cr (VI) Adsorption from Aqueous Solution by $CaCO_3$

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Summary: Calcium carbonate was synthesized, characterized, and utilized in water purification. The adsorption of Co(II) and Cr(VI) ions from aqueous solutions in $CaCO_3$ was studied as a function of different optimal conditions, such as contact time, initial metal ion concentration and temperature, at fixed solid/solution rations by using batch adsorption experiments. Characterization studies confirmed that synthesized $CaCO_3$ is crystalline with a high phase purity and specific surface area of 9.68 m^2/g. The kinetic processes of the systems were described in order to provide a more clear interpretation of the rate of adsorption mechanism. Langmuir, Freundlich and Dubinin-Radushkevich isotherms were used as the model adsorption equilibrium data. The maximum amounts (q_{max}) of Co(II) and Cr(VI) adsorbed in $CaCO_3$ were 2.29 and 1.06×10^{-2} mg/g, respectively. The pseudo-second order kinetic model was found to better fit the experimental data measured for both metallic ions. The adsorption processes of both systems were adjusted by the Freundlich isotherm. The adsorption energies calculated from Dubinin-Radushkevich isotherm show that the adsorption processes were physical in nature. Based on the thermodynamic data of $\Delta H°$, $\Delta S°$ and ΔG obtained, it can be concluded that the processes of Co(II) and Cr(VI) ion adsorption in $CaCO_3$, were endothermic, spontaneous, and are the result of physical adsorption process. These features make the $CaCO_3$ a potential adsorbent for both Co(II) and Cr(VI) adsorption from wastewater.

Keywords: Purification, Adsorption, Optimal conditions, Crystalline, Radushkevich Isotherms.

Introduction

The adsorption of heavy metals from aqueous solutions on solids has been object of many investigations in methods that allow decreasing the indices of contamination in the effluents from diverse industrial technologies [1]. The efficiency of this process depends to a great extent on the chemical, structural, and superficial characteristics of solids that are used as adsorbent materials (i.e., the specific surface area, crystalline phases, size of the particle, porosity, etc.), the properties of the chemical species in solution (i.e., cations, anions, size, and electrical charge), the conditions of the process (i.e., agitation time, concentration of the adsorbent and adsorbate, pH, and temperature), the forces that control the process (i.e., Van der Waals, electrostatic, and chemical bonds) and of the type of adsorption mechanisms that can occur between the solid and liquid phases of the process [2].

Some natural or synthetic inorganic materials have shown important applications in the processes of water demineralization and the adsorption of radioactive materials that are present in aqueous solution because they are porous structures that are subject to selectivity, which favors the ion adsorption [3]. Organic resins have been displaced by inorganic materials because they are thermally unstable and are easily degraded as a result of the radiation; such behavior is incompatible with the adsorption of radioactive materials [4]. There actually exists a great amount of inorganic materials which can be used as adsorbents, such as, activated charcoal, metallic oxides, aluminosilicates, carbonates, and phosphates, among others, due to the fact that they are economic materials that are resistant to the chemical changes, temperature, and radiation.

The calcium carbonate is a white crystalline mineral that is abundant in nature. It is quite cheaply and widely used in the production of paper, polymers, and iron [5]. Due to its structural and superficial properties, it has been investigated intensely as an adsorbent substance that is used for the removal of metal ions from aqueous solution [6].

On the other hand, heavy metals, such as cobalt and chromium, are significant environmental contaminants. In relative high concentrations, they can be carcinogenic, mutagenic and toxic. They are extremely soluble and their presence in water is restricted and indeed possesses a significant threat to aquatic life as well as public health [7].

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Therefore, the aim of this work is to examine the Co(II) and Cr(VI) ions adsorption behavior from an aqueous solution by synthesized $CaCO_3$ in batch experiments as a function of different experimental parameters on the adsorption process: contact time, initial metal ion concentration and temperature. Additionally, the isotherm models and some of the kinetic and thermodynamic parameters were determined to interpret and elucidate how the adsorption mechanisms of cobalt and chromium ions work.

Results and Discussions

The synthesis of calcium carbonate by the precipitation method produces a fine and white powders. Particles were analyzed by X-ray diffraction (XRD). Fig. 1 shows the X-ray diffraction pattern of the synthetic calcium carbonate ($CaCO_3$) sample. It is clear that all of the sharp and well defined peaks correspond to the pure phase of a single crystalline $CaCO_3$ (calcite structure, JCPDS 20-1088 card); no peaks of impurities were detected, which confirms that a well-crystallized $CaCO_3$ crystal was easily obtained. The specific surface area of synthesized calcium carbonate was 9.68 m^2/g, the total pore volume was 0.0095 cm^3/g and the mean pore diameter was 39.33 nm. The micrographs, which were obtained by SEM (Fig. 2), show that the synthetic $CaCO_3$ is composed of square block particles that are fairly uniform and ranged in size from 1 to 5 µm. EDS analysis revealed only the presence of carbon (element % 15.50), oxygen (element % 45.38), and calcium (element % 39.12) in the synthesized $CaCO_3$.

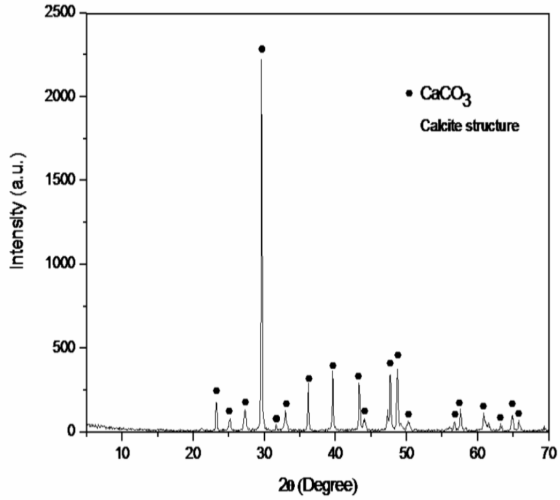

Fig. 1: XRD pattern of $CaCO_3$ particles synthesized from precipitation method.

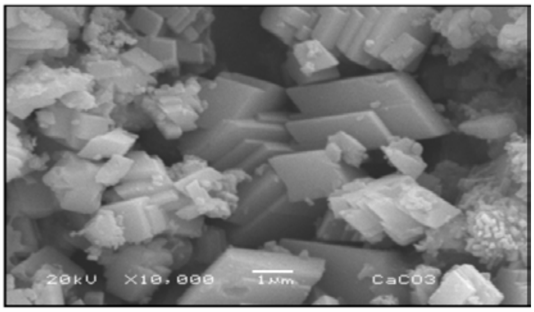

Fig. 2: SEM image of $CaCO_3$ synthesized from precipitation method.

The batch-type kinetic adsorption studies of Co(II) and Cr(VI) ions in synthesized $CaCO_3$ were carried out at room temperature. Fig. 3 indicates that the time required to attain the equilibrium for Co(II) adsorption on $CaCO_3$ was 4 h of contact between the solid-liquid phases of the system, with a maximum adsorption capacity of 2.29 mg/g. In contrast, Cr(VI) adsorption with the same adsorbent showed an equilibrium after a contact time of 3 h after contact with a maximum capacity of adsorption of Cr(VI) of 1.06 x 10^{-2} mg/g. Therefore, the $CaCO_3$ presents better adsorption properties for Co(II) than for Cr(VI). This behavior indicates that adsorption of Co(II) and Cr(VI) ions occurred in a single step and that the slow adsorption (i.e., less than 3 h or 4 h) can be explained by an exchange of the cobalt and chromium ions on the surface of calcium carbonate.

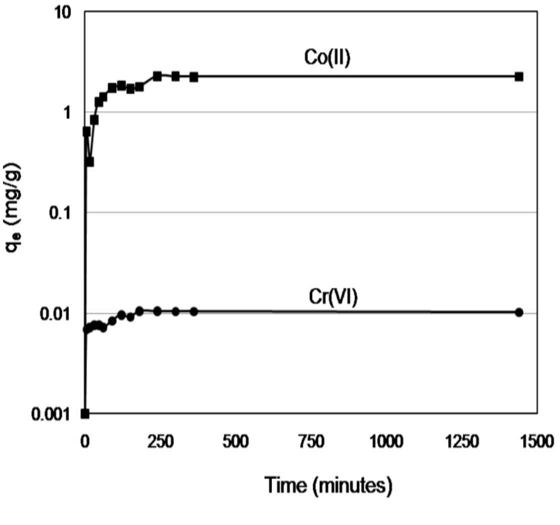

Fig. 3: Co(II) and Cr(VI) ions adsorption on synthesized $CaCO_3$ as a function of contact time.

On the other hand, in order to understand the kinetics for Co(II) and Cr(VI) adsorption process by $CaCO_3$ at room temperature and at equilibrium pH= 7.5 and 6.5 respectively were realized and Table-1 shows kinetic models analysis developed with pseudo-first order equation [8], pseudo-second order equation [9], Elovich [10], and intraparticle mass transfer diffusion model [11]. The associated kinetics parameters, which have been evaluated from the slopes and intercepts of the respective linear plots of kinetics equations, are shown in Table-1. The conformity between experimental data and the model-predicted values was expressed by the correlation coefficients (R^2 values close or equal to 1). The results obtained from the analysis of the present data indicated that the both Co(II) and Cr(VI) adsorptions on $CaCO_3$ have been described ($0.995 < R^2 < 0.999$) (Table 1) by the pseudo-second order equation and the data for the other equations were rather poor. Hence, the pseudo-second order kinetic equation in general, has best agreed to the present kinetic reactions. The Elovich equation no has been satisfactorily applied to both systems in which the adsorbing surface is heterogeneous.

An assessment of the effect of initial concentrations on the adsorption of cobalt and chromium on $CaCO_3$ were carried out by varying the adsorptive concentrations ($1 \times 10^{-2} - 7 \times 10^{-2}$ mol/L) at 293 K for 4 h for cobalt and ($1 \times 10^{-5} - 7 \times 10^{-5}$ mol/L) at 293 K for 3 h for chromium. The results of the adsorption of Cr(VI) ions are shown in Fig. 4. It was found that the adsorption of Co(II) and Cr(VI) ions onto $CaCO_3$ was strongly dependent on the initial concentration of metal ions. As is seen in Fig. 4, the percentage of adsorption decreased when initial concentration of cobalt and chromium ions increased. The increases of adsorption are explained by the interaction of metal ions that were adsorbed onto the surfaces by a mechanism that involves specific metal ion adsorption at a limited number of surface sites because there are more surface-active sites per gram of adsorbent available for deposition at a higher level of dilution.

The equilibrium distribution of Co(II) and Cr(VI) ions between the liquid phase and the solid adsorbent phase (calcium carbonate) as a function of initial concentrations (1×10^{-2} mol/L for Co(II) and 1×10^{-5} mol/L for Cr(VI) and equilibrium pH= 7.5 and 6.5 respectively), were surveyed by using three adsorption isotherms models: Langmuir, Freundlich and Dubinin-Radushkevich, therefore, the mathematical isotherm model were applied to fit the equilibrium data of the adsorption systems.

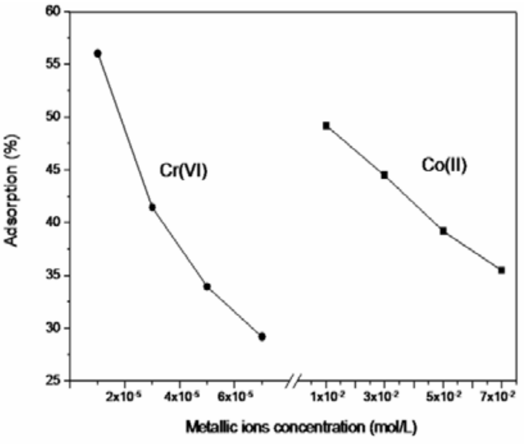

Fig. 4: Adsorbate concentration effect on Co (II) and Cr (VI) ions adsorption on synthesized $CaCO_3$.

The adsorption isotherm equations were used in their linearized form for both Co (II) and Cr(VI) ions, as shown in Table-2. They have been analyzed by the Langmuir equation model; that assumes monolayer adsorption onto a surface that contains a finite number of adsorption sites of uniform strategies of adsorption with no transmigration of adsorbate in the plane of surface [12]. We also employed the Freundlich equation model, which is an empirical equation based on adsorption on a heterogeneous surfaces supporting sites of varied affinities. It assumed that the stronger binding sites are the first to be occupied and that the binding strength decreases with the increasing degree of site occupation [12]. The Dubinin-Radushkevich equation model postulates a fixed volume or "adsorption space" that is close to the adsorbent surface where adsorption takes place and this model assumes the heterogeneity of adsorption energies within this adsorption space. The Polanyi adsorption potential, ε, is the work required to remove a molecule or ion to infinity from its location in adsorption space independent of temperature. The Dubinin-Radushkevich equation was formulated from the Polanyi theory especially for applications to microporous materials; however, it can be applied to experimental data for low concentrations of adsorbates and very good correlations can be obtained [13]. On the other hand, the Dubinin-Radushkevich equation was used to predict the nature of adsorption processes as physical or chemical by calculating the mean adsorption energy.

Table-1: Kinetic equation models applied to experimental data, the mathematical linear from of the equations and kinetic parameters evaluated for Co(II) and Cr(VI) adsorption on synthesized $CaCO_3$ at room temperature and equilibrium pH=5.5.

Kinetic equation models	Metallic ions	Constants				
		k (g/mg.min)	q_e (mg/g)	*α* (mg/g.min)	*β* (g/mg)	R^2
Pseudo-first order,	**Co(II)**	**-0.008**	**1.973**			**0.860**
$\ln(q_e - q_t) = \ln 1.973 + 0.008t$ **$\ln(q_e - q_t) = \ln 0.001 + 0.001t$**	**Cr(VI)**	**-0.001**	**0.001**			**0.146**
Pseudo-second order,	**Co(II)**	**0.0111**	**2.352**			**0.995**
$t/q_t = 1/(0.011)(2.352)^2 + (1/2.352)t$ **$t/q_t = 1/(10.939)(0.010)^2 + (1/0.010)t$**	**Cr(VI)**	**10.939**	**0.010**			**0.999**
Elovich,	**Co(II)**			**0.207**	**2.445**	**0.841**
$q_t = -0.277 + 0.408 \ln t$ **$q_t = 0.004 + 0.001 \ln t$**	**Cr(VI)**			**0.148**	**1000.0**	**0.757**

Table-2:Langmuir, Freundlich and Dubinin-Radushkevich isotherms constants for Co(II) and Cr(VI) adsorption on synthesized $CaCO_3$ at room temperature and equilibrium pH= 5.5.

Isotherm models and lineal equations	Metallic ions	Constants					
Langmuir,	**Co(II)**	q_{max} **(mg/g)** **500**	K_L **(L/mg)** **2.10×10^{-4}**	*1/n*	K_F**(mg/g(L/mg)$^{1/n}$)**	*E* **(kJ/mol)**	R^2 **0.931**
$\frac{C_e}{q_e} = \left(\frac{1}{q_{\max}}\right)C_e + \frac{1}{K_L q_{\max}}$	**Cr(VI)**	**0.132**	**0.5405**				**0.992**
Freundlich,	**Co(II)**			**0.770**	**2.677**		**0.992**
$Ln\ q_e = \left(\frac{1}{n}\right)\ln C_e + \ln K_F$	**Cr(VI)**			**0.682**	**22.398**		**0.990**
Dubinin-Radushkevich,	**Co(II)**	**0.001**				**0.318**	**0.892**
$\ln C_e = \ln q_{\max} - K_{DR}\varepsilon^2$	**Cr(VI)**	**0.884**				**0.436**	**0.988**

The linearized equations have been given without detail in Table-2. The associated isotherms constants for Co(II) and Cr(VI) adsorption on $CaCO_3$ at room temperature and pH= 7.5 and 6.5 respectively, have been evaluated from the slopes and intercepts of the respective linear plots of isotherm equations and are shown also in Table 2. The results obtained from the analysis of the present data indicated that the both Co(II) and Cr(VI) adsorptions on $CaCO_3$ have been described by the Freundlich equation and the data for the other equations were poor. A list of the obtained parameters values is provided in Table 2. A comparison of these results indicates, that the most appropriate isotherm equations for both Co(II) and Cr(VI) ions were Freundlich, with R^2 = 0.992 and R^2 = 0.990, respectively. Parameters of the Freundlich equations assume heterogeneous surfaces that support the sites of varied affinities.

On the other hand, the values for the mean adsorption energies (*E*) that were obtained for the systems that were studied according to the Dubinin-Radushkevich equation were found to be lower than the interval 1-16 kJ/mol for a physisorption process [14]. *E* = 0.3181 kJ/mol and *E* =0.4361 kJ/mol for cobalt and chromium, respectively, then, the retention processes are not controlled by an ion exchange processes. The low adsorption energy values that were found for the present systems indicate that the forces of attraction that work during the Co(II) and Cr(VI) adsorption on calcium carbonate are relatively no stronger and the adsorption processes can occur under ordinary conditions. Therefore, those results indicate a physisorption as ion-exchange mechanism between metal ions species and the functional groups of adsorbent.

Regarding, when the q_{max} value obtained for the Co(II) and Cr(VI) ions adsorption on calcium carbonate was compared with the prior data that has been collected from literature for these metallic ions adsorption on various organic e inorganic adsorbents [15-22] are shown in Table-3. Therefore, the results of this study indicated that the calcium carbonate can be used in technologies that are aimed at water remediation to remove cobalt and chromium from aqueous solutions.

Table-3: Maximum adsorption capacity of adsorbents (q_{max}) for cobalt and chromium ions; Langmuir (L) and Freundlich (F) models.

Adsorbents	Co(II)	Cr(VI)	
	q_{max} **(mg/g)**	q_{max} **(mg/g)**	**Reference**
$CaCO_3$	**2.10×10^{-4} (L)** **2.67 (F)**	**0.13 (L)** **22.39 (F)**	**Present work** **Present work**
Kaolinite	**0.91 (L)**		**[15]**
Bagasse fly ash		**4.35 (L)** **1.86 (F)**	**[16]**
TiO_2		**4.76 (F)** **10.83 (L)**	**[17]**
Bentonite	**25.8 (L)** **4.95 (F)**		**[18]**
Attapulgite	**0.11 (L)**		**[19]**
Rice husk		**11.39 (L)**	**[20]**
Dolomite		**10.01 (L)** **3.17 (F)**	**[21]**
Fe-Mn binary oxide	**32.25 (L)** **0.05 (F)**		**[22]**

It is known that $CaCO_3$ is acid sensitive because is soluble in acids. The formation of hydrolyzed cobalt and chromium species depends on metal concentration and pH of solution [23]. Then, in the present work, at equilibrium pH= 7.5 and 6.5 respectively of the metallic solutions, divalent cationic cobalt (Co^{2+}) and hexavalent chromium anionic chemical species (CrO_4^{2-}, $HCrO_4^-$ and $Cr_2O_7^{2-}$) are the only ionic species present in the solutions. Previous studies for cobalt adsorption in MnO_2 [24] and Cr(VI) on boehmite [25], indicate that cation adsorption is not important to the acid pH values; rather, the anion adsorption is important to these values such as occurs with chromium ions. Therefore, it can be inferred that adsorption of these cobalt and chromium ions on $CaCO_3$ at our studied equilibrium pH=7.5 and 6.5 were carried out.

Temperature dependence of equilibrium constants K_d, were used to determine the thermodynamic parameters: ΔH^o, ΔS^o and ΔG^o for adsorption process. These values were calculated using following the equations:

$$\log K_d = -\frac{\Delta H^o}{2.303R}\frac{1}{T} + \frac{\Delta S^o}{2.303R} \qquad (1)$$

$$\Delta G^o = -RT\ln K_d \qquad (2)$$

$$\Delta G^o = \Delta H^o - T\Delta S^o \qquad (3)$$

where ΔH^o is the change of enthalpy, T is the absolute temperature, R is the universal constant of gases, K_d is the distribution coefficient, ΔS^o is the change of entropy and ΔG^o signifies the Gibbs free energy. The changes of enthalpy were calculated from linear slopes of K_d versus $1/T$ of Fig. 5. The Van´t Hoff equation was used to evaluate the variation of equilibrium constant with temperature in its linearized form:

$$\log K_d = \frac{-\Delta H^o}{2.303\ RT} + \text{constant} \qquad (4)$$

The ΔH^o values that were obtained were 31.38 kJ/mol for Co (II) and 18.59 kJ/mol for Cr(VI), respectively. The magnitudes of these values indicate that the adsorption systems were carried out under physical adsorption, where the type of interaction between adsorbent and adsorbate are predominantly the Van der Waals type. Further, the enthalpy values that were obtained are relatively of low energy versus those that facilitate chemisorption. In an exothermic process, the adsorption decrease with the increase of the temperature, favoring the adsorbate desorption. When this occurs, the behavior increased the tendency to allow the retained metallic ions to scarp in the solid phase to the aqueous phase [26]. However, when the adsorption occurs as an endothermic process, the increasing temperature favors the adsorption of the adsorbate. The degree of covering on the surface of the adsorbate is increased if the pressure is constant, as has occurred in some studies in which the adsorption reactions are physical and proceed predominantly through ion exchange [27]. The negative values of ΔG^o of an adsorption system will confirm the viability of the process and spontaneity to carry out the adsorption. On the other hand, if the values of ΔG^o are very small and negative, surely the adsorption increases when the temperature of the system rises. Therefore, such an outcome confirms that the best adsorption is obtained with the temperature increase. The previous behavior can be attributed to the fact that, when the temperature increases, the chemical species (i.e., cations or anions) which are present in the aqueous solution of the system move more and more vigorously. As a result, chemical species interact more easily with the active sites of the adsorbent surface and result in greater retention. Further, some stages of the adsorption that are originally slow are accelerated by the increase of the activation energy of the system. Such a process generates the efficiency of adsorption creates some new active sites in the adsorbent surface.

The ΔS^o values were calculated with the intercept of linear plot of Fig. 5 whereas that ΔG^o was obtained using the equation (3). Table-4 shows the summary of the values calculated for studied thermodynamic parameters. The ΔG^o value for Co(II) ions on $CaCO_3$ was to be -10.56 kJ/mol, in the case of Cr(VI) ions on $CaCO_3$ was to be -8.29 kJ/mol, its negative sign and magnitude show the spontaneity of the adsorption processes. Meanwhile, the ΔS^o obtained values were 14.27 x 10^{-2} kJ/mol.K and 9.15 x 10^{-2} kJ/mol.K, for Co(II) and Cr(VI) ion on $CaCO_3$, respectively. The positive value of the entropy indicates the increase in the randomness in the interface of the solution with the solid by the fixation of Co(II) and Cr(VI) ions on $CaCO_3$, due to the fact that when the ions are adsorbed on the surface of calcium carbonate, water molecules that were previously united with metallic ions are released and dispersed in the solution. As a result, there is an increase in the change of entropy that facilitates the adsorption of ions on the adsorbent surface.

Table-4: Obtained values of change of enthalpy, entropy and energy of Gibbs of Co(II) and Cr(VI) ions on $CaCO_3$.

Adsorbent	**Co(II)**			**Cr(VI)**		
	ΔH^o (kJ/mol)	**ΔS^o(kJ/mol.K)**	**ΔG^o (kJ/mol)**	**ΔH^o (kJ/mol)**	**ΔS^o (kJ/mol.K)**	**ΔG^o (kJ/mol)**
$CaCO_3$	**31.38**	**14.27×10^{-2}**	**-10.56**	**18.59**	**9.15×10^{-2}**	**-8.29**

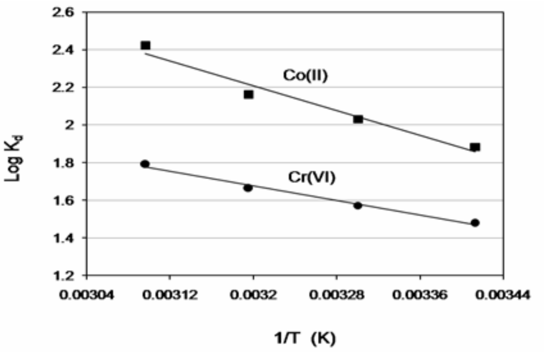

Fig. 5: Plot of log K_d vs. $1/T$ for the thermodynamics parameter determination of Co (II) and Cr (VI) ions adsorption on synthesized $CaCO_3$.

Experimental

All chemical and reagents used in this work had a pure analytical quality. In all experiments, distilled water was used for preparation, dilution, and analytical purposes of solutions. The calcium carbonate was synthesized by the precipitation method at 298 K: $Ca(NO_3)_2 \cdot 4H_2O$ (Sigma-Aldrich, 99.9% wt. purity) was mixed with $Na_2CO_3 \cdot 10H_2O$ (Merk, 99% wt. purity) (wt. ratio of 1:1) in 100 mL of distilled water under vigorous continuous stirring by 60 minutes. The obtained solid was filtered and washed with distilled water in order to obtain a neutral pH solution. Then, the material was dried to 342 K in an oven. The synthesized solid sample was characterized by X-ray diffraction in a Siemens D-5000 diffractometer coupled with a copper anode X-ray tube. The K_a radiation was selected with a diffracted beam monochromator. The compound was identified by comparing it with the Joint Committee on Powder Diffraction (JCPDS) cards in the conventional way. The specific surface area, total pore volume, and mean pore diameter of $CaCO_3$ were obtained by N_2–sorption measurements in a surface area analyzer (Belsorp-max, Japan); the samples were heated at 473 K for 2 h before that the specific surface area was measured. The morphology and grain size of the prepared $CaCO_3$ powders was determined by using a JEOL-JMS 5900 LV Scanning Electron Microscopy (SEM). The chemical composition of the synthesized $CaCO_3$ was analyzed by Energy Dispersive X-ray Spectrometry (EDS) connected to a JEOL-JMS 5900 system.

Adsorption experiments of Co(II) and Cr(VI) ions in synthesized $CaCO_3$ as a function of contact time were carried out in a batch mode. Separately, 0.1 g of $CaCO_3$ and 10 mL of solutions that contain 1×10^{-2} mol/L of $Co(NO_3)_2 \cdot 9H_2O$ or 1×10^{-5} mol/L of $K_2Cr_2O_7$, respectively, were mixed in close vials and continuously shaken at room temperature for different lengths of contact times. The liquid phases were later separated by centrifugation (3000 RPM) for 5 minutes. Aliquot part of 1 and 5 mL of liquid was analyzed by ultraviolet visible spectrometry (UV-Vis) to determine the Co(II) and Cr(VI) ion concentrations by using a Perkin-Elmer Spectrometer Lambda 10 ultraviolet-visible spectrophotometer analyzer at λ=260 nm for Co(II) and at λ=540 nm for Cr(VI), peroxide with bicarbonate method [28] and 1,5 diphenylcarbazide method were used respectively for colour development [29]. All experimental data were considered as the average of duplicate determinations; a good reproducibility was obtained (i.e., standard deviations were usually lesser than 5% of mean values). The pHs of the supernatants that were measured at the end of the experiments were assumed to be equilibrium pH. The amounts of Co(II) and Cr(VI) ions adsorbed by a gram of $CaCO_3$ at a specific contact time (q_t) or at equilibrium (q_e) were determined by the following equation:

$$q_t \ or \ q_e = \frac{(C_i - C_e)V}{w} \tag{5}$$

where q_t and q_e are the amounts of metallic ions that were adsorbed in mg/g at time t or at equilibrium, respectively; C_i and C_e are the initial and equilibrium metallic ion concentrations in the solution (mg/L); V is the volume of the solutions (0.01 L), and w is the mass of $CaCO_3$ (0.1 g). Furthermore, experimental data obtained from this study were evaluated by using several kinetic models.

The Co(II) and Cr(VI) adsorption on calcium carbonate as a function of initial adsorbate concentration was carried out at room temperature at 4 and 3 h of equilibrium contact time, respectively, and equilibrium pH = 7.5 and 6.5 of the systems. A constant amount of $CaCO_3$ 0.1 g and 10 mL of metal concentrations: (1 x 10^{-2} mol/L to 7 x 10^{-2} mol/L) for cobalt and (1 x 10^{-5} mol/L to 7 x 10^{-5} mol/L) for chromium. The metal solutions were prepared by successive dilutions of a stock solution of each metal and separately, batch adsorption experiments were carried out. The experimental data that was based on the equilibrium experiments obtained from this study were evaluated with Langmuir, Freundlich and Dubinin-Radushkevich isotherms models.

The temperature effect on the Co(II) and Cr(VI) adsorption on the synthesized material, was investigated by batch experiments carried out by varying the system temperature (293 K, 303 K, 313 K and 323 K) and using constant initial concentrations of 1 x 10^{-2} mol/L for cobalt and 1 x 10^{-5} mol/L for chromium. Later, several thermodynamic parameters, such as enthalpy $\Delta H°$, entropy $\Delta S°$ and free energy of Gibbs $\Delta G°$ of the adsorption process were determined.

Conclusions

The calcium carbonate was synthesized by precipitation method. A fine, white, crystalline powder was produced. It was determined that the time which was necessary to reach the equilibrium between the phases solid-liquid for the Co(II) ions was 4 h and 3 for Cr(VI). The Co(II) and Cr(VI) ions´ adsorption on the synthesized material was dependent of the adsorbate concentration and temperature. At smaller concentrations of the adsorbate and major systemic temperatures, the adsorption capacity was greater. The adsorption systems that were studied were adjusted to the Freundlich adsorption isotherm. The pseudo-second order kinetic model was found to fit better the experimental data that was measured for both metallic ions. The values of ΔH^o, ΔS^o, and ΔG^o show that the cobalt and chromium ion adsorption on $CaCO_3$ was carried out by means of an endothermic and spontaneous adsorption process. The positive entropy values indicate the increase in the randomness in the interface of the solution with the solid by the fixation of the Co(II) and Cr(VI) ions on the $CaCO_3$. The values of the enthalpies in the adsorption systems were smaller than 31 kJ/mol, which indicate that physical adsorption processes were carried out. The Co(II) ion adsorption on calcium carbonate was better than for the Cr(VI) ion adsorption.

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