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Marble slurry waste as a scavenger material for Cr(III) ions from aqueous medium

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ABSTRACT

The present paper reports removal of chromium from aqueous solution using marble slurry waste material at room temperature. Optimum conditions such as concentration of Cr(III) and adsorbent, solution pH, stirring time, effect of foreign ions, and effect of temperature were studied. The adsorption of Cr(III) ion onto marble slurry is well described by Langmuir and Freundlich adsorption isotherm. The maximum Cr(III) removal was 139.92 mg of Cr(III) per gram of marble slurry as evaluated from Langmuir isotherm. Thermodynamic parameters like enthalpy, entropy, and Gibbs free energy have been found to be 30.92 kJ/mol, 118.14 J/mol K, and −4.21 kJ/mol, respectively. These parameters indicated that the process was spontaneous and endothermic in nature. It has been found that 1 g/L marble slurry is capable to remove ≈100% of Cr(III) ions in the pH range of 5–10.

Keywords: Marble slurry; Chromium(III); Langmuir isotherm; Freundlich isotherm

1. Introduction

The discharge of heavy metals into environment has become a serious problem over the last few decades. Heavy metals are carcinogenic and mutagenic in nature for animals. The heavy metal pollutants of serious concern include zinc, chromium, cadmium, mercury, etc. Chromium is an essential nutrient for humans and its deficiency may cause disruptions of metabolism, diabetes, and cardiovascular disorder. Sometimes, higher uptake of Cr(III) can also cause skin problems. Steel, leather, and textile manufacturing [1–3] industries are continuously releasing Cr(III) which is a major source of Cr(III) pollutant to environment.

The commonly used method for removing metals from effluents includes ion exchange, coagulation/flocculation [4,5], reverse osmosis, and solvent extraction. These techniques are expensive, consume more time and energy, required more reagent concentration, low efficiency, and produce waste sludges that again required disposal. Thus, removal of heavy metals using waste inorganic and biosorbent is a good technique because of cheap material, easy to handle and does not require much technology. Several studies reveal that few inorganic adsorbents and bioadsorbents are effective in the removal of heavy metal ions. Some reported inorganic sorbents and bioadsorbents are fly ash [6–8], fuller earth [9], clarified sludge [10], red mud [11], coal [12], wood saw dust [13,14], rubber

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saw dust [15], agriculture waste material [16], rice husk [17,18], rice husk ash [19–21], mustard husk [22] fertilizer industry waste [23], lime stone [24,25], magnetic nanoparticles [26], etc. Therefore, efficient low cost and environment-friendly methods are needed to be developed to remove heavy metals from effluents.

Marble slurry is a processing and polishing waste of marble mining industry which is composed of CaO, SiO_2, MgO, Al_2O_3, and FeO_2. This is excellent adsorbent easily available, waste material, and creating number of problems to environment and human health. Marble is a major product being mined in Udaipur region, during the processing of marble, 20% out of mined resource is produced as fine marble slurry which is left as a waste material. It is creating serious threat to surrounding areas. Thus, the present work is designed to develop marble slurry as useful and cheap adsorbent for removal of Cr(III) from effluent.

2. Experimental

2.1. Apparatus

Atomic absorption spectrophotometer (Elico SL 168) has been used to determine the concentration of Cr(III) ion in various aqueous solutions. The pH studies were performed using pocket-sized pH meter (pH 600 milwaukee). An auto stop magnetic stirrer (model DIGMAG) was used for experiments. The FTIR of marble slurry was recorded on Bruker TENSOR 27.

2.2. Materials

Marble slurry taken from dumping area was thoroughly washed many times with double-distilled water so as to remove any soluble impurities. The washed sample was dried in an oven at 373 K for 24 h to make it moisture free. Finally, this treated adsorbent was used throughout the course of investigation. The particle size of marble slurry was sieved using sieve size less than 200 μm. Marble slurry contained CaO 17.10%, SiO_2 28.50%, MgO 26.61%, Al_2O_3 1.63%, FeO_2 4.63%, and loss on ignition 21.32%. Presence of carbonates in marble slurry was characterized through FTIR analysis. The observed peaks at about 711, 878, 1,432, 1,810, and 2,500 cm^{-1} coincided with pure $CaCO_3$.

Stock solution of Cr(III) (5.1 g/L) was prepared using chromium(III) chloride of LR grade in double-distilled water. Further solutions were prepared by diluting the stock solution as per requirement.

2.3. Experimental procedure

All studies excluding temperature dependence were done at room temperature that is 298 ± 1 K. Initial concentration of marble slurry was assessed from 100 to 2,000 mg/L of marble slurry taken for 1,500 mg/L of Cr(III) solution at pH 7. Different concentrations of Cr(III) in the range of 500–4,000 mg/L have been taken to optimize the best concentration at which adsorbent adsorbed ≈ 100% Cr(III). Stirring time has also been studied ranging from 2 to 100 min at 250 rpm of magnetic stirrer. Effect of temperature on adsorption of Cr(III) onto marble slurry were examined in the range 298–358 K. Thus, entire studies have been done to optimize different parameters.

After each study, samples were filtered off on whattman filter (no. 1) and in filtrate residual concentration of Cr(III) was determined by atomic absorption spectrophotometer. The percent adsorption of Cr(III) on marble slurry has been calculated using Eq. (1) and metal up tack (q) was calculated by Eq. (2).

$$\text{Adsorption}\ (\%) = C_i - C_r/C_i \times 100 \tag{1}$$

where C_i is initial concentration of Cr(III), C_r is residual concentration of Cr(III)

$$q_e = [(C_i - C_r)/m]V \tag{2}$$

where V is volume of suspension and m is weight of the adsorbent.

3. Result and discussion

3.1. Effect of amount of marble slurry, Cr(III) concentration, and pH

Amount of adsorbent plays an important role in adsorption. To evaluate effect of marble slurry as adsorbent on the adsorption of Cr(III) ion, various quantity of marble slurry have been taken in the range of 200–2,000 mg/L in the optimized condition. The result in Fig. 1 show that adsorption efficiency increases with increasing amount of marble slurry, adsorption reach 100% at 1,000 mg/L of marble slurry. It can be explained, since amount of marble slurry will increase surface area as well as binding sites of adsorbent. Therefore, 1,000 mg/L marble slurry was fixed for further experiment.

The result obtained from Fig. 2, is effect of varying Cr(III) concentration indicated that almost 100% adsorption occurs in the range of 500–1,500 mg/L. Decreased adsorption can be explained in terms of relatively small number of active sites of adsorbent at higher concentration of Cr(III).

The pH also plays an important role in most adsorption processes. In the present experiment, the

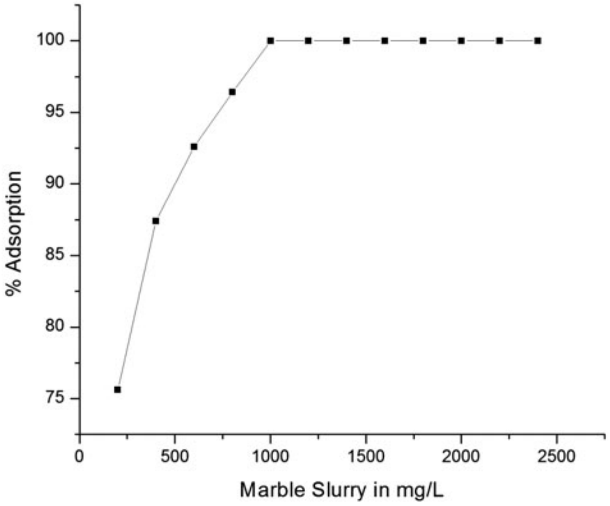

Fig. 1. Effect of amount of marble slurry on adsorption of Cr(III) [Experimental conditions pH 7, Cr(III) 1,530 mg/L, temp 298 ± 1 K].

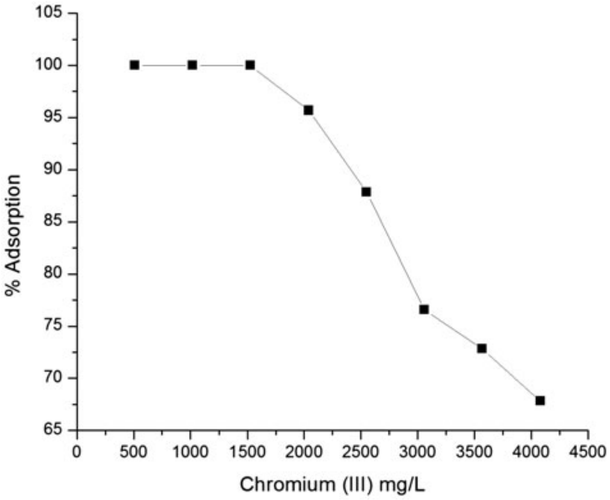

Fig. 2. Effect of Cr(III) concentration on adsorption [Experimental conditions pH 7, marble slurry 1,000 mg/L, and temp 298 ± 1 K].

effect of pH was studied ranging from 2 to 14. At pH below 2 the removal of Cr^{3+} reach to zero because of almost complete solubility of the adsorbent ($CaCO_3$, $MgCO_3$) thereby hindering the adsorption. In between pH 2–5 adsorption increases sharply. This may be attributed to a possible ion exchange mechanism between Cr(III), Ca^{2+}, and Mg^{2+} in the marble slurry. At pH 6–9 chromium undergoes hydrolysis to $Cr(OH)^{2+}$ and $Cr(OH)_2^+$, trivalent chromium is precipitated as $Cr(OH)_3$ at pH 7.5. Thus, pH 7 has been selected for further study because at this pH almost 100% adsorption occurs.

3.2. Kinetics of the adsorption process

Variation of percent adsorption of Cr(III) onto marble slurry with stirring time has been studied at different concentration of Cr(III) ions. The data shown in Fig. 3 elucidate that the adsorption of Cr(III) ions was quite rapid initially, which indicate that adsorption occurred mostly at the surface of adsorbent and to some extent of pores. With the passage of time, the percent of adsorption increased and reached at constant value and then rate of adsorption decreased. Slow adsorption may be attributed to diffusion of Cr (III) ions into the pores of marble slurry. The time required to reach adsorption equilibrium was found to be 20 min in concentration range 100–500 mg/L Cr(III) ions, 30 min for 1,000–1,500 mg/L Cr(III) ions, and 70 min for more than 2,000 mg/L Cr(III) ions concentration. Therefore, 30 min stirring time was chosen for further experiment.

Kinetics of adsorption of Cr(III) onto marble slurry was checked by Morris–Weber equation to correlate mechanism of adsorption [27]. Data depicted in Fig. 3 (1,530 mg/L of Cr) plotted against square root of stirring time. The obtained pattern of plot may verify the Morris–Weber equation. The equation may be written as:

$$q_t = K_d(t)^{1/2} \tag{3}$$

where q_t is amount of Cr(III) ions adsorbed (mg/g) at time t, $t^{1/2}$ is square root of different stirring time and K_d is rate constant. Two distinct regions were observed when q_t was plotted against $t^{1/2}$. In Fig. 4,

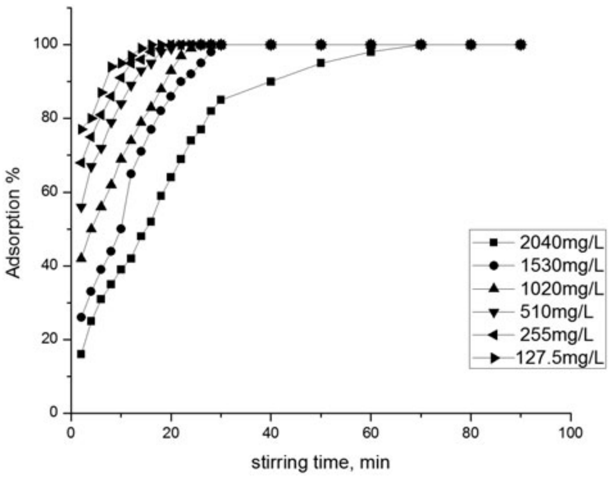

Fig. 3. Effect of stirring time on adsorption of various concentrations of Cr(III) ions [Experimental conditions pH 7, temp 298 ± 1 K].

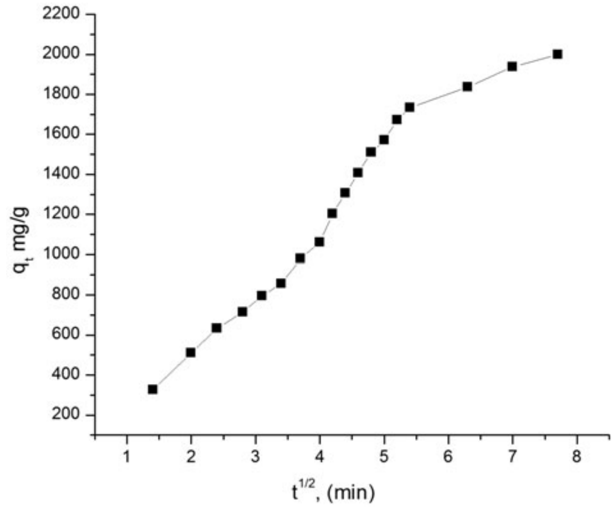

Fig. 4. Plot of the amount of Cr(III) ions adsorbed at against square root of time [Experimental conditions; pH 7, marble slurry 1,000 mg/L, temp 298 ± 1 K, Cr(III) 1,530 mg/L, and r^2 0.974].

first linear portion was boundary line diffusion effect [28] and second portion due to the intraparticle diffusion effect [29]. However, in Fig. 4, line does not pass through the origin indicates that intrapore diffusion is not controlling step in adsorption of Cr(III) ions onto marble slurry [30,31]. Rate constant which was 299.837 mg/g/min, show mobility of Cr(III) ions towards the marble slurry surface.

Again the kinetic data obtained in Fig. 3 (1,530 mg/L of Cr) for Cr(III) adsorption by marble slurry were tested by Lagergren equation [32]. Lagergren equation may be written as:

$$\log (q_e - q_t) = \log q_e - (k_1/2.303)t \qquad (4)$$

where q_e is the amount of Cr(III) ions adsorbed at equilibrium (mg/g), k_1 is the first-order rate constant for Cr(III) ions adsorption onto marble slurry. A graph is drawn between $\log(q_e - q_t)$ and time, t (min) are liner and indicate fitness of the model for the present system. log q_e is calculated by Fig. 5 (intercept) and compared with the experimental q_e, both values are almost same that indicate first-order kinetics is involved. The value of k_1 was calculated to be 0.0681 min^{-1}.

3.3. Adsorption isotherm

Both Langmuir and Freundlich adsorption isotherm were studied at various concentration of Cr(III) ions and it was observed that the system followed both adsorption isotherms at 298 ± 1 K (Fig. 6). The Freundlich equation may be written in linear form as:

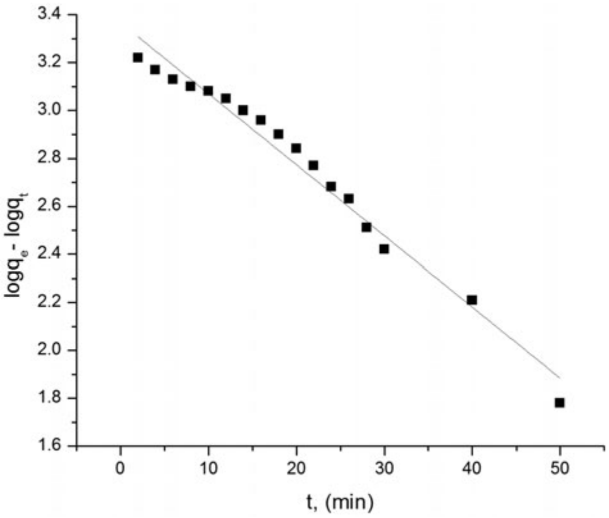

Fig. 5. Plot of log ($q_e - q_t$) against stirring time t [Experimental conditions; pH 7, marble slurry 1,000 mg/L, temp 298 ± 1 K, Cr(III) 2,040 mg/L, and r^2 0.995].

$$\log q_e = \log K_f + 1/n \log C_e \qquad (5)$$

where q_e (mg/g) amount of Cr(III) ions adsorbed, K_f is the indicator of adsorption capacity, $1/n$ is intensity of the adsorption and C_e is equilibrium concentration of Cr(III) mg/L.

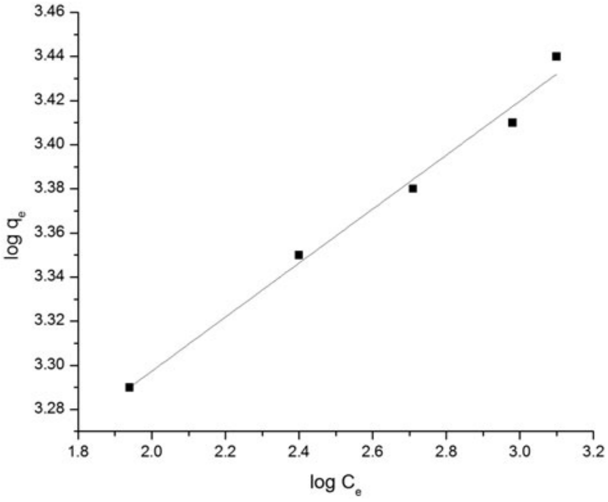

Fig. 6. Freundlich plot for Cr(III) ions adsorption by marble slurry [Experimental conditions; pH 7, marble slurry 1,000 mg/L, temp 298 ± 1 K, and r^2 0.9985].

Freundlich equation was applied to the experimental data (Fig. 2) and linear plot was obtained when graph was plotted between log q_e and log C_e. Parameters n and K_f were calculated from slope and intercept which were found to be 8.169 L/g and 3.052, respectively, with correlation coefficient of 0.9985. Favorable adsorption of Cr(III) ion onto marble slurry was suggested by the fact that the value of n is greater than unity [33,34] Langmuir isotherm was also tested to determine adsorption capacity of marble slurry. The Langmuir isotherm may be written as:

$$C_e/q_e = C_e/q_m + 1/q_m b \tag{6}$$

where C_e is equilibrium concentration of solute (mg/L), q_m is adsorption capacity (mg/g), $1/b$ is free energy of adsorption, and q_e is amount of Cr(III) adsorbed at equilibrium time (mg/g). When Langmuir equation applied on Fig. 2, plotted C_e/q_e vs. C_e a linear slope has been obtained (Fig. 7), straight line shows the applicability of Langmuir equation, q_m, and b were calculated by intercept and slope which were 139.92 mg/g and 2,859 ml/g, respectively. This model also suggested that monolayer coverage of Cr(III) ions occur onto the outer surface of marble slurry.

The Temkin isotherm model [35] correlates adsorbent-adsorbate interactions of Cr(III) onto marble slurry (Fig. 8). Temkin isotherm may be written in linear form as:

$$q_e = RT/b_T \ln(A_T) + (RT/b_T) \ln(C_e) \tag{7}$$

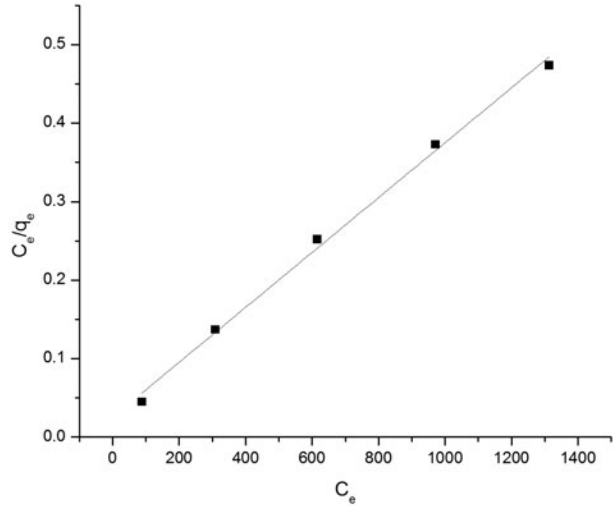

Fig. 7. Langmuir plot for Cr(III) ions adsorption by marble slurry [Experimental conditions pH 7, marble slurry 1,000 mg/L, temp 298 ± 1 K, and r^2 0.995].

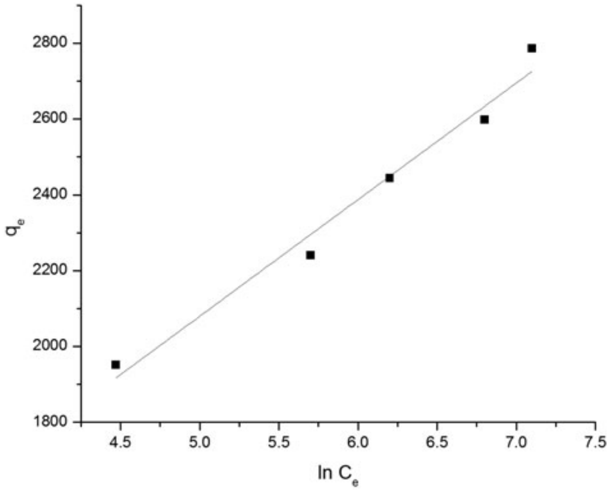

Fig. 8. Temkin isotherm for the adsorption of Cr(III) [pH 7, marble slurry 1,000 mg/L, and temp 298 ± 1 K r^2 0.981].

q_e and C_e were defined above, R is universal gas constant and T is absolute temperature. A_T is the equilibrium binding constant corresponding to the maximum binding energy, and b_T is related to the heat of adsorption.

A graph is drawn between q_e vs. ln C_e. A_T and b_T were calculated by intercept and slope which were 5.8 L/g and 8.05, respectively. Therefore, the Freundlich and Langmuir model showed better fit followed by Temkin model. Thus, also indicates that the metal adsorption by the adsorbents was mainly governed by physical adsorption [36].

3.4. Thermodynamics of adsorption

According to Van't Hoff equation Gibbs free energy change is calculated by following equation:

$$\Delta G = RT \ln K_D \tag{8}$$

where K_D is equilibrium constant which is obtained by the following equation:

$$K_D = q_e/C_e \tag{9}$$

where q_e and C_e are concentrations of chromium on the solid surface and in the liquid at equilibrium.

$$\Delta G = \Delta H - T\Delta S \tag{10}$$

$$\ln K_D = -\Delta H/RT + \Delta S/R \tag{11}$$

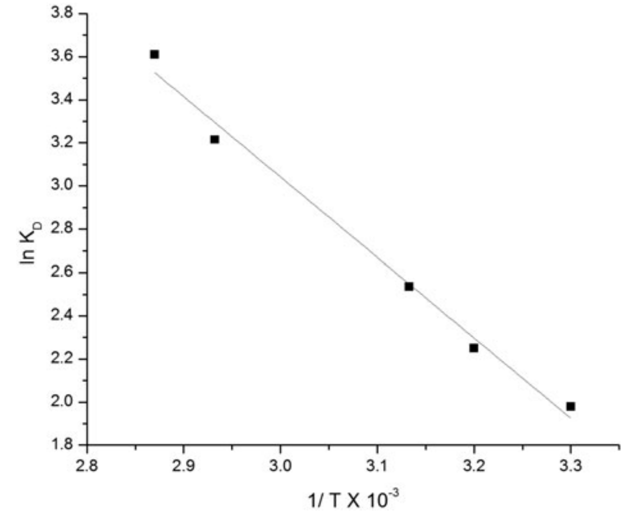

Fig. 9. Thermodynamic distribution coefficient calculated for the adsorption of Cr(III) ions by marble slurry [Experimental conditions pH 7, marble slurry 1,000 mg/L, Cr(III) 2, 040 mg/L, and r^2 0.986].

where T is temperature and R is universal gas constant (8.314 J/mol K).

To calculate the thermodynamic parameters a graph is plotted between ln K_D vs. $1/T$. In Fig. 9 slope and intercept indicates $-\Delta H/RT$ and $\Delta S/R$ which were −3.723 and 14.21, respectively.

ΔH = 30.92 kJ/mole
ΔS = 118.14 J/(mol-K)
ΔG = −4.21 kJ/mol

Positive value of ΔH indicates that adsorption process is endothermic and positive value of ΔS indicates that adsorption process is irreversible. On increase in temperature ΔG value becomes negative which indicates that the adsorption process is spontaneous and feasible.

4. Conclusions

Marble slurry is a waste product, cheap, and effective inorganic adsorbent for the removal of Cr(III) ions from aqueous solutions. The experimental result revealed the following.

(1) Adsorption occurred mainly at the surface of the adsorbent and slightly by internal pores.
(2) The experimental data for the adsorption process were well described by Freundlich and Langmuir models over the concentration range studied. The Langmuir adsorption capacity was determined as 139.92 mg/g for Cr(III) adsorption.
(3) The adsorption of Cr(III) ions followed the pseudo-first-order kinetic.
(4) The adsorption capacity increased with increasing temperature showing that the adsorption process was partialy chemical in nature, endothermic, and spontaneous as confirmed by the evolution of the relevant thermodynamic parameters, viz. ΔH, ΔS, and ΔG.

List of Symbols

C_i — initial concentration of Cr(III)
C_r — residual concentration of Cr(III)
C_e — equilibrium concentration of Cr(III)
q_e — amount of Cr(III) ion adsorbed at equilibrium
q_t — amount of Cr(III) ion adsorbed at time
K_d — rate constant
K_f — indicator of adsorption of Cr(III)
$1/n$ — intensity of adsorption
q_m — adsorption capacity
A_T — equilibrium binding constant
b_T — heat of adsorption
ΔG — Gibbs free energy
K_D — equilibrium constant
ΔH — enthalpy change
ΔS — entropy change

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