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Characterization of Cr(III) interaction with kaolinite – Effect of the presence of Cr(VI)

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Abstract: *In the present study, experiments were performed to characterize the effectiveness of kaolinite in Cr(III) removal from water in the absence and in the presence of Cr(VI). The results of batch experiments, show that the efficiency of Cr(III) removal by kaolinite increases with the increase of pH and temperature in both cases. The effect of the presence of Cr(VI) on the adsorption of Cr(III) by kaolinite depends on the solution pH and on the concentrations of the two ions. Whatever the system, the removal kinetic of Cr(III) is well described by the pseudo-second order model. Spectroscopic analyses reveal that Cr(III) interaction with kaolinite is mainly electrostatic.*

Keywords: kaolinite, Cr(III), Cr(VI), adsorption, water treatment

Introduction

Environment contamination by heavy metals is a major and a well-known issue. Among these metals, chromium is one of the most toxic contaminants of surface and groundwater due to its widespread use in industrial applications [1]. Chromium is extensively used in electroplating, leather tanning, metal finishing, nuclear power plant, dying, photography industries and textile industries [2, 3]. Elevated chromium concentration in industrial processes ends up in waste water. The main chromium species in water are Cr(III)

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and Cr(VI) depending on pH and oxidation potential. They are characterized by different mobility and bioavailability. Cr(VI) is much more toxic than Cr(III). In wastewater treatment, Cr(VI) is converted to Cr(III) by reducing reagents, then Cr(III) is removed. Many processes can be applied for heavy metals removal from aqueous solutions, such as chemical precipitation, adsorption, ion exchange, electrochemical treatment, reverse osmosis and membrane technologies [4-10]. Adsorption which is one of the most widely used process in water treatment, due to its high efficiency and low cost, provides an additional alternative attractive if the adsorbent is inexpensive and available. Therefore, special attention has been given to the use of natural materials available in large quantities such as clays for metals removal [11-14]. Clays such as bentonite and kaolinite have been tested for Cr(III) removal from synthetic water [15, 16] and from tannery wastewater [17]. However, in our knowlegment, no study can be found in literature about Cr(III) removal by clays in binary system with Cr(VI) which is the case when Cr(VI) is not totally reduced in industrial waste water.

The main aim of the present work is the study of Cr(III) removal by adsorption on kaolinite in the presence of Cr(VI). Kinetic, thermodynamic, equilibrium and spectroscopic studies were carried out.

Materials and methods

All chemicals used were of analytical grade and no purification was used. The used kaolinite is a commercial product (BIOCHEM CHEMOPHARMA). Cr(III) and Cr(VI) solutions in distilled water were prepared from chromium nitrate ($Cr(NO_3)_3.9H_2O$) and potassium chromate (K_2CrO_4) respectively. NaOH (1 $mol.L^{-1}$) and HCl (1 $mol.L^{-1}$) solutions were used for adjusting the solutions pH.

The used kaolinite was characterized by EDX, X-ray diffraction, ATR-FTIR, TGA and surface area measurement. The kaolinite composition was determined with an EDAX KEVEX SIGMA LEICA analyser. X-ray powder diffraction pattern was recorded by using a Thermo Electron ARL'XTRA diffractometer using a Curved Position-Sensitive Detector (INEL CPS 120) by Reflection Asymmetric Powder Diffraction with Flat-Plate Sample. The diffractometer was equipped with a cobalt anticathode (λ=1.79Å). N_2-adsorption desorption isotherm of the kaolinite sample was recorded at 77 K using a Micromeritics ASAP2020 sorptometer, after degassing the sample at 150°C for 96 hours. The BET surface area was determined in the 0.05-0.35 P/P° range. Thermal analysis (TGA-DTA) was performed on a Setaram Labsys TG apparatus under constant nitrogen flow (10 $mL.min^{-1}$) with a heat rate of 5°$C.min^{-1}$. Infrared analysis by attenuated total reflection (ATR-FTIR) performed on a Thermo Scientific NICOLET iS10 Smart spectrometer was used to characterize kaolinite samples before and after Cr(III) adsorption in single and binary systems. The pH of zero point of charge (pH_{PZC}) was determined by drift method [18].

Cr(III) removal was studied in single system and in binary system with Cr(VI). Effects of pH, temperature in the range 295 to 318 K, contact time, Cr(III) and Cr(VI) concentrations were evaluated.

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Adsorption experiments were conducted in batch. Suspensions formed by kaolinite and Cr(III) or mixed Cr(III)/Cr(VI) solutions at adjusted pH were agitated for a desired time, then final pH was measured and suspensions were centrifuged for 15 min. In the recovered solutions, Cr(III) concentration was determined after conversion to Cr(VI) by oxidation using H_2O_2 in alkaline medium at elevated temperature. Cr(VI) concentration was determined by diphenyl carbazide method using UV-Visible SCHIMADZU 1650 PC spectrophotometer.

Results and Discussion

The X-ray diffraction pattern of the used kaolinite (Figure 1) shows the presence of the characteristic kaolinite peaks at 2θ = 14°, 2θ = 23°, 2θ = 29°, 2θ = 41° and 2θ = 45° observed in others studies [19, 20]. EDX analysis (data not shown) reveals the absence of any other metallic species than Al and Si.

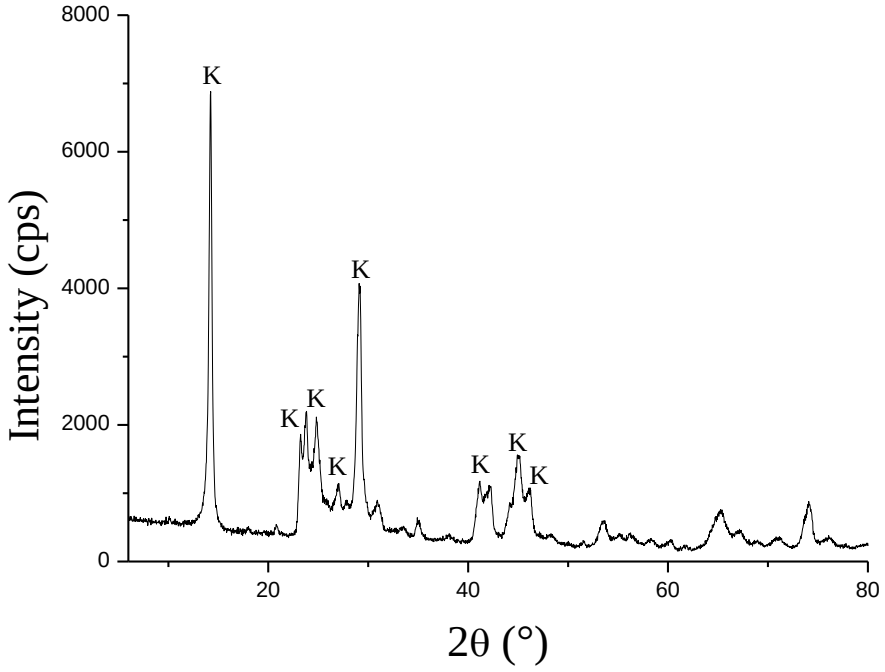


Figure 1. X-ray diffraction spectrum of the pristine kaolinite

Nitrogen adsorption-desorption isotherm is typical of multi-layer adsorption at the particles surface of the used kaolinite. The measured BET specific surface area is 24.1 m^2/g. This value is slightly higher than that reported in literature [21-23]. The measured pH at point of zero charge (pHPZC) which is about 2.2 is in agreement with pH_{PZC} values of others commercial kaolinite (pH_{PZC}< 3) [22, 24]. The thermal behavior of

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kaolinite (Figure 2) shows a minor mass loss of 0.5% below 100°C attributed to the evaporation of the adsorbed water and a major mass loss of about 10% between 445 and 600°C, corresponding to dehydroxylation which is characterized by the endothermic peak observed in DTA analysis at 550°C.

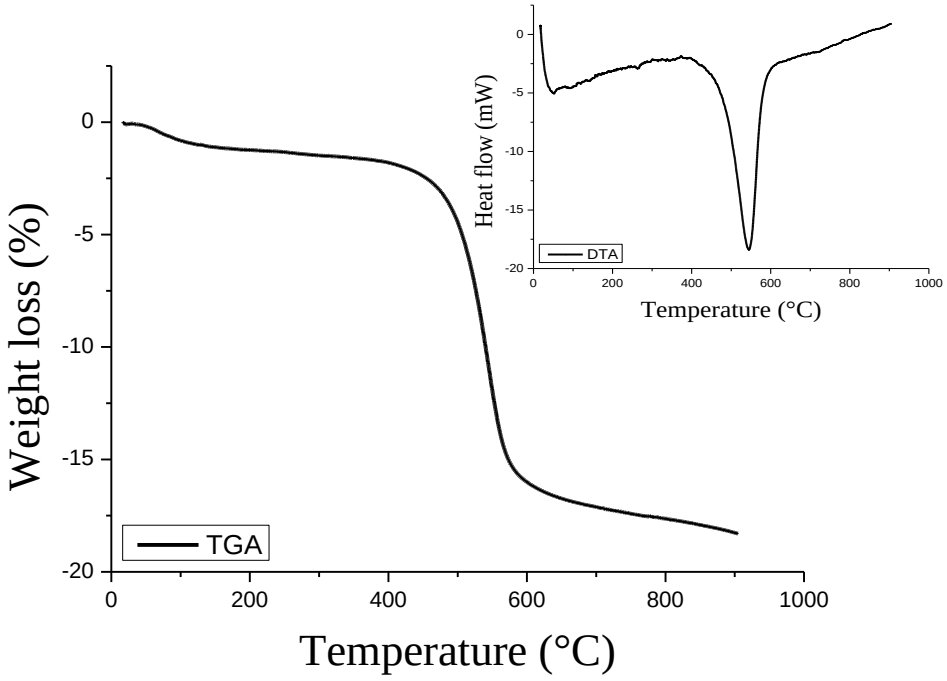


Figure 2. Thermal analysis of the raw kaolinite

Cr(III) uptake by kaolinite in single and binary systems is pH-dependent (Figure 3). In the two systems, Cr(III) removal increases as increasing pH. This is in agreement with results of other studies on adsorption of heavy metals by clays [14, 25]. Such evolution is explained by the zeta potential decrease together with the pH increase due to aluminol and silanol groups deprotonation. The measured pH_{PZC} in the present work shows that the edges of the used kaolinite particles are negatively charged at pH>2.2. Consequently, Cr(III) interaction with kaolinite surface seems to be mainly electrostatic. In the case of a mixture of Cr(VI) and Cr(III) at the same concentration a decrease in Cr(III) removal is observed. At pH<4.5, Cr(III) removal is totally hindered. Cr(VI) adsorption on the pristine kaolinite in single system is observed only at pH<4. Consequently, the effect of Cr(VI) on Cr(III) adsorption in this pH range can be related to competition. At pH higher than 7, in addition to Cr(III) uptake by the clay, precipitation occurs.

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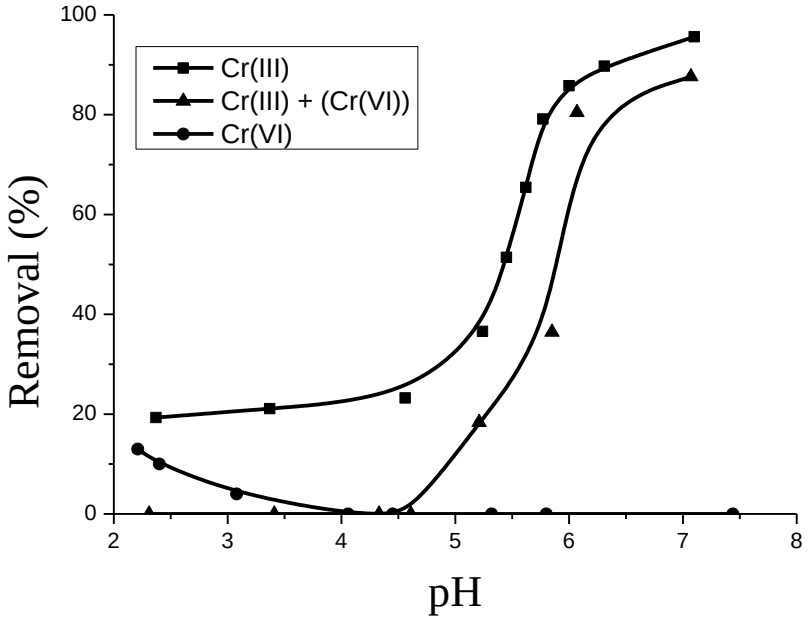


Figure 3. Effect of pH on Cr (III) removal by kaolinite
($C_{0(Cr(III))}$: 10 mg/L, $C_{0(Cr(VI))}$: 10 mg/L, t: 60 min, kaolinite dose:1g/L)

In binary system, the effect of increasing Cr(VI) concentration on Cr(III) uptake by kaolinite depends on solution pH (Figure 4). At pH: 3, whatever the Cr(VI) concentration, the Cr(III) removal does not occur. However, at pH: 6, it increases when Cr(VI) concentration increases. It can be noted that the reduction of Cr(VI) ions by the used kaolinite is ruled out as no iron has been detected. Indeed, Kwak et al. [26] have shown that Cr(VI) reduction by clays is related to the presence of Fe(II).

In the FTIR spectrum of the raw kaolinite (Figure 5), the observed bands at about 3684 and 3618cm^{-1} are attributed to –OH stretching vibrations. Bands observed at about 1026 cm^{-1} and 912 cm^{-1} are attributed to Si-O-Si vibration in the plane and to the Al-OH deformation respectively [21]. Those observed at 798 cm^{-1} and 746 cm^{-1} are due to Si-O-Al vibrations, they are the typical bands of kaolinite. In all cases, ATR-FTIR spectra obtained after Cr(III) adsorption, show no change in the SiO vibrations bands (Fig. 5), implying no incorporation of chromium ions in kaolinite and confirming electrostatic interaction.

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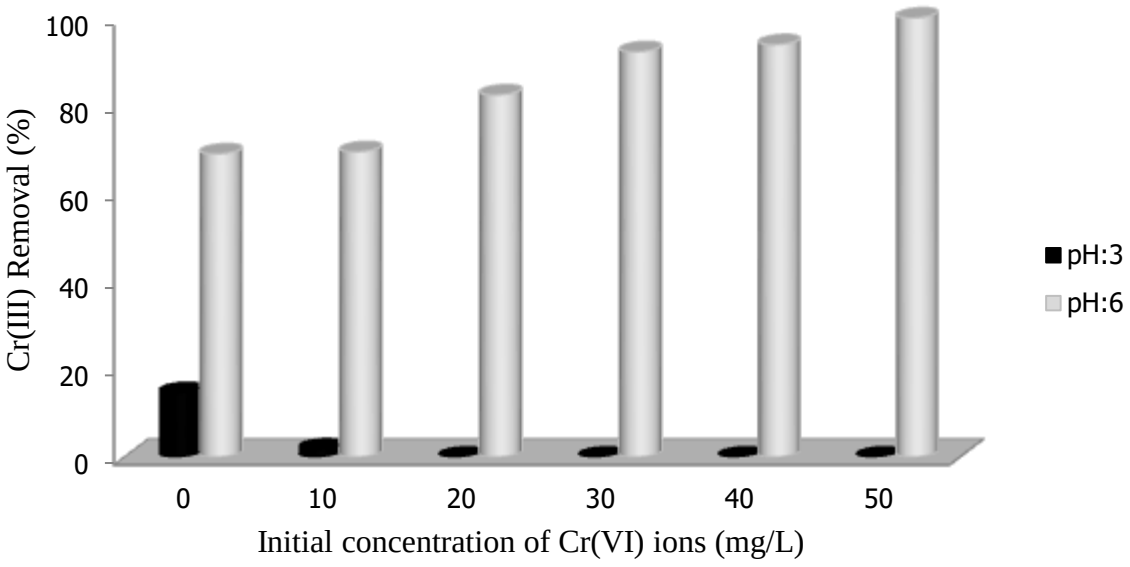


Figure 4. Effect of increasing Cr(VI) concentration on Cr(III) adsorption on kaolinite ($C_{0(Cr(III))}$: 10 mg/L, kaolinite dose:1 g/L, t: 60 min)

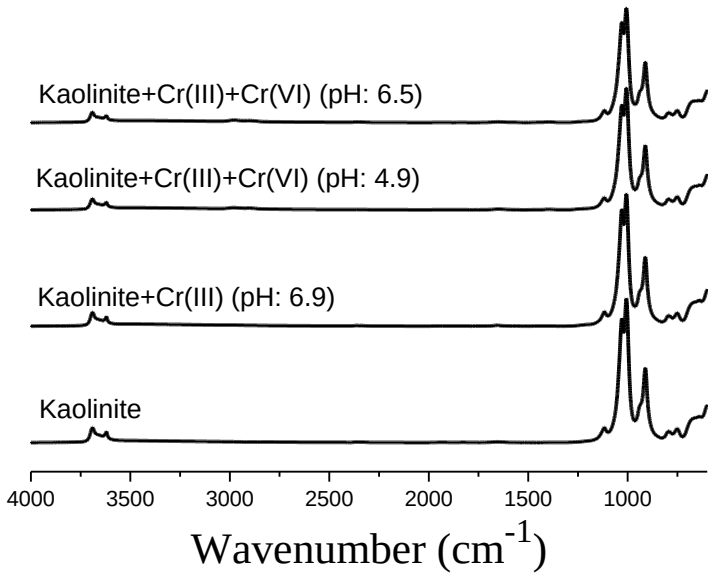


Figure 5. ATR-FTIR spectra of kaolinite after chromium adsorption

In the two systems, Cr(III) removal increases with increasing temperature (Figure 6). The same evolution has been observed by Turan and coauthors [16]. However, it has been reported that Cr(III)

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adsorption on bentonite is exothermic [25]. The presence of Cr(VI) has no effect on the kaolinite behavior towards Cr(III) adsorption. At 45°C, the increase in Cr(III) removal is more important in single system. The calculated values of enthalpy variation (ΔH) are 79.8 and 47.3 Kj/mol in the absence and in the presence of Cr(VI) respectively.

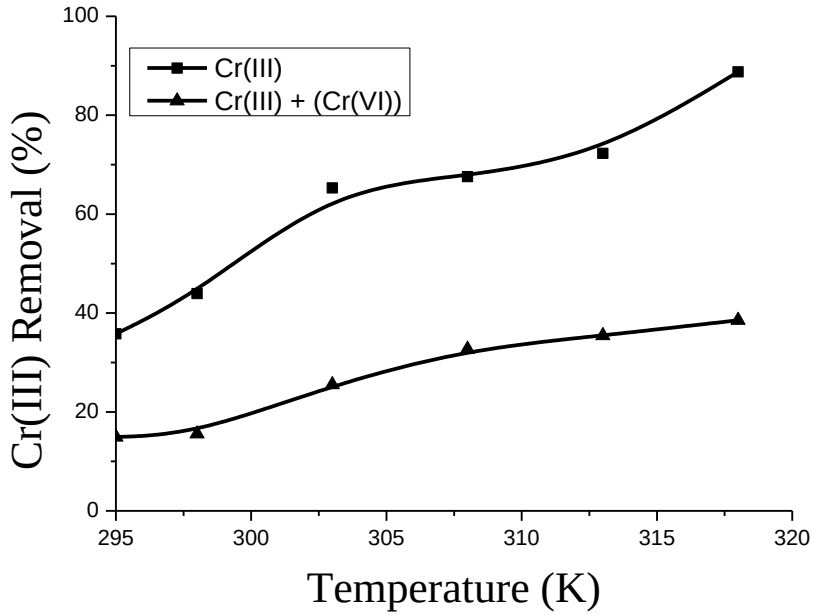


Figure 6. Effect of temperature on Cr (III) adsorption on kaolinite
($C_{0(Cr(III))}$:10 mg/L, $C_{0(Cr(VI))}$: 10 mg/L, kaolinite dose:1 g/L, pH: 5, t: 60 min)

The presence of Cr(VI) has no significant effect on Cr(III) adsorption kinetics. In both cases, the same time evolution is observed with a first rapid step during the three first hours (Figure 7). Then, Cr(III) removal increases gradually to attain equilibrium. Application of various kinetics models to experimental data shows that the second order model is more suitable. The calculated rate constant decreases in the presence of Cr(VI) (Table 1), implying that Cr(III) adsorption reaction slows down. In single system, kinetics of Cr(III) adsorption by kaolinite is limited by external diffusion. However, it is limited by intraparticular diffusion in binary system. Consequently, the Cr(III) diffusion to kaolinite surface is favored in the presence of Cr(VI) in bulk solution. For the two diffusion models, the calculated diffusion constants are higher in the presence of Cr(VI).

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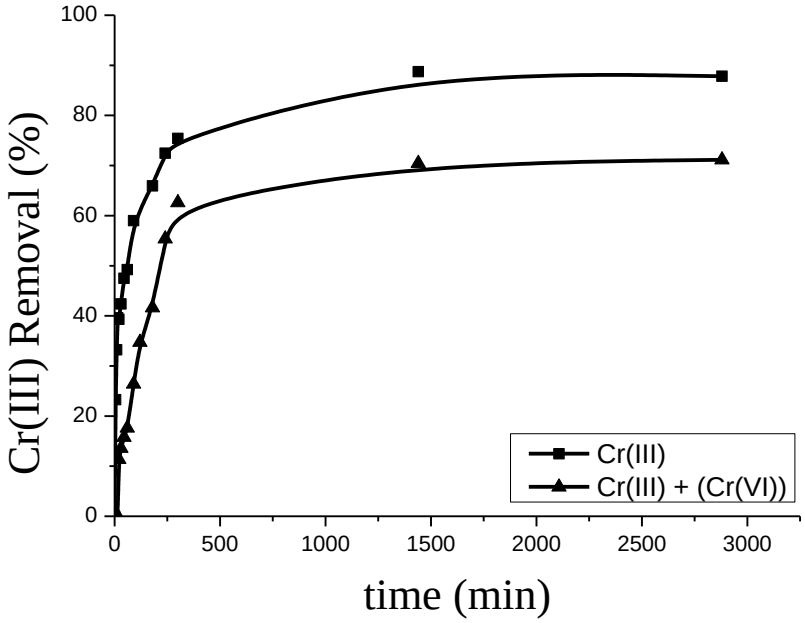


Figure 7. Effect of time on Cr (III) adsorption on kaolinite

($C_{0(Cr(III))}$:10 mg/L, $C_{0(Cr(VI))}$: 10 mg/L, kaolinite dose:1 g/L, pH: 5, t: 60 min)

Table 1. Kinetic parameters

Model	Second ordre	Intraparticular Diffusion	External Diffusion
Cr(III) alone	R^2: 0.999 Q_e: 8.92 ($mg.g^{-1}$) K_2: 0.003 ($g.mg^{-1}.min^{-1}$)	R^2: 0.878 K: 0.376 ($mg.g^{-1}.min^{-1/2}$)	R^2: 0.965 K: 0.004 (min^{-1})
Cr(III)+Cr(VI)	R^2: 0.993 Q_e: 6.73 ($mg.g^{-1}$) K_2: 0.001 ($g.mg^{-1}.min^{-1}$)	R^2: 0.982 K: 0.422 ($mg.g^{-1}.min^{-1/2}$)	R^2: 0.731 K: 0.010 (min^{-1})

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In both systems, experimental isotherms of Cr(III) adsorption (Figure 8) show a gradual decrease of available adsorption sites as increasing its concentration. The effect of the presence of Cr(VI) depends on the Cr(III) concentration. As Cr(III) concentration increases, the presence of Cr(VI) implies an increase of Cr(III) adsorption capacity. In the concentration range tested, saturation is only observed in the binary system. At pH: 5, Cr(III) adsorption capacity calculated by the Langmuir equation is greater in the presence of Cr(VI) (Table 2). In single system, Langmuir model is more suitable. However, Freundlich and Temkin models can better describe the experimental isotherm in binary system.

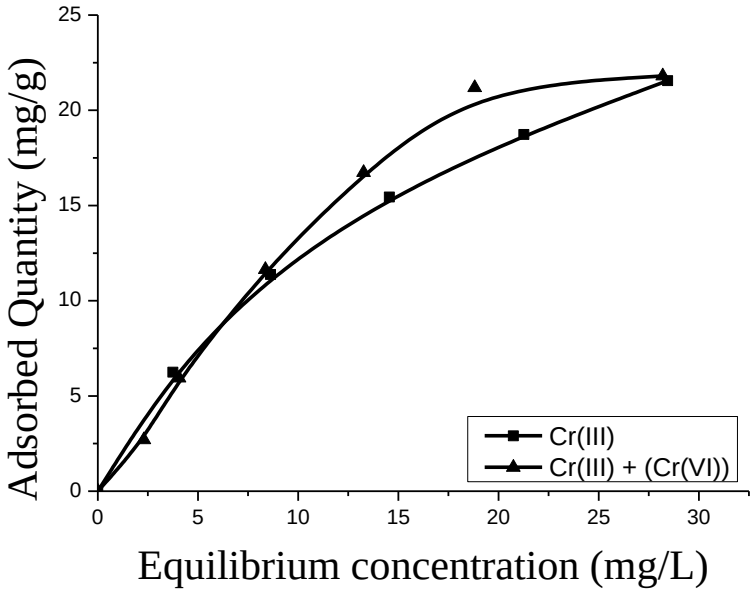


Figure 8. Isotherm of Cr (III) adsorption on kaolinite (kaolinite dose: 1 g/L, $C_{0(Cr(VI))}$: 10 mg/L, pH: 5, t: 24 h)

Table 2. Isotherms parameters

Model	Langmuir	Freundlich	Temkin
Cr(III) alone	R^2: 0.859 Q_m: 22.70 (mg.g^{-1}) K: 0.22 (L.mg^{-1})	R^2: 0.776 n: 3.55 K: 6.89	R^2: 0.649 ΔQ: 18,97 (J.mol^{-1}) K: 14.42 (L.mg^{-1})
Cr(III)+Cr(VI)	R^2: 0.544 Q_m: 33.27 (mg.g^{-1}) K: 0.07 (L.mg^{-1})	R^2: 0.942 n:1.17 K: 1.63	R^2: 0.975 ΔQ: 9.84 (J.mol^{-1}) K: 0.55 (L.mg^{-1})

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Conclusion

The results obtained in the present study show that Cr(III) removal by kaolinite is favored at pH>5 and at elevated temperature. In the presence of Cr(VI), Cr(III) removal by kaolinite is inhibited at pH<4.5. At pH:5, Cr(III) diffusion to kaolinite surface in binary system with Cr(VI) increases but the adsorption processes slows down. The Cr(III) adsorption capacity calculated by the Langmuir equation increases from 22.70 mg/g in single system to 33 mg/g in binary system with Cr(VI). In the two systems, Cr(III) interaction with tha kaolinite surface is mainly electrostatic.

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