Cr^{6+} adsorption by modified vermiculite

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Introduction

The work shows the adsorption of hexavalent chromium (Cr^{6+}) investigated using exfoliated vermiculite. Removing of Cr^{6+} from the environment is essential because it is harmful to biological organisms, including humans, due to its high toxicity, carcinogenicity and bioaccumulation in the food chain. The choice of using vermiculite as absorbent was due to its high cation exchange capacity (CEC) and surface reactive area, that can make it a valid material for removing Cr^{6+} with concomitantly low costs.

Research Goals

This work aimed at investigating the adsorption of Cr^{6+} in water by exfoliated vermiculite. Three effects were studied:

- contact time;
- initial concentration of Cr^{6+};
- adsorbent mass.

The adsorption mechanism were also characterized.

Materials and Methods

The adsorbent tested in this experiment was a vermiculite (produced in China) which has been subjected to heating at 1000 °C for 1 minute, resulting in an exfoliated vermiculite (Fig.1).

In order to test the 3 effects mentioned above, the adsorption experiment were performed using the following Cr^{6+} concentration/adsorbent mass/contact time combinations listed below:

- 1 ppm Cr^{6+} / 0.3 g vermiculite at 2, 4, 8, 14, 24, 48, 72 hours contact time;
- 0.125, 0.25, 0.50, 0.75, 1 ppm Cr^{6+} / 0.5 g vermiculite at 24 hours contact time;
- 1 ppm Cr^{6+} / 0.1, 0.2, 0.3, 0.5, 0.7, 1 g vermiculite at 24 hours contact time.
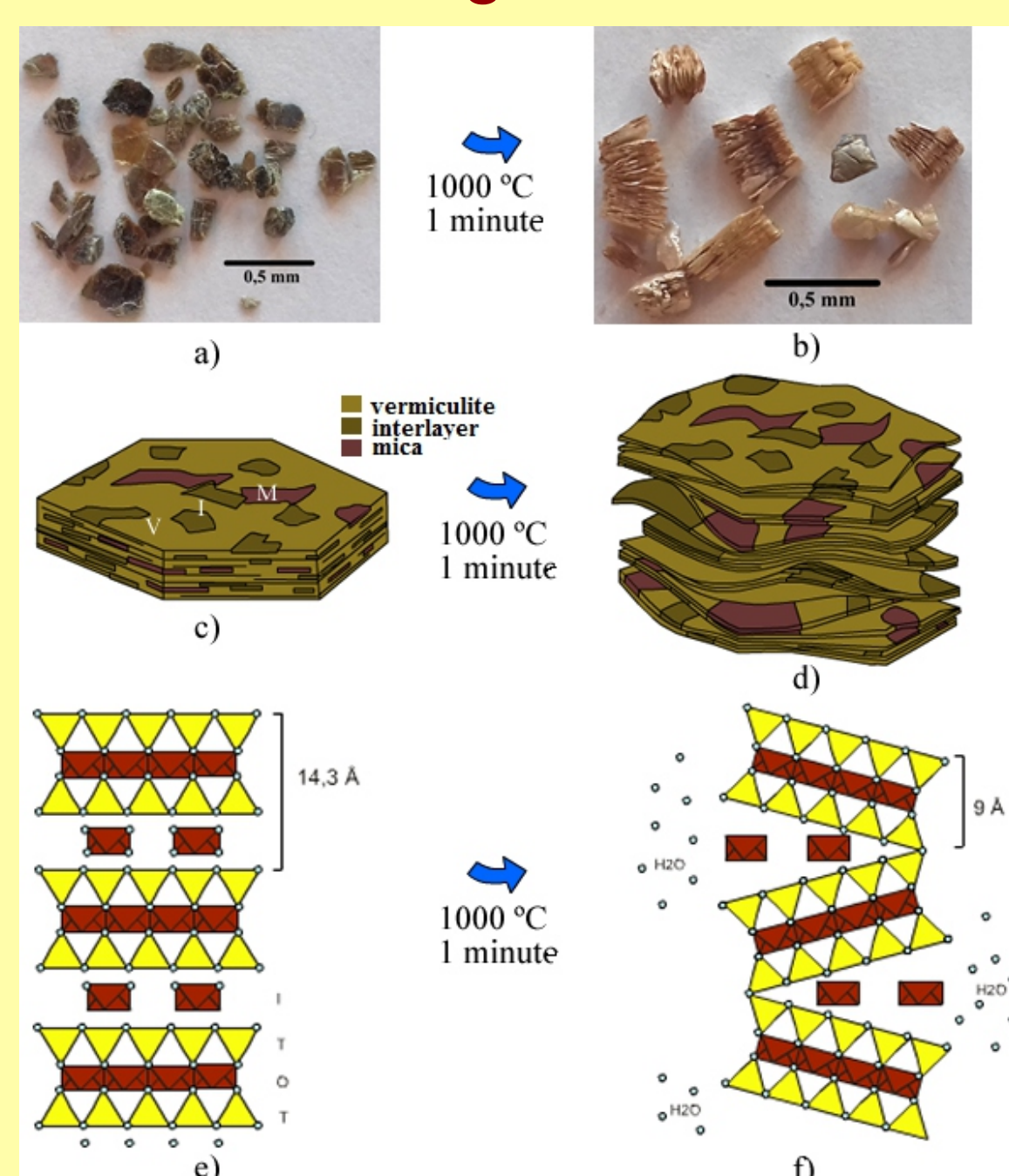

Fig. 1.- Vermiculite exfoliation: a) initial vermiculite, b) exfoliated vermiculite, c) single particle composition of initial vermiculite, d) single particle composition of exfoliated vermiculite, e) framework of initial vermiculite, f) framework of exfoliated vermiculite.

Samples were analyzed by X Ray Fluorescence (XRF), X- Ray Diffraction (XRD) and the solutions with Inductively Coupled Plasma Mass Spectrometry (ICP-MS) to quantify the adsorbed Cr^{6+} by the vermiculite. The adsorption of Cr^{6+} was studied by Langmuir, Freundlich and Dubinin-Kaganer-Radushkevich (DKR) isotherm models (their linearized form are shown in Table 1).

Langmuir	Freundlich	DKR
$1/q_e = 1/a + 1/(a\ b\ C_e)$	$\log q_e = \log k^f + 1/n \log C_e$	$\ln C_{ads} = \ln X_m - \beta \varepsilon^2$

Table 1.- linear equations used in the work to the study of adsorption.

Results and Discussion

Concerning the XRF analysis, the highest values of major elements were SiO_2, followed by MgO and Al_2O_3. The most important trace elements were Cr (1740 ppm) and Ba (2480 ppm).

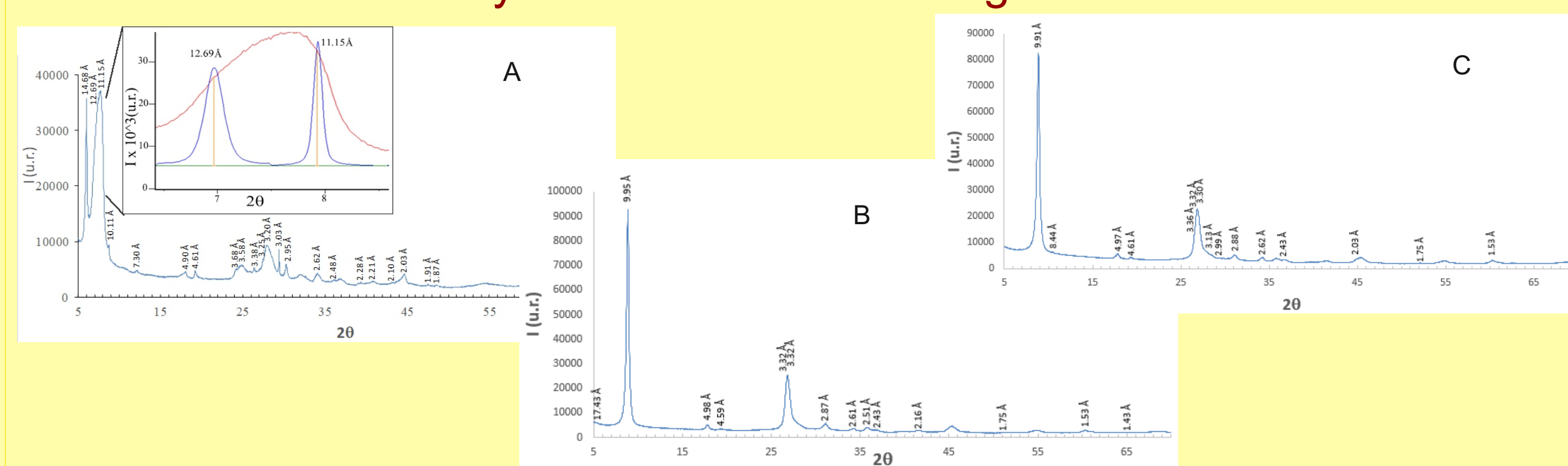The results of XRD analysis hare shown in the Fig. 2.

Fig. 2.- A) X-ray diffraction pattern shows the natural vermiculite with 4 phases (vermiculite with 2 and 1 layers of water at 14.68 Å and 11.15 Å; hydrobiotite at 12.69 Å; mica at 10.11 Å). B) X-ray diffraction pattern shows the exfoliated vermiculite that became a mica phlogopite. C) X-ray diffraction pattern shows the exfoliated vermiculite after the contact with the Cr^{6+} solution (1 ppm) and it's comparable with B).

Concerning the results from ICP-MS, the best adsorption was obtained with a contact time between 16 and 24 hours, 1 ppm of Cr^{6+} and 0.5 g of vermiculite. An interesting adsorption behavior was observed when the concentration of Cr^{6+} was varied while keeping constant the vermiculite mass and contact time (Fig. 3).
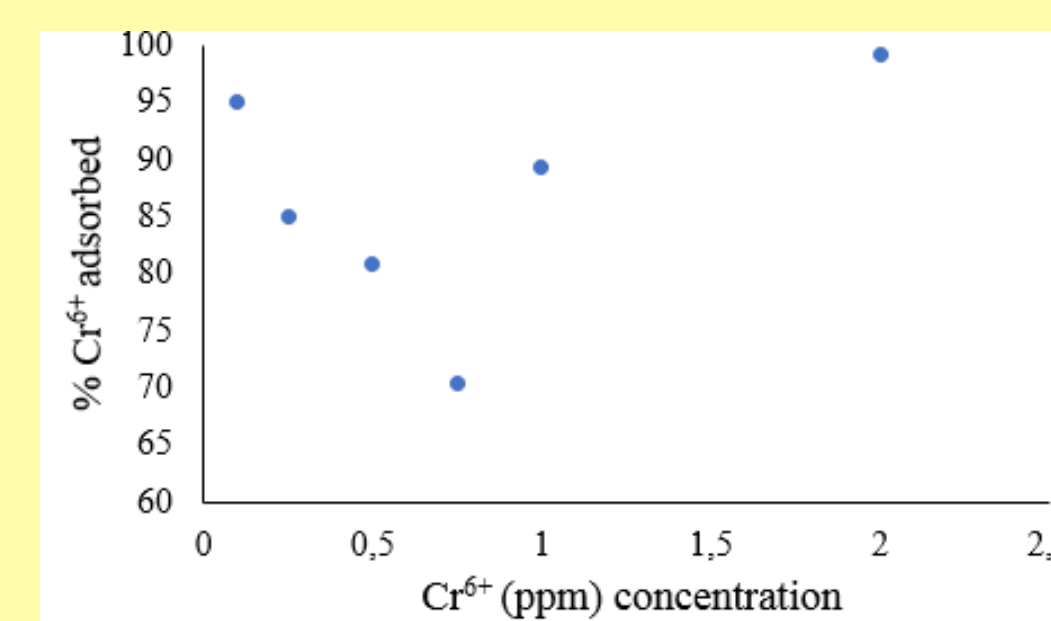

Fig. 3.- % of adsorbed Cr^{6+} in relation to its initial concentration in the solutions using 0.5 g of vermiculite and 24 hours of contact time.

The Cr^{6+} adsorbed rate depend on its initial concentration: at the beginning there were active sites that could be ocupied by Cr^{6+}; with higher initial concentrations, the adsorption rate decreased until the active sites weren't availables to the Cr^{6+} adsorption due to the saturation; finally the trend showed an inversion in the process, due to the active sites have released the adsorbed ions, so there were active sites availables to a new Cr^{6+} adsorption (increase in adsorbtion rate in the Fig. 3) .

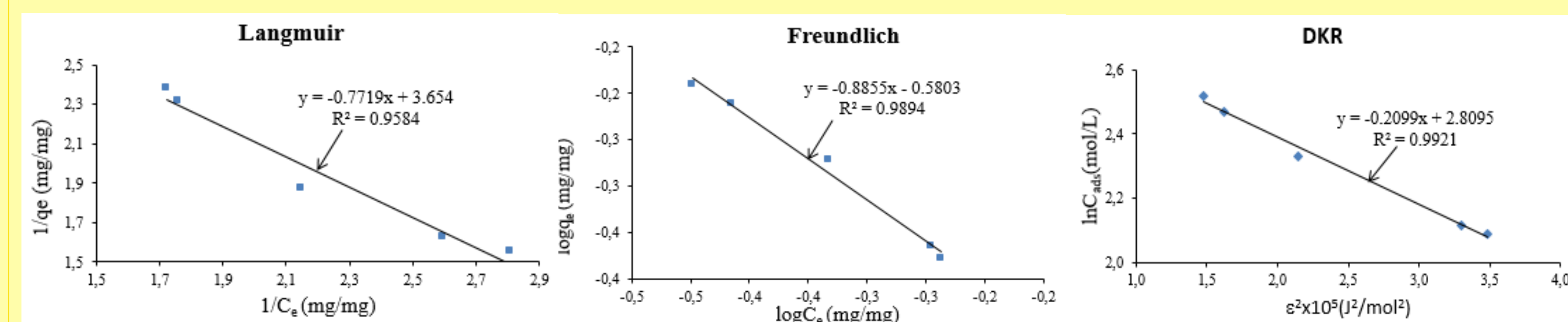The study of the mechanism of adsorption with the isotherm models is illustrated in Fig. 4.

Fig.4.- The Langmuir, Freundlich and DKR isotherm models gave a good correlation coefficient (R^2). The DKR model gave the best fit with the experimental data (R^2=0.9921).

The DKR model describes a cooperative adsorption: among these processes, the physical adsorption and ionic diffusion overcame in the present work the Cr^{6+} sorption.

Conclusions

The exfoliated vermiculite from China was a good Cr^{6+} adsorbent in water solutions.

The vermiculite mineral, after being heated at high temperatures, became a mica phlogopite but it showed no further transformations after the contact with Cr^{6+} solution due to the absence of hydration-dehydration processes.

The best sorption was obtained at 24 hours contact time, 1 ppm of Cr^{6+} and 0.5 g of vermiculite. The DKR isotherm model gave the best fit with the obtained results, describing the sorption process as a cooperative adsorption.