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ORIGINAL PAPER

# Separation of Cr(VI) from aqueous solutions by adsorption on the microfungus *Ustilago maydis*

**J. Serrano-Gómez · M. T. Olguín**

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**Abstract** Cr(VI) adsorption from aqueous solutions on the microfungus *Ustilago maydis* modified with formaldehyde (*Um*F) was studied as a function of the initial pH, contact time, chromium concentration and temperature. The pH results showed that Cr(VI) adsorption on *UmF* is higher at acidic pH values and decreases as the pH increases to alkaline values. Cr(VI) adsorption also depends on the chromium concentration and temperature. The Cr(VI) adsorption data as a function of concentration obey the Freundlich and Langmuir isotherms at pH values of 2 and 6.5. The maximum sorption capacity of *UmF* for Cr(VI) at pH 2 was $2.53 \times 10^{-3}$ mol/g (131.55 mg/g), which is significantly higher than that at pH 6.5 ($0.33 \times 10^{-3}$ mol/g or 17.60 mg/g). The negative value of ΔH° and the positive values of ΔG° indicate that the chromium adsorption process is exothermic and non-spontaneous. The pHpzc value was 5 for UmF and it played a role in the Cr(VI) adsorption.

**Keywords** Chromium · *Ustilago maydis* · Adsorption · Isotherms · Thermodynamic parameters

## Introduction

Over the last decades, the utilization and release of chemicals to the environment have significantly increased due to rapid worldwide industrialization (Gupta et al. 2013a, b). Among the released chemicals, heavy metals, such as Cr, Hg, Pb, Ni and Cd, constitute a major concern because they are toxic, even in very small quantities, and can be found in surface and underground water bodies. Chromium contamination can occur through waste discharges from leather tanning, paints and pigments, electroplating and finishing industries, among others. Chromium is found in aqueous systems in both the trivalent Cr(III) and hexavalent Cr(VI) forms, and Cr(VI) is significantly more toxic due to its high water solubility, high mobility and easy reduction. According to the United States Environmental Protection Agency, the content of chromium in effluents should be reduced to the allowable limit of 0.05 mg/L before the effluents are discharged to aqueous systems.

Chemical precipitation, ion exchange, reduction, solvent extraction and membrane separation are a few of the conventional methods utilized to remove heavy metals from industrial wastewater (Gupta et al. 2012). Furthermore, materials like activated carbon developed from waste rubber tires, porous carbon, carbon nanotubes and fullerenes have been investigated as adsorbents of pollutants from aqueous media (Gupta et al. 2011, 2013a; Gupta and Saleh 2013). Recently, because of the pursuit for less costly adsorbents that are more effective at small metal concentrations, biomasses, living and non-living have become widely used to search the separation of heavy metals from aqueous solution. Algae (Dziwulska and Bajguz 2004), fungi (Marandi 2011), bacteria (El-Zahrani and El-Saied 2011), yeast (Machado et al. 2008) and plants (Ucun et al. 2008) are among the investigated biological materials used as adsorbents to separate Cr(VI) from waste waters. Certain advantages of the biosorption process over conventional treatment methods are that biosorption is a non-polluting process because it does not produce chemical sludge, and it is more efficient and easy to operate. In the case of fungal

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biomass, removal of heavy metal ions from aqueous solutions has been investigated with strains of *Aspergillus niger* to separate $Cu^{2+}$, $Mn^{2+}$, $Zn^{2+}$, $Ni^{2+}$, $Fe^{3+}$, $Pb^{2+}$ and $Cd^{2+}$ (Tsekova et al. 2010); *Rhizopus Arrhizus* to remove $La^{3+}$, $Mn^{2+}$, $Cu^{2+}$, $Zn^{2+}$, $Cd^{2+}$, $Ba^{2+}$, $Hg^{2+}$, $Pb^{2+}$, $UO_2{}^{2+}$ and $Ag^{+}$ (Tobin et al. 1982); *Mucor rouxii to* adsorb $Pb^{2+}$, $Zn^{2+}$, $Cd^{2+}$ and $Ni^{2+}$ (Yan and Viraraghavan 2003); *Phanerochaete chrysosporium* for the adsorption of $Cd^{2+}$, $Pb^{2+}$ and $Cu^{2+}$ (Say et al. 2001); and *Amanita rubescens* for the sorption of $Pb^{2+}$ and $Cd^{2+}$ (Sari and Tuzen 2009), among others. Tewari et al. (2005) found that *Mucor hiemalis* exhibited the highest Cr(VI) uptake of 53.5 mg/g at an initial pH of 2 and a temperature of 50 °C. At this pH value, the negative chromate ions interact more strongly with the positively charged functional groups of the *M. hiemalis* biomass, resulting in a high Cr(VI) uptake. *Ustilago maydis* (ethnic name huitlacoche) is an edible corn smut fungus consumed in México and is currently internationally known as a delicacy. Studies on the *Ustilago maydis* biomass in the literature are related to the determination of its organic components (Lizárraga-Guerra and López 1996, 1998; Muñoz et al. 2005) but none are related to its use as an adsorbent of heavy metals. Hence, because the fungal biomasses mentioned above can also be investigated as adsorbents of toxic metals (substances), in this paper the sorption behavior of Cr(VI) on the *U. maydis* biomass, the maize mushroom, was investigated as a function of pH, contact time, chromium concentration and temperature.

## Materials and methods

### Formaldehyde-modified *Ustilago maydis*

The raw *U. maydis* biomass was collected from a local market in México City and dried for several days at room temperature. Then, it was crushed in an agatha mortar and sieved to the desired particle size (25 mesh). The nonliving *U. maydis* biomass was washed several times with a 0.2 % formaldehyde aqueous solution until the solution ran clear. The obtained formaldehyde-modified material was referred as to *Um*F. It is important to mention that formaldehyde was used to prevent the organic leaching from the non-living biomass after the chromium adsorption processes (Chen and Yang 2005; Nadeau and Carlson 2007).

### Effect of the initial pH

Samples of *Um*F (100 mg) were shaken for 24 h in separate glass vials with 10 mL of 25 ppm Cr ($K_2CrO_4$) aqueous solution at pH values from 2 to 12 and at a temperature of 20 °C. After shaking, the suspension was centrifuged for phase separation. The liquid was recovered with a pipette, and the solid was discarded. The Cr content in the liquid was determined as described below. All of the experiments were performed in duplicate.

### Kinetics

The experimental conditions used to obtain the kinetics of the adsorption processes were similar to those previously described; however, in this case, the initial pH value of the Cr solution was maintained at 5.5, and the mixtures were shaken from 0.25 to 24 h. The experimental data were examined using a pseudo-second-order kinetic adsorption model.

### Isotherms

For the isotherm measurements, 100 mg of sample were mixed in glass vials with 10 mL of either a 50–500 ppm Cr solution or a 500–1,000 ppm Cr solution for 24 h at 20 °C with pH values of 6.5 and 2, respectively. Two separate vials were used for each Cr concentration. The Cr measurements were performed as described in Sect. 2.6. The experimental data were examined using the Freundlich and Langmuir adsorption models.

### Thermodynamics of the sorption

The effect of temperature on Cr(VI) adsorption on *Um*F was investigated by varying the temperature from 293 to 313 K, considering the contact of 100 mg of *Um*F with 10 mL of Cr(VI) solution (25 mg/L) for 24 h with a pH value of 5.5.

### Chromium determination

The chromium concentration was quantified in the remaining solutions using a UV–Vis spectrophotometer (Shimadzu, model 265) at a wavelength of 372 nm. For each experiment, a Cr calibration curve was obtained using standard Cr aqueous solutions.

### Characterization of *Um*F

#### *Scanning electron microscopy*

The unmodified and modified non-living biomasses were mounted directly onto sample holders for scanning electron microscopy. The images were observed at 20 keV with a Phillips XL30 electron microscope. Elemental chemical analyses of the materials were performed by energy X-ray dispersive spectroscopy (EDS) with a DX-4 probe.

### *IR spectroscopy*

Infrared (IR) spectra in the 4,000–400 $cm^{-1}$ range were recorded for the *Um*F samples before and after the Cr(VI) adsorption at pH 2 using a Nicolet Magna-IR 550 FTIR. The samples were prepared using the standard KBr pellet method.

### *The pH of the point of zero charge (pHpzc)*

The value of the pHpzc of the *Um*F adsorbent was determined using the modified pH drift method (Faria et al. 2004; Zaini et al. 2009; Ma et al. 2011), in which 0.15 g of *Um*F were mixed with 50 mL of 0.01 M NaCl at different initial pH values. The initial pH of the solution was adjusted between 2 and 12 by the addition of a 0.1 M HCl or 0.1 M NaOH solution. The suspensions were allowed to equilibrate for 48 h under agitation at 25 °C, and the final pH values were measured using a pH STAT Controller (MeterLab PHM 290). The pH of the point of zero charge corresponds to the pH at which the curve intersects the straight line that fits the points pHinitial = pHfinal.

## Results and discussion

### Effect of the initial pH

The pH value affects the surface charge of the adsorbent, determines the chemical species of the adsorbate in the solution and also determines the degree of ionization of those chemical species. Figure 1 shows the effect of the initial pH value on the adsorption of chromium on *Um*F. The removal of chromium decreases as the pH increases from 2 to 12. In addition, the percent removal value of the chromate ions is highest at pH 2. At this pH value and with 25 ppm Cr, the MEDUSA program (Puigdomenech) results indicated that $HCrO_4^-$ (approximately 99 %) and $H_2CrO_4$ (approximately 1.0 %) are the chromium chemical species present in the aqueous solutions, whereas at pH 4, the unique chemical species of chromium in the solution is the anion $HCrO_4^-$. At pH 6, two chromium chemical species are present in the aqueous solution, $HCrO_4^-$ (approximately 85 %) and $CrO_4^{2-}$ (approximately 15 %). At pH 8, these two chromium chemical species are also present in the solution with different percentages ($CrO_4^{2-}$ ions at 97 % and $HCrO_4^-$ ions at 3 %). Finally, at the pH values of 10 and 12, only $CrO_4^{2-}$ exists in the aqueous solutions. Thus, the anions $HCrO_4^-$ and $CrO_4^{2-}$ are the chemical species adsorbed by the *Um*F non-living biomass. At acidic pH values, the surface of the *Um*F material becomes positively charged because of the formation of the positive $-NH_3^+$ groups, resulting from the attachment of protons to the $-NH_2$ chemical groups present in the amino acids lysine, glycine, valine, leucine and glutamic acid, which are organic components of *U. maydis* (Lizárraga-Guerra and López 1996). Thus, the adsorption of chromium by *Um*F occurs through the electrostatic binding of the anions $HCrO_4^-$ and $CrO_4^{2-}$ to the positively charged $-NH_3^+$ groups. Lizárraga-Guerra and López (1998) have also determined the monosaccharide and alditol contents of *U. maydis*, and they found that glucose (143.2 mg/g) and fructose (71.10 mg/g) were the most abundant monosaccharides, whereas glycerol (8.5 mg/g), sorbitol (4.45 mg/g) and mannitol (3.17 mg/g) were the most abundant alditols. These monosaccharides and alditols contain $^-OH$ groups that can also be protonated in an acidic medium to form positively charged $^-OH_2^+$ groups, to which the anions $HCrO_4^-$ and $CrO_4^{2-}$ are also attached by an electrostatic attraction. These adsorption reactions are based on the finding that at low pH values, Cr(VI) adsorption increases, and at high pH values, Cr(VI) adsorption decreases (Saha and Orvig 2010) because of a decrease in the number of positive groups on *Um*F.

### Kinetics

The results of the Cr(VI) adsorption on *Um*F as a function of contact time are shown in Fig. 2. Cr(VI) uptake by *Um*F was rather slow, and the corresponding equilibrium was reached in approximately 20 h at pH 5.5.

To clarify the sorption kinetics of Cr(VI) on *Um*F, the experimental data were fitted to a pseudo-second-order model (Fig. 3), which has been applied in similar systems (Tewari et al. 2005; Ho et al. 2000). The pseudo-second-order kinetic model, developed by Ho and McKay (1999), is based on experimental data for solid-phase sorption and has generally been applied to heterogeneous systems in

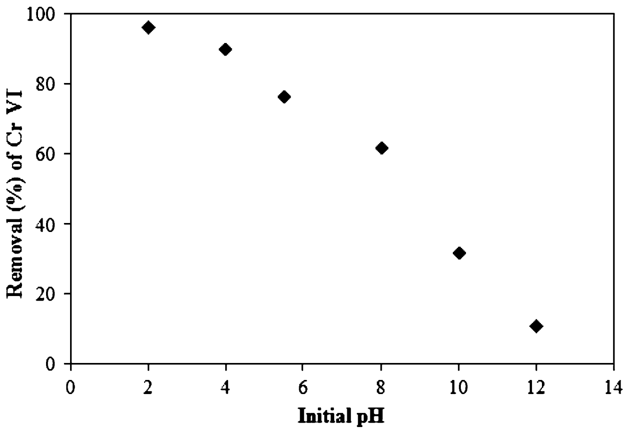

**Fig. 1** Effect of the initial pH of the aqueous solution on Cr(VI) removal by *Um*F

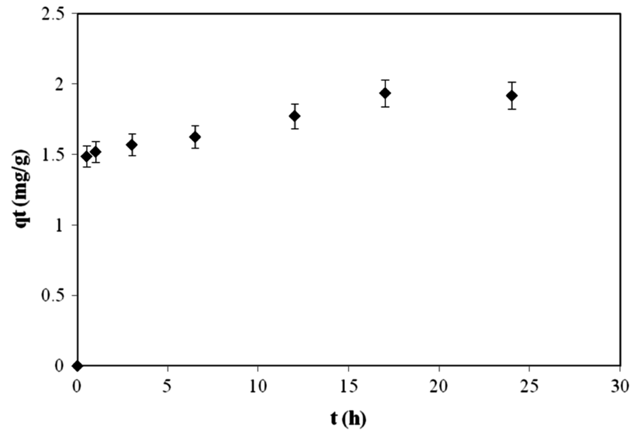

**Fig. 2** Sorption of Cr(VI) by *Um*F as a function of contact time. The pH of the Cr(VI) solution was 5.5

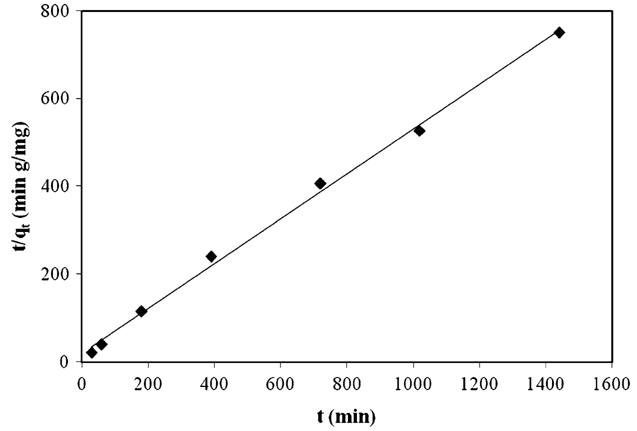

**Fig. 3** Sorption kinetics of Cr(VI) by *Um*F fitted to the pseudo-second-order model

which chemical sorption is the primary mechanism. The model is described with the following equation:

$$1/(q_\mathrm{e} - q_t) = 1/(q_\mathrm{e} + k_2 t) \tag{1}$$

Rearranging this equation to a linear form provides the following equation:

$$t/q_t = \left(1/k_2 q_\mathrm{e}^2\right) + t/q_\mathrm{e} \tag{2}$$

where $k_2$ (g/mg h) is the rate constant of the pseudo-second-order reaction, $q_t$ (mg/g) is the amount of Cr(VI) sorbed at time $t$, and $q_\mathrm{e}$ (mg/g) is the amount of Cr(VI) sorbed at equilibrium. The pseudo-second-order model assumes that chemisorption is the rate-limiting step, which involves valence forces from the sharing or exchange of electrons between the sorbent and the sorbate. Based on the determination coefficients ($R^2$), the experimental data fit the pseudo-second-order kinetics model better. According to the $q_\mathrm{e}$ values, *Um*F sorbs 1.95 mg/g from the aqueous solution. The parameter $k_2$, which corresponds to the rate constant of the pseudo-second-order model, is 0.0137 g/mg min, and the sorption rate (h) is 0.0523 mg/g min. Tewari et al. (2005) found that the sorption of Cr(VI) by *M. hiemalis* followed the pseudo-second-order kinetic model. Tewari et al. (2005) also found that with an initial concentration of 10 mg/L Cr(VI), the $q_\mathrm{e}$, $k_2$ and $h$ values were 7.7 mg/g, 0.0167 g/mg min and 0.9900 mg/g min, respectively. These values are 3.9, 1.2 and 18.9 times higher than those obtained in the present study. This result indicates that the characteristics of the non-living biomasses determine the sorption kinetics of Cr(VI).

## Isotherms

The effect of the chromium concentration on the adsorption of Cr(VI) by *Um*F was investigated using chromium solutions with pH values of approximately 6.5. However, when the effect of the initial pH was investigated, the optimum pH value for Cr(VI) adsorption on *Um*F was determined to be 2. Thus, the effect of the chromium concentration was also investigated by adjusting the pH of the aqueous solutions with HCl to that acidic value to compare the Cr(VI) adsorption capacities of *Um*F at the pH values of 2.0 and 6.5. Because of the Cr(VI) sorption was very high at pH 2, the following two chromium concentration intervals were used: 50–500 and 500–1,000 ppm with aqueous solution pH values of 6.5 and 2, respectively.

The capacity of an adsorbent can be surveyed by sorption isotherms, which are characterized by certain constants, and the values of these constants provide information about the surface properties of the adsorbent. The experimental data were fitted to the Freundlich and Langmuir isotherm models to describe the Cr(VI) adsorption behavior by *Um*F. In Figs. 4 and 5, the logarithm of the amount of Cr(VI) adsorbed at equilibrium ($q_\mathrm{e}$, mol/g) is plotted versus the logarithm of the Cr(VI) concentration in the residual solutions at equilibrium ($C_\mathrm{e}$ in mol/L) for the pH values 2 and 6.5, respectively. The obtained straight lines are described by the following linearized Freundlich equation:

$$\mathrm{Log}\, q_\mathrm{e} = (1/n)\ \log\ C_\mathrm{e} + \log K_\mathrm{F} \tag{3}$$

where $1/n$ and $K_\mathrm{F}$ are the Freundlich constants indicating the adsorption intensity and the adsorption capacity, respectively. From the slopes and intercepts of the plots, the numerical values of the Freundlich constants, i.e., $1/n$ and $K_\mathrm{F}$, were computed using the least square technique, and they changed with the pH value as follows: for pH 2, $1/n = 0.52$ and $K_\mathrm{F} = 2.4 \times 10^{-2}$ (mol/g) (L/mol)$^{1/n}$, and for pH 6.5, $1/n = 0.57$ and $K_\mathrm{F} = 4.66 \times 10^{-3}$ (mol/g) (L/mol)$^{1/n}$. In this work, the observed value of $1/n < 1$ in both cases (pH values 2 and 6.5) confirms that the Freundlich model is valid for the Cr(VI) adsorption on *Um*F, with

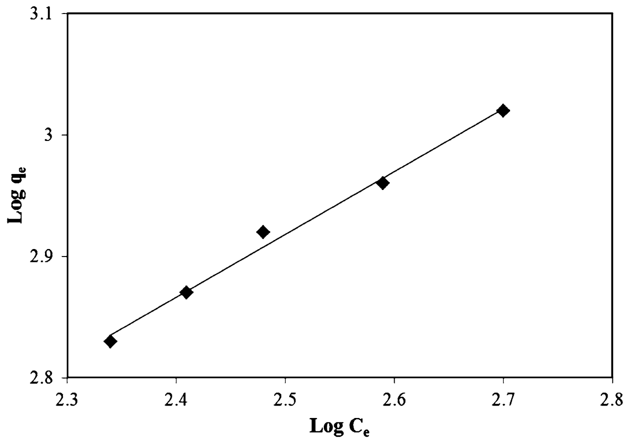

**Fig. 4** Sorption isotherm of Cr(VI) by UmF at pH 2.0 fitted to the Freundlich model

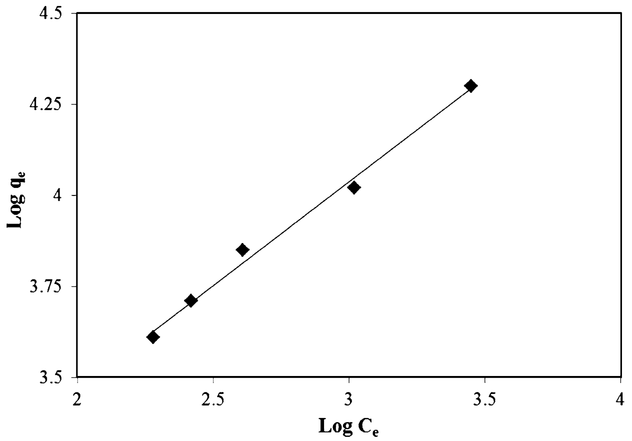

**Fig. 5** Sorption isotherm of Cr(VI) by *Um*F at pH 6.5 fitted to the Freundlich model

$R^2 = 0.9908$ for pH 2 and $R^2 = 0.992$ for pH 6.5. Furthermore, the $1/n$ constant values found in this study suggest that the adsorbent surface is heterogeneous with an exponential distribution of the active centers and that the adsorbed species have no appreciable interaction.

The Langmuir isotherm was also tested with the Cr(VI) adsorption data on *Um*F using its linearized form:

$$C_e/q_e = (1/K_L q_{max}) + (C_e/q_{max}) \tag{4}$$

where $C_e$ and $q_e$ were defined above, and $K_L$ and $q_{max}$ are the Langmuir constants, which are related to the adsorption energy and the maximum adsorption capacity, respectively. The Langmuir constants $K_L$ and $q_{max}$ were calculated for both pH values (2 and 6.5) from the intercepts and slopes of the plots of $C_e/q_e$ versus $C_e$, respectively. The values were found to be the following: for pH 2, $K_L = 299.61$ L/mol, $q_{max} = 2.53 \times 10^{-3}$ mol/g (131.55 mg/g), and $R^2 = 0.9782$, whereas for pH 6.5, $K_L = 466.82$ L/mol, $q_{max} = 0.33 \times 10^{-3}$ mol/g (17.6 mg/g), and $R^2 = 0.9649$. These values indicate that the maximum adsorption capacity for *Um*F by Cr(VI) at pH 2 is 8.5 times higher than that at pH 6.5, with a slightly higher $R^2$ value.

**Table 1** Maximum capacities of different fungus for chromium adsorption

| Fungus | $q_{max}$ (mg/g) | Experimental conditions | | Reference |
|---|---|---|---|---|
| | | pH | *T* (°C) | |
| *Aspergillus niger* | 117.33 | 1.0 | 50 | Khambhaty et al. (2009) |
| *Coriolus versicolor* (HT) | 62.89 | – | RT* | Sanghi et al. (2009) |
| *Mucor hiemalis* | 47.40 | 2.0 | 27 | Tewari et al. (2005) |
| *Penicillium* sp. | 35.97 | 2.0 | 40 | Zhang et al. (2011) |
| *Phanerochaete chrysosporium* (surface-modified) | 344.8 | 3.0 | 25 | Chen et al. (2011) |
| *Pleurotus ostreatus* | 10.75 | 2.5 | RT* | Javaid et al. (2011) |
| *Rhizopus arrhizus* | 78.00 | 2.0 | RT* | Aksu and Balibek (2007) |
| *Rhizopus nigricans* | 38.76 | 2.0 | RT* | Bai and Abraham (2002) |
| *Ustilago maydis* | 131.55 | 2.0 | 20 | Present work |

*RT** room temperature

A comparison was made between the Cr(VI) maximum adsorption capacity of *U. maydis* found in this study and the corresponding values of other fungal materials, such as *A. niger*, *Coriolus versicolor* (HT), *M. hiemalis*, *Penicillium* sp., polyethylenimine (PEI)-modified *P. chrysosporium*, the macrofungus *Pleurotus ostreatus*, *R. arrhizus* and *Rhizopus nigricans*. It can be observed in Table 1 that *U. maydis* at pH 2 shows a high maximum Cr(VI) adsorption capacity and the best performance because the corresponding $q_{max}$ was obtained at 20 °C and no surface modification was done.

## Thermodynamics of the sorption

It was found that the amount of Cr(VI) adsorbed at equilibrium at various temperatures decreases with increasing temperature from 303 to 333 K. The thermodynamic parameters of standard enthalpy (ΔH°), standard entropy (ΔS°) and Gibbs free energy (ΔG°) for the adsorption of Cr(VI) on *Um*F were calculated using the equilibrium constant, $K_c$ (Ucun et al. 2008):

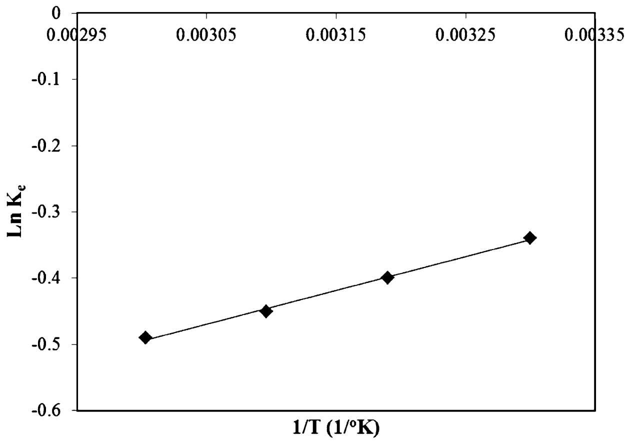

**Fig. 6** Log $K_c$ as a function of 1/*T* for the Cr(VI) sorption by *Um*F

$$K_c = q_e / C_e \tag{5}$$

where $q_e$ and $C_e$ have the same meaning as in Eqs. 3 and 4. Thus, ΔH° and ΔS° were obtained from the slope and intercept of the van't Hoff plots (ln $K_c$ vs. $1/T$), as displayed in Fig. 6:

The van't Hoff equation in its linearized form is:

$$\ln K_c = (-\Delta H^\circ / 2.303RT) + \Delta S^\circ / 2.303R \tag{6}$$

where *T* is the absolute temperature in degrees Kelvin, and the gas constant is $R = 8.3143$ kJ/Kmol.

The adsorption standard free energy changes (ΔG°) can be calculated according to Eq. 7:

$$\Delta G^\circ = -RT \ln K_c \tag{7}$$

Table 2 shows the thermodynamic parameters of the chromate ion adsorption process. The values of ΔH° and ΔS° obtained using Eq. 6 were found to be −9,736.7 kJ/mol and −38.68 J/K mol, respectively. The negative value of ΔH° shows that the Cr(VI) sorption process is exothermic. The negative value of ΔS° suggests the decreasing randomness at the solid/liquid interface (Tewari et al. 2005) during the sorption of Cr(VI) on *Um*F. The values of ΔG° obtained at 303, 313, 323 and 323 K are all positive, which indicates that the adsorption process involved in the Cr(VI) sorption on *Um*F is not spontaneous. The increase in the change of ΔG° with the rise in temperature indicates that a better adsorption is obtained at a lower temperature.

**Table 2** Thermodynamic parameters for the adsorption of Cr(VI) by *UmF*

| *T* (K) | Equilibrium constant ($K_c$) | ΔH° kJ mol$^{-1}$ | ΔS° kJK$^{-1}$ mol$^{-1}$ | ΔG° KJ mol$^{-1}$ |
|---|---|---|---|---|
| 303 | 0.7117 | −9,745.1450 | −38.6846 | 856.54 |
| 313 | 0.6703 | | | 1040.96 |
| 323 | 0.6353 | | | 1208.49 |
| 333 | 0.6143 | | | 1356.65 |

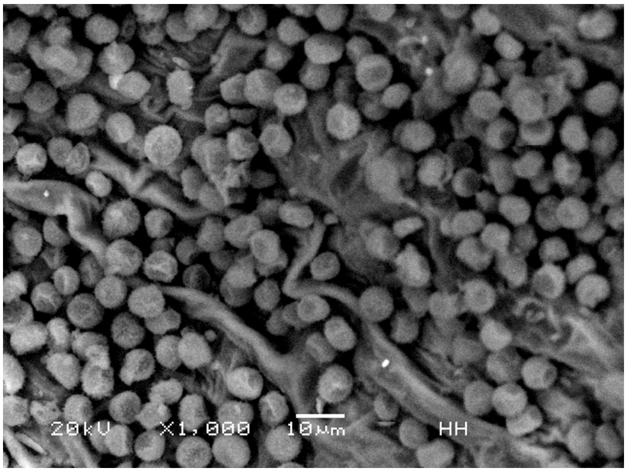

**Fig. 7** SEM image of *Um* modified with formaldehyde

## Characterization of *Ustilago maydis*

### *Scanning electron microscopy*

Figure 7 shows the images of *Um*F$_{(b)}$ before performing the chromate ion adsorption. As can be observed in this figure, the microfungus *U. maydis* is made up of very small spheres with diameters of approximately 8 µm, and no changes were observed after the contact of *Um*F$_{(b)}$ with the Cr(VI) aqueous solution at pH 2 (*Um*F$_{(a)}$). The elemental composition, as found by the EDS analyses of *Um*F$_{(b)}$, was the following: $C = 43.58 \pm 2.0$ wt%, $N = 22.58 \pm 1.6$ wt%, $O = 32.87 \pm 0.20$ wt%, $\mathrm{Cl} = 0.42 \pm 0.14$ wt% and $\mathrm{Ca} = 0.56 \pm 0.08$ wt%. For *Um*F$_{(a)}$, in addition to the elements detected in *Um*F$_{(b)}$, Cr was also observed, and the elemental composition was found to be the following: $C = 42.99 \pm 0.06$ wt%, $N = 21.07 \pm 0.06$ wt%, $O = 35.33 \pm 0.01$ wt%, $\mathrm{Ca} = 0.10 \pm 0.01$ wt% and $\mathrm{Cr} = 0.51 \pm 0.01$ wt%.

### *IR spectroscopy*

The *Ustilago maydis* modified with formaldehyde (*Um*F) shows a characteristic fungus IR spectrum (Fig. 8a); therefore, the C–H (2,000–2,800 cm$^{-1}$), ester C=O (1,740 cm$^{-1}$), amide O=C–N– (1,700–1,490 cm$^{-1}$) and C–O groups (1,140–930 cm$^{-1}$) are observed. After the Cr(VI) adsorption process at pH 2, other bands were found only between 1,000 and 400 cm$^{-1}$ in the IR spectra of *Um*F-Cr (Fig. 8b), and they were assigned to the principal bands of

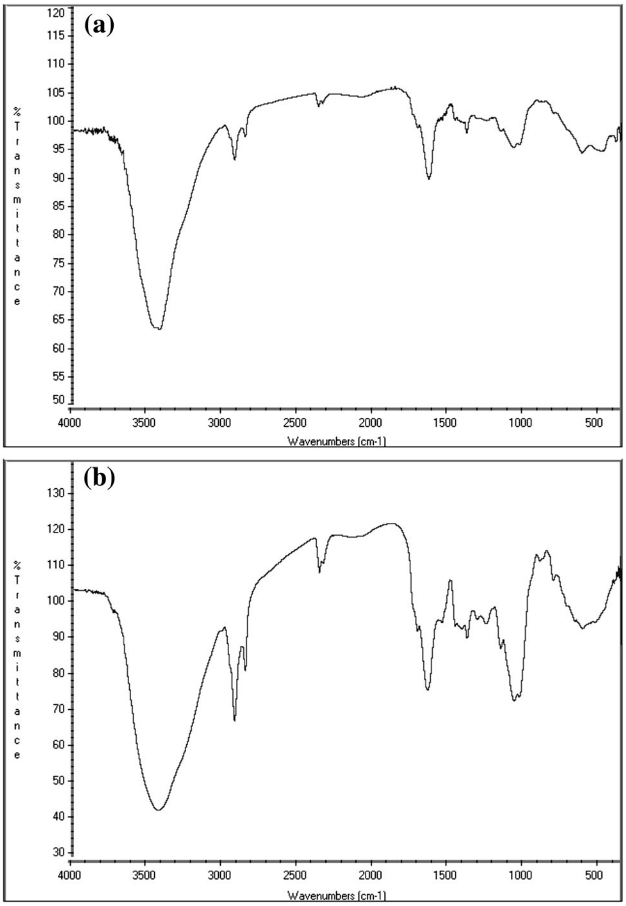

**Fig. 8** IR spectra of **a** *Um*F before Cr(VI) sorption and **b** *Um*F after Cr(VI) sorption (*Um*F-Cr) at pH 2

$CrO_4^{2-}$ at 733, 871 and 928 $cm^{-1}$ (Malherbe and Besse 2000); thus, no degradation of the *Um*F was observed (Table 2).

### *The pH value of the point of zero charge (pHpzc)*

The pHpzc value is an important indicator of the net surface charge and the preference for the ionic species for a sorbent. Using the modified drift method, the graphs of the final pH versus the initial pH were obtained for *Um*F, as shown in Fig. 9.

The pH of the point of zero charge, pHpzc, is the pH at which the curve intersects the straight line that fits the points pHinitial = pHfinal (Lopez-Ramon et al. 1999). Therefore, the pHpzc value is 5 for *Um*F. When the pH is lower than 5, the material has positively charged sites and sorbs anions, and when the pH is higher than 5, the surface has negatively charged sites and predominantly sorbs cations. For *Um*F, when the pH is lower than 5 (Fig. 9), the surface has positively charged sites and sorbs anions in a higher percentage. Thus, this material sorbs $HCrO_4^{-}$ or $CrO_4^{2-}$ preferentially at pH 2 rather than at pH 6.5.

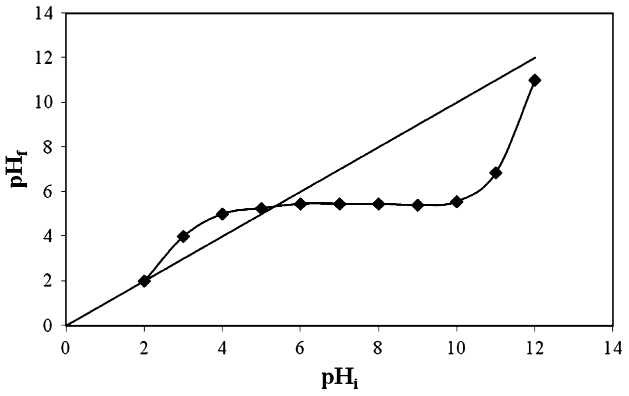

**Fig. 9** pH value of the point of zero charge for *Um*F

## Conclusion

The chromium adsorption on *U. maydis* modified with formaldehyde (*UmF*) strongly depends on the pH value. At pH 2, the Cr(VI) adsorption is the highest and then decreases as the pH rises to alkaline pH values. The Cr(VI) adsorption equilibrium was reached in approximately 20 h, and the experimental data fitted well with the pseudo-second-order model. The chromium (VI) initial concentration and temperature affected the chromate adsorption. Experimental adsorption isotherms of Cr(VI) on *UmF* fit Freundlich and Langmuir isotherms at pH values of 2 and 6.5. The $q_{max}$ value was found to be $2.53 \times 10^{-3}$ mol/g (131.55 mg/g) at pH 2 and 20 °C. The temperature influence on the Cr(VI) adsorption by *UmF* indicated an exothermic and non-spontaneous sorption process. The microfungus formaldehyde-modified *U. maydis* consists of very small spheres with diameters of approximately 8 µm. The presence of Cr was found in the *Um*F sample after contact with Cr(VI) solution.

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**Conflict of interest** The authors declare that they have no conflict of interest.

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