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Chromium(VI) sorption from dilute aqueous solutions using wool

Nilgün Balkaya[a]*, Nilden Bektas[b]

[a]*Department of Environmental Engineering, Faculty of Engineering, Istanbul University, 34320 Avcilar-Istanbul, Turkey*
Tel: +90 212 473 70 70/17643; Fax: +90 212 473 71 80; email: nbalkaya@istanbul.edu.tr
[b]*Department of Environmental Engineering, Faculty of Engineering, Ondokuz Mayıs University, 55139 Kurupelit-Samsun, Turkey*

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ABSTRACT

Removal of chromium(VI) from a dilute aqueous solution was investigated using the sorption technique. Locally available wool from merino sheep was used as an sorbent for the removal of chromium(VI). The influence of operating parameters such as sorbent amount, contact time, pH and initial metal concentration in solution on the sorption capacity were studied in a batch system. Optimum conditions for sorption were determined as wool amount, 50 g L^{-1}; pH 2; and contact time, 20 min. It was seen that when initial metal concentration in solution was increased, the uptake of Cr(VI) increased. Chromium(VI) sorption for different types of wool was also examined. Kinetic data were processed using the intraparticle diffusion model. The results suggest that the Cr(VI) uptake process seems to be controlled by external mass transfer at earlier stages and by intraparticle diffusion at later stages.

Keywords: Wool; Chromium(VI); Sorption; Kinetics; Isotherm

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1. Introduction

Heavy metals can be present at low concentrations in contaminated water sources and some industrial effluents. Removal of heavy metals at low concentrations from aqueous environment is generally difficult. In very low metal concentrations, processes such as chemical precipitation are not adequate and sufficient. Sorption using activated carbon is an effective method for the removal or reduction of heavy metals from wastewaters. However, the process is generally expensive [1].

Therefore, various materials have been recently investigated as alternative sorbents for activated carbon in heavy metal removal from aqueous solutions. It was reported that low cost abundantly available materials such as soya cake [2], bagasse and fly ash [3], *Fagus orientalis L.* [4], bacterial biofilm supported on zeolite [5],treated pine sawdust [6], and fly ash [7] were potentially useful in the removal of Cr(VI) ions from aqueous solution.

Up to now, researchers have studied the sorption of metals by wool, a polypeptide loose fibre, as a low-cost sorbent [8–14]. However, as far as we can find in the literature, they did not consider the sorption of Cr(VI) for water treatment purposes. Bektas and Balkaya [15], Balkaya [16], and Daikiky et al. [17] studied Cr(VI) sorption from aqueous solution using kıvırcık wool [15], wool from merino sheep [16], and wool from sheep [17], respectively. In these studies on Cr(VI) sorption, wool samples were also not subjected to any kind of pretreatment such as soxhlet extraction, modification by polyethylenimine etc., following the procedure performed by the other researchers who studied metal removal using wool.

In this study, the performance of locally available wool fibres for Cr(VI) sorption from wastewaters including low Cr(VI) concentrations such as paint manufacturing was evaluated. In batch sorption experiments, the influence on

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*Corresponding author.

Cr(VI) sorption of sorbent amount, contact time, pH and initial Cr(VI) concentration is investigated by using wool from merino sheep. The different types of locally available wool on Cr(VI) sorption was also studied. The preliminary experimental data of kinetic study were fitted using the intraparticle diffusion model.

In the previous study carried out by Balkaya [16] on Cr(VI) sorption from dilute aqueous solution using wool from merino sheep, the linear Langmuir and Freundlich models were applied to describe equilibrium isotherms. The first- and second-order reaction rate constants were calculated. Also, under laboratory conditions, a study was made to determine whether the parameters which were more easily measured, such as pH, conductivity and potential values, could be used instead of Cr(VI) concentration to indicate treatment efficiency in a treatment plant where a Cr(VI) removal process by wool will be used. The previous study mentioned above can be considered as the first part of this study. In the present work, Cr(VI) sorption by wool from merino sheep was investigated in more detail.

2.. Materials and methods

2.1. Wool

Locally available wool in loose form from merino sheep, goats and lambs used in this study was obtained from a commercial firm. The wool samples were first cleaned by hand to remove animal and plant debris, washed carefully with detergent for the removal of the lipid layer, and then rinsed with tap water. They were dried at 25°C for 24 h. The wool samples were not subjected to any pretreatment, except for washing with detergent. Before use, they were not sized to any long fibres.

2.2. Chemicals

The chemicals used were of analytical reagent grade. One hundred milligrams per litre Cr(VI) stock solution was prepared by dissolving anhydrous $K_2Cr_2O_7$ in deionised water. Different initial concentrations of Cr(VI) solutions were prepared by proper dilution from stock Cr(VI) standard.

2.3. Sorption experiments

Batch sorption experiments were carried out at room temperature by shaking the mixture wool–Cr(VI) solution in Erlenmeyer flasks at 100 rpm using a horizontal bench shaker (Nüve SL-350) throughout the contact time. Before the experiments, dry wool samples were swollen by immersion in 100 mL distilled water for a few min. After carefully blotting excess water between two filter papers [10,12], the wetted wool samples were put into 250 mL Erlenmeyer flasks containing 100 mL of the test solutions. As stated above, the effect of sorbent amount, contact time, pH and initial Cr(VI) concentration on Cr(VI) sorption was investigated. In the experimental studies, the sorbent amount was varied from 5 to 130 g L^{-1}, the contact time from 5 to 90 min, pH from 1.0 to 5.0 and initial Cr(VI) concentration from 0.1 to 0.9 mg L^{-1}.

The Cr(VI) contents in the aqueous solutions were determined spectrophotometrically at 540 nm using diphenyl carbazide as the complexing agent [18]. The pH of the solutions was adjusted to the required value with 0.1 mol L^{-1} HNO_3 or 0.1 mol L^{-1} NaOH solutions where it was necessary.

Each cycle of the sorption test run was repeated at least twice to ensure the accuracy of the test data collected. The mean values are presented below. The standard deviations did not exceed 5% of the respective means.

3. Results and discussion

The sorption of Cr(VI) from dilute aqueous solution on the wool was examined as a function of sorbent amount, contact time, pH, initial metal concentration and types of sorbent.

3.1. Effect of sorbent amount

Firstly, the effect of sorbent amount on Cr(VI) sorption was searched. As seen from Fig. 1a and b, while Cr(VI) removal (%) was increasing with increase in sorbent amount, Cr(VI) sorption decreased with increase in sorbent amount. The decrease in amount of Cr(VI) sorbed (mg g^{-1}) with increasing wool amount is because of the split in the flux or the concentration gradient between solute concentration in the solution and the solute concentration in the surface of the sorbent [19]. This decrease may also be attributed to the electrostatic interactions, interference between binding sites, or reduced mixing at higher sorbent densities [20–22].

3.2. Effect of contact time

The effect of contact time on the amount of Cr(VI) sorbed is shown in Fig. 2 where the majority of Cr(VI) ions are sorbed in the first 5 min. When the contact time was increased, the Cr(VI) uptake increased. This can be explained by the affinity of the support towards Cr(VI) [23].

3.3. Sorption kinetics

The mechanisms involved in the sorption process can be identified by fitting the experimental data in an

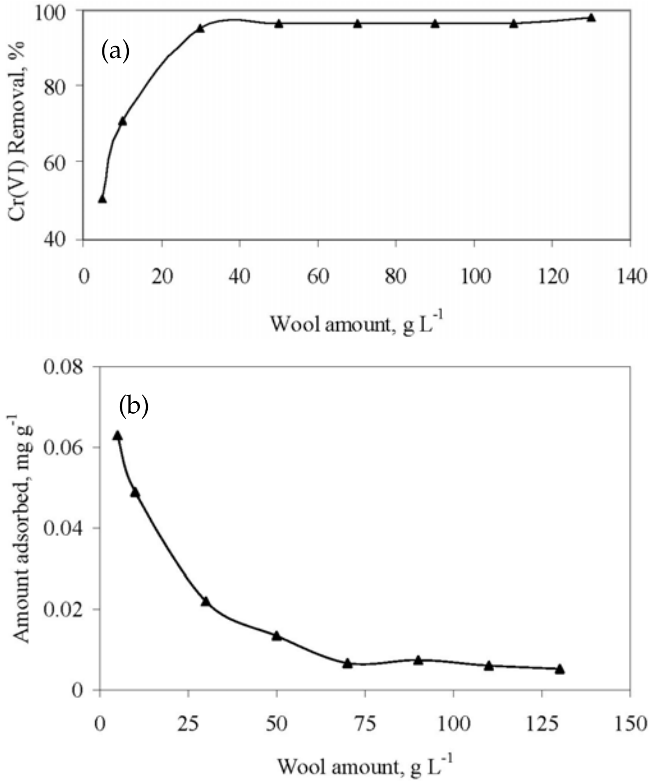

Fig. 1. Effect of wool amount on Cr(VI) removal (initial Cr(VI) concentration: 0.70 mg L^{-1}; initial pH: 1.0; contact time: 45 min). (a) Cr(VI) removal (%) vs. wool amount; (b) metal uptake (mg g^{-1}) vs. wool amount.

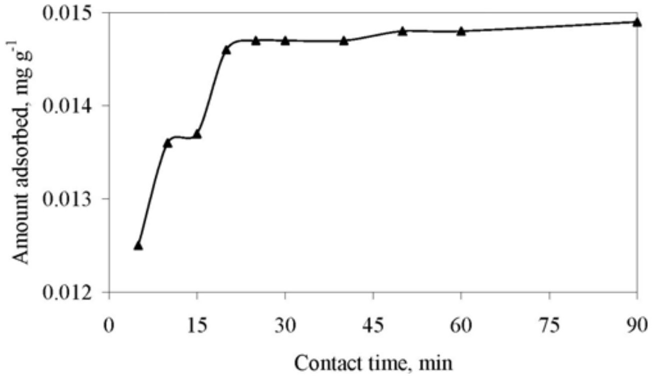

Fig. 2. Effect of contact time on Cr(VI) removal (initial Cr(VI) concentration: 0.80 mg L^{-1}; pH: 0.9; wool amount: 50 g L^{-1}).

intraparticle diffusion plot. This is the most commonly used technique [19]. In the present paper, the kinetic of sorption of Cr(VI) ions onto the wool was studied by using intraparticle diffusion equation.

The rate parameter (K_i) for intraparticle diffusion is defined as follows [24–26]:

$$q = K_i t^{1/2} \tag{1}$$

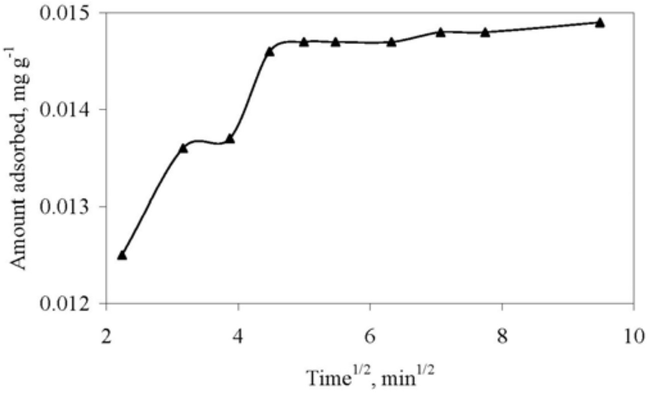

Fig. 3. Plot of q vs. $t^{1/2}$ for initial diffusion rate parameter (initial Cr(VI) concentration: 0.80 mg L^{-1}; pH: 0.9; wool amount: 50 g L^{-1}).

where K_i is the intraparticle diffusion rate coefficient (mg g^{-1} $min^{-1/2}$).

To determine the intraparticle diffusion coefficient (K_i), q was fitted against $t^{1/2}$ (Fig. 3). As can be seen from Fig. 3, the plot of this figure is of a double nature, an initial curved portion followed by a linear portion and plateau. A similar result has been interpreted for sorption of Cr(VI) on chitin by Sag and Aktay [27], *Microcystis* by Singh et al. [25], and synthetic hydrous stannic oxide by Goswami and Ghosh [28].

As pointed out by Singh et al. [25], Vadivelan and Kumar [19] and Singh et al. [29], a double nature of the plot suggests that the sorption process proceeds by surface sorption and intraparticle diffusion. The initial curved portion is attributed to the boundary layer effect. The final linear portion is attributed to the intraparticle or pore diffusion. The slope of the second linear portion of the plot has been defined as the intraparticle diffusion parameter K_i (mg g^{-1} $min^{-1/2}$). On the other hand, the intercept of the plot reflects the boundary layer effect. If the intercept is large, the contribution of the surface sorption in the rate-limiting step will be greater. The intraparticle diffusion coefficient (K_i) value was calculated as 5×10^{-5} mg g^{-1} $min^{-1/2}$.

The kinetic data were further analyzed using the Boyd kinetic expression in order to predict the actual slow step involved. This kinetic expression predicts the actual slowest step involved in the sorption process for different sorbent sorbate systems [19]. The Boyd kinetic expression is given by Boyd et al. [30]:

$$F = 1 - \left(6/\pi^2\right)\exp(-Bt) \tag{2}$$

and

$$F = q/q_0 \tag{3}$$

where q_0 is the amount of Cr(VI) sorbed at infinite time (mg g^{-1}) and *q* represents the amount of Cr(VI) sorbed at any time *t* (min), *F* represents the fraction of solute sorbed at any time *t*, and *Bt* is a mathematical function of *F*.

Substituting Eq. (3) in (2), Eq (2) simplifies to:

$$1-F=\left(6/\pi^2\right)\exp(-Bt) \tag{4}$$

or

$$Bt=-0.4977-\ln(1-F) \tag{5}$$

The *Bt* values at different contact times can be calculated using Eq. (5). The calculated *Bt* values were plotted against time (*t*) as shown in Fig. 4. The linearity test of *Bt* vs. *t* plot was employed. It was observed that the *Bt* vs. *t* plot was not linear and did not pass through the origin. In this work, the external mass transfer was not calculated. However, it may be concluded that according to the findings obtained from Fig. 4, the external mass transfer process can mainly govern the sorption process [19,30–34].

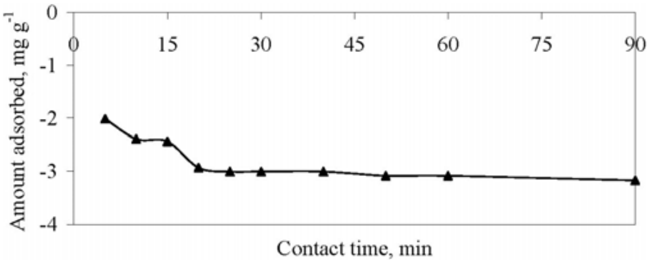

Fig. 4. Plot of *Bt* vs. *t* (Boyd plot) (initial Cr(VI) concentration: 0.80 mg L^{-1}; pH: 0.9; wool amount: 50 g L^{-1}).

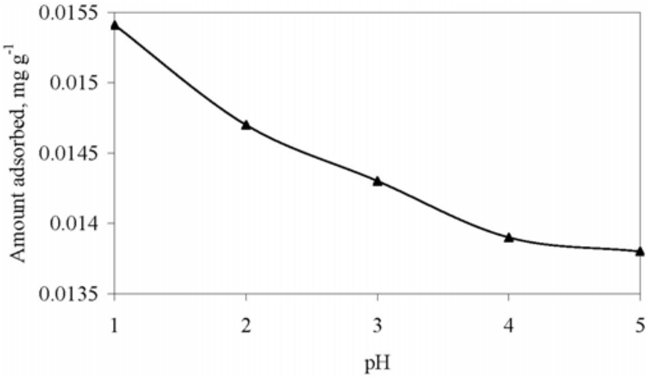

Fig. 5. Effect of initial pH on Cr(VI) removal (initial Cr(VI) concentration: 0.80 mg L^{-1}; wool amount: 50 g L^{-1}; contact time: 20 min).

3.4. Effect of pH

The range from pH 1.0 to 5.0 was used in this study. In Fig. 5, the effect of initial pH on the sorption of Cr(VI) is presented. The amount of Cr(VI) sorbed increased as the initial pH of the solution decreased. This result is consistent with the finding of Dakiky et al. [17] on Cr(VI) removal by wool from sheep. They revealed that wool has a high sorption capacity in acidic medium and the optimum pH for removal was found to be 2. Also, various sorbents such as Sphagnum moss peat [35], *Cladophora crispata* [36], phosphate-treated sawdust [37], hazelnut shell [38], dried anaerobic activated sludge [39], activated carbon [40], coal [41], persimmon tannin gel [42], Fe-modified steam exploded wheat straw [43], activated alumina and activated charcoal [44], *Tamarindus indica* seeds [45], eucalyptus bark [46], Turkish brown coals [47], pine needle [48], olive oil industry waste [49], modified rice husk [50], *Hevea brasilinesis* sawdust activated carbon [51], agricultural waste biomass [52], immobilized cyanobacterium [53] and treated pine sawdust [6] have exhibited a high sorption capacity in an acidic medium for Cr(VI) ion. A pH of 2 was the optimum value for these sorbents.

In basic solutions above pH 6.0, the predominant species is CrO_4^{2-}. Between pH 2.0 and 6.0, $HCrO_4^-$ and $Cr_2O_7^{2-}$ are present in equilibrium. At pH <1.0 the main species is H_2CrO_4. At pH 2.0, the sorbent surfaces are highly protonated, which favour the uptake of Cr(VI) in the predominant anionic form ($HCrO_4^-$) [54].

Wool is a protein-based animal fibre, with many amino and carboxylic groups that are potential binding sites for metal cations [17]. It can be said that at pH values up to 5.0, due to deprotonation of carboxylic groups, the wool fibres build up an increasing negative charge accompanied with a concomitant repulsion towards the Cr(VI) ions [16]. This behaviour is specific for the chromium ions and it is different for the divalent metals. Chromium ions release hydroxide ions to the solution instead of proton [55]. At low pH, the active sites on the wool fibres are beared an overall positive charge. Thus, the anionic Cr(VI) ions are electrostatically attracted by these sites [6,16, 50,53].

At lower pH values the attraction between the functional groups of the wool and anionic chromium ions gets stronger because of higher protonation extent of active sites [27]. The protonated sites are likely to have taken part in the sorption process, as revealed by Laurie and Barrachlough [11] for anionic $HgCl_3^-$ and $HgCl_4^{2-}$ and Tabak and Afsin [56] for ammonia and pyridine species. These sites possibly induce the hydrogenation of negative regions of the related species on the wool surface.

Also, it can be said that the efficient sorption of Cr(VI) by the wool at very low pH values may be due to the ion exchange mechanism. During the sorption process, probably one of the carboxylate, amine, amide groups may be exchanged with Cr(VI) ions. It can be said that increase in pH during the Cr(VI) sorption as stated by Balkaya [16] seems prove to this conclusion.

3.5. Effect of initial Cr(VI) concentration

The effect of initial Cr(VI) concentration on the sorption of Cr(VI) was studied by treating 5 g wool with 100 mL of Cr(VI) solution for 20 min at pH 2.0. Experimental studies were carried out at Cr(VI) concentrations of 0.1 to 0.9 mg L^{-1}, since these concentrations are known as the minimum Cr(VI) concentration range in paint manufacturing wastewaters. These concentrations can also be found in the some other industrial effluents and contaminated water sources. Paint manufacturing wastewaters contain Cr(VI) in a concentration range of 0.4 to 7.5 mg L^{-1} [57]. It was seen that increasing the initial metal concentration resulted in an increase in the amount of Cr(VI) sorbed from solution (Fig. 6).

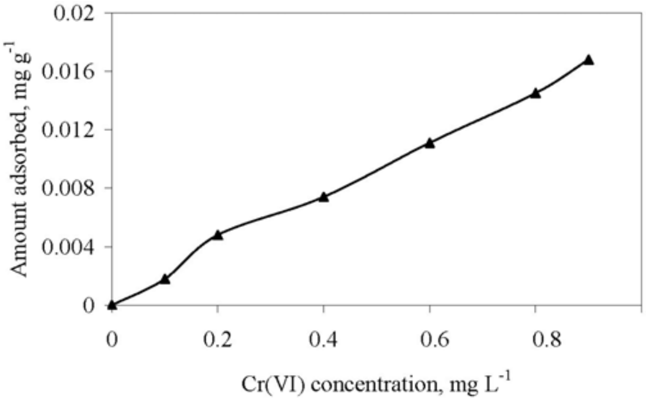

Fig. 6. Effect of initial Cr(VI) concentrations on Cr(VI) removal (wool amount: 50 g L^{-1}; initial pH: 2.0; contact time: 20 min).

3.6. Cr(VI) uptake depending on kind of fibre

The morphological structure of wool fibres (cuticle, ortho and para cortex, medulla) and functional groups in wool keratin exhibits differences from each other [12]. Since the interaction between fibre and metal depends on the kind of fibre and its chemical nature in addition to the kind of metal and its valence state, the solution concentration, pH, time, temperature, etc. [12,14]; in the laboratory-scale studies, the variation of Cr(VI) removal for different kinds of wool, respectively two kinds of wool from merino sheep, wool from lamb and wool from goats were investigated. As illustrated in Fig. 7, the Cr(VI) removal (%) obtained by wool from goat was higher than that obtained by the other wool samples. It can be said that Cr(VI) uptake by wool samples exhibits differences from each other due to differences in their morphological structure and functional groups.

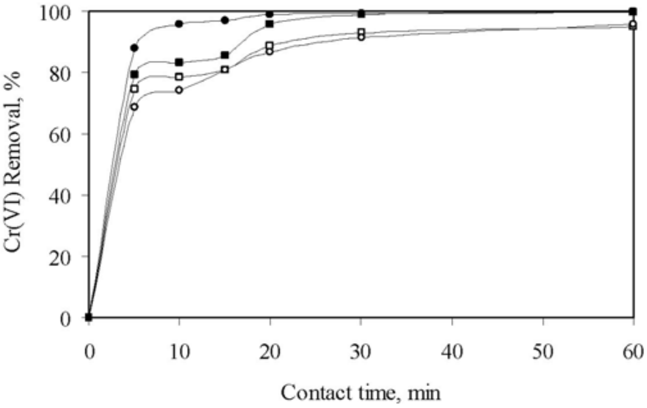

Fig. 7. Variation of Cr(VI) removal for different samples of wool, respectively, wool 1 from merino sheep, wool 2 from merino sheep, wool from lamb and wool from goat (initial Cr(VI) concentration: 0.90 mg L^{-1}; wool amount: 50 g L^{-1}; initial pH: 2.0) (Symbols; ●: wool from goat, ○: wool from lamb, □: wool 1 from merino sheep, ■: wool 2 from merino sheep). Wool 1 from merino sheep used in all of the experimental studies was revealed in this paper.

3.7. Method and cost evaluation

It is known that the cost of activated carbon or ion-exchange resins are approximately US $2000 and $4000 per ton [58]. In Turkey, the known cost of the cheapest commercial carbon available is US $1500 per ton. Wool is abundantly available in Turkey at low cost. For example, in Turkey the cost of raw wool from lamb is approximately US $550 and $750 per ton. Therefore, it can be considered as an economical alternative for commercially available active carbon in Cr(VI) sorption.

When the waste wool discharged from wool manufacturing is used for the present system, the relative cost of this material would be lower than that of raw wool. Reusability and elimination of exhausted sorbent loaded with Cr(VI) ions are expected to cut down operating costs and render the process attractive.

In practice, it can be suggested that after each adsorption cycle, wool packing can be regenerated by an alkaline solution or an anion exchanger. Then the regenerated wool can be used again in the sorption experiments. As another option, as revealed by Kadakuro et al. [59], the sorbent loaded with Cr(VI) ions can be hydrolyzed by concentrated sulfuric acid. Thus, the problem of solid waste disposal can also be solved.

4. Conclusions

The results indicate that when the amount of wool was increased, the amount of Cr(VI) sorbed (mg g^{-1}) decreased. The wool has a high sorption capacity in acidic medium, and pH 2 is the optimum pH value.

Cr(VI) kinetics suggests that the Cr(VI) uptake process seems to be controlled by external mass transfer at earlier stages and by intraparticle diffusion at later stages. The

Boyd plot shows that the external mass transfer may be the slowest step involved in sorption process.

From the data it can be concluded that a high amount of the wool was used here (50 g L^{-1}) as sorbent, and sorption capacity of the wool was low. It should be noted that the wools used in this study were of original length, and also not subjected to any pre-treatment like cutting in any size. It can be said that size reduction of sorbent would increase the sorption capacity. Also, if temperature optimization was improved, the sorption capacity could increase. It can be said that when the temperature is increased, the pores of the wool fibre may enlarge. Consequently, surface for the sorption may increase and the diffusion and penetration of Cr(VI) ions within the pores of the wool may be easier [60]. It is thought that such pre-treatment possibilities should be further investigated in our future work. Furthermore, more detailed studies including binary and multicomponent sorption and continuous study about Cr(VI) sorption using wool from aqueous solution will be the subject of a future study.

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