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The Removal of Cr(III) from Aqueous Solution Using Modified Wool

Ganchimeg Yunden[1], Naoki Kano[2] and Hee-Joon Kim[2]

1. Chemical Engineering Department, School of Applied Sciences, Mongolian University of Science and Technology, Ulaanbaatar, Mongolia

2. Department of Chemistry and Chemical Engineering, Faculty of Engineering, Niigata University, Niigata, Japan

Abstract: Mongolian sheep wool was modified by maleic anhydride at different temperatures to obtain new adsorbent for the removal of Cr(III). Adsorption of Cr(III) from aqueous solution onto the modified wool was investigated in batch system. In this work, the effect of various parameters such as pH, contact time, temperature and initial concentration on the adsorption capacity was determined by ICP-OES (Inductively Coupled Plasma-Optical Emission Spectrometry). Modified wool was characterized by SEM (scanning electron microscopy) and FT-IR (Fourier transform infrared spectrometer). The thermodynamic and kinetic studies were carried out and the results confirmed that the adsorption process was spontaneous in nature, thermodynamically favourable and endothermic. Kinetically, the adsorption process obeys the pseudo-second order model. The modified wool can be an effective adsorbent for the removal of Cr(III) from aqueous solution.

Key words: Adsorption, chromium, modified wool, kinetics, thermodynamics.

1. Introduction

In the past few years, special attention has been given to environmental contamination with heavy metal ions because of their toxicity to human health. Metal ions such as chromium, cadmium, copper, lead zinc, manganese, nickel, and iron are commonly detected both natural and industrial effluents. Industrial processes that generate Cr(III) wastes include the production of stainless steel and other metal alloys, the processing of leathers [1, 2].

In Ulaanbaatar city, water resource pollution with wastewater containing chromium from the tanneries, wool and cashmere industries has been a serious problem [3]. At the present, there are over 30 tanneries which are processing about 9 million of hide and skins per year.

Cr mainly consists of two stable oxidation states such as trivalent state Cr(III) and hexavalent state Cr(VI) in natural aqueous environment [4]. The typical mobile forms of Cr(VI) in natural environment are CrO_4^{2-}, $HCrO_4^{-}$, the relative distribution of each species depends on the solution pH, on the concentration of Cr(VI) and redox potential [5], Cr(III) tends to form $[Cr(H_2O)_6]^{3+}$, $Cr(H_2O)_5(OH)^{2+}$, $Cr(H_2O)_4(OH)^{2+}$, or Cr(III) organic complexes. The maximum level permitted in waste water is 5 mg/dm^3 for trivalent Cr and 0.05 mg/dm^3 for hexavalent Cr [6]. Therefore, exposure to chromium in high concentrations has a negative effect on fertility, the respiratory system and also cause cancer [7-9]. Removing chromium ion from aqueous mediums is significant for both human health and the environment. On the other hand, Mongolia is also abundant in raw wool, which is expected to be developed. Twenty-two (22) million of sheep in Mongolia as of today and producing about 26,000 ton of wool per year which account about 1.3% of world's raw wool production. Produce felts, carpets and other products with 10,000 ton of it, and rest of the all wool exported cheaply. Raw wool is a potential cheap, biodegradable and effective adsorbent for water treatment. Keratinous

Corresponding author: Ganchimeg Yunden, Dr., research field: environmental chemistry.

materials such as wool, human hair, and bird feathers are being investigated in the form of particles, loose fibers, non-woven fabrics, membranes and colloidal dispersions for removal of toxic metal ions from waste water streams [10]. Adsorption is most suitable method for removal of low concentration metal ion from aqueous media [11]. The aim of this work is to obtain modified wool at different temperature, to investigate the adsorption capacity of chemically modified wool for Cr(III) and optimize the various adsorption parameters in order to maximize metal recovery and estimate thermodynamic and kinetic parameters of the process.

2. Experimental Section

2.1 Materials

Mongolian sheep raw wool was used as a precursor in this investigation. Chemical reagent including hydrogen peroxide, N,N-dimethylformamide, maleic anhydride were purchased from Kanto Chemical Co., Inc (Japan). Cr(III) standard solutions were prepared by diluting a standard solution (1,000 mg·dm^{-3} $Cr(NO_3)_3$ solution).

All reagents were of an analytical grade, and water (18.2 MΩ) which was treated by ultrapure water system (Advantec aquarius: RFU 424 TA) was employed throughout this work. The pH meter (Horiba F-72) was used for measurement of pH while adjusting the pH of solution using 0.1 mol/L of NaOH and 0.1 mol/L of HNO_3.

2.2 Modification of Raw Wool

Raw wool was washed for 3-4 times, then dried at room temperature for use. Dried wool was vibrated with some detergent to remove the oily matters, then thoroughly rinsed with cold water, squeezed, and dried at room temperature. The cleaned wool placed in hydrogen peroxide with a mass concentration of 7%, the pH of the liquid 8.0, temperature of bath fixed 90 °C, and contact time was 60 min. After this pretreatment the treated wool placed in a solution of maleic anhydride and N,N-dimethylformamide in a certain volume ratio (w/v) of maleic anhydride was 12% at temperatures of 65 °C, 70 °C, 75 °C, 80 °C and 85 °C respectively. The treated wool was washed with distilled water, and the modified wool was totally dried at room temperature [12]. SEM and FT-IR were used to characterize the surface and functional groups.

2.3 Adsorption of Modified Wool

To investigate adsorption properties of the modified wool it carried out at different pH, contact time, temperature. Adsorbent was mixed with 50 mL of solution, containing certain amount of Cr(III) in a 200 mL conical flask, and the mixer was shaken. The suspension containing modified wool and chromium solution was filtered through a 0.1 μm membrane filter (Advantec Mixed Cellulose Ester, 47 mm) to remove Cr(III) that have been adsorbed into modified wool. The concentration of this metal in the filtrate was determined with an ICP-OES (SPS 1500, Seiko Instrument Inc.).

The percentage of removal Cr(III) was calculated as:

$$R\% = \frac{(C_0 - C_e)}{C_0}\,100\% \tag{1}$$

The amounts of Cr(III) up taken by modified wool were calculated as:

$$q_t = \frac{(C_0 - C_t)V}{m};\ q_e = \frac{(C_0 - C_e)V}{m} \tag{2}$$

where, C_o, C_t and C_e are the initial, time t and equilibrium concentrations of Cr(III) in the solution (mg/L); V is the volume of aqueous phase (L); m is the dry weight of the modified wool (g); q_t and q_e are the amount of Cr(III) ion up taken onto modified wool at time t and equilibrium, respectively (mg/g);

The thermodynamic parameters of the adsorption, i.e. the standard Gibb's free energy change (ΔG^0, kJ/mol), a change in standard enthalpy (ΔH^0, kJ/mol) and entropy (ΔS^0, J/mol·K), were calculated from the Van't Hoff equation.

$$\Delta G^0 = -RTlnK_c;\ K_c = \frac{C_0 - Ce}{C_e} \quad (3)$$

$$lnK_c = \frac{\Delta H^0}{-RT} + \frac{\Delta S^0}{R} \quad (4)$$

where, R is the gas constants (8.314 J/mol·K) and T (K) is the absolute temperature. The slope and intercept of the plot of lnK_c versus $1/T$ were used to determine the ΔH^0 and ΔS^0.

The sorption kinetic data of Cr(III) on the adsorbent studied were analyzed in terms of pseudo-first order and pseudo-second order rate equation. The linearized form of pseudo-first order rate equation is given as:

$$lg(q_t - q_e) = lgq_e - \frac{K_1 t}{2.303} \quad (5)$$

The linearized form of pseudo-second order rate equation is given as:

$$\frac{t}{q_t} = \frac{1}{q_t} + \frac{1}{K_2 q_e^2} \quad (6)$$

where, K_1 (min^{-1}), K_2 (g/mg min) are rate constants of pseudo-first order, pseudo-second order rate equation, respectively; t is the adsorption period (min).

3. Results and Discussion

3.1 Characterization of Modified Wool

Fig. 1 shows SEM images of raw wool and pretreated by hydrogen peroxide wool, Fig. 2 shows SEM images of wool, modified at temperatures of 65 °C, 70 °C, 75 °C, 80 °C and 85 °C respectively.

From Fig. 1a, it can be seen that the surface of raw is very uniform and the scale layer can be clearly seen. Fig. 1b shows that scale layer of pretreated by hydrogen peroxide wool is partly destroyed, which indicates successful surface dissolution.

Fig. 2 shows that surface was changed differently due to modification temperature and modified wool samples show heterogeneous particle size distribution.

Fig. 3 shows FT-IR spectra of wool, modified at different temperatures.

The full mid-IR spectra 4,500-250 cm^{-1} for this study, can be divided into four main regions:

(1) The O-H stretching region, 3,700-3,000 cm^{-1};

(2) The C-H stretching region, 3,000-2,700 cm^{-1};

(3) The O-H bending region, 1,800-1,300 cm^{-1};

(4) The fingerprint region with multiple C-O vibrations, 1,250-850 cm^{-1}.

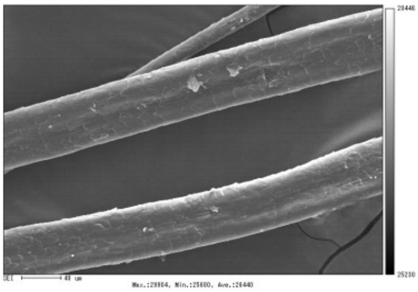
The most notably, there is marked intensity change for the O-H vibration at 1,375 cm^{-1}.

3.2 Effect of pH

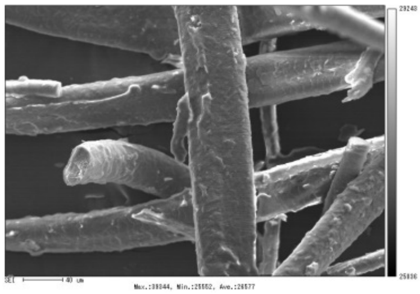
Solution pH is most important parameter affecting adsorption characteristics. The effect of pH was studied at 25 °C with initial concentration of 5 mg/L Cr(III) for 1 hour at wide range of pH (Fig. 4). While in the pH range of 3–8, the adsorption rate of Cr(III) was increased from 1.23% to 94.19% and, attains a maximum value at pH of 9. But the adsorption rate of Cr(III) is decreased from 98.53% to 21.19% in pH range of 9-14.

The increase in removal percentage at higher pH (up to 9) value can be explained by the precipitation of $Cr(OH)_3$. Cr(III) becomes more insoluble as pH is increased to its minimum solubility point which is pH 8-9.

Species distribution of Cr(III) at different pH based on theoretical calculation is shown in Fig. 5.



(a)



(b)

Fig. 1 SEM image of raw wool (a) and pretreated wool (b).

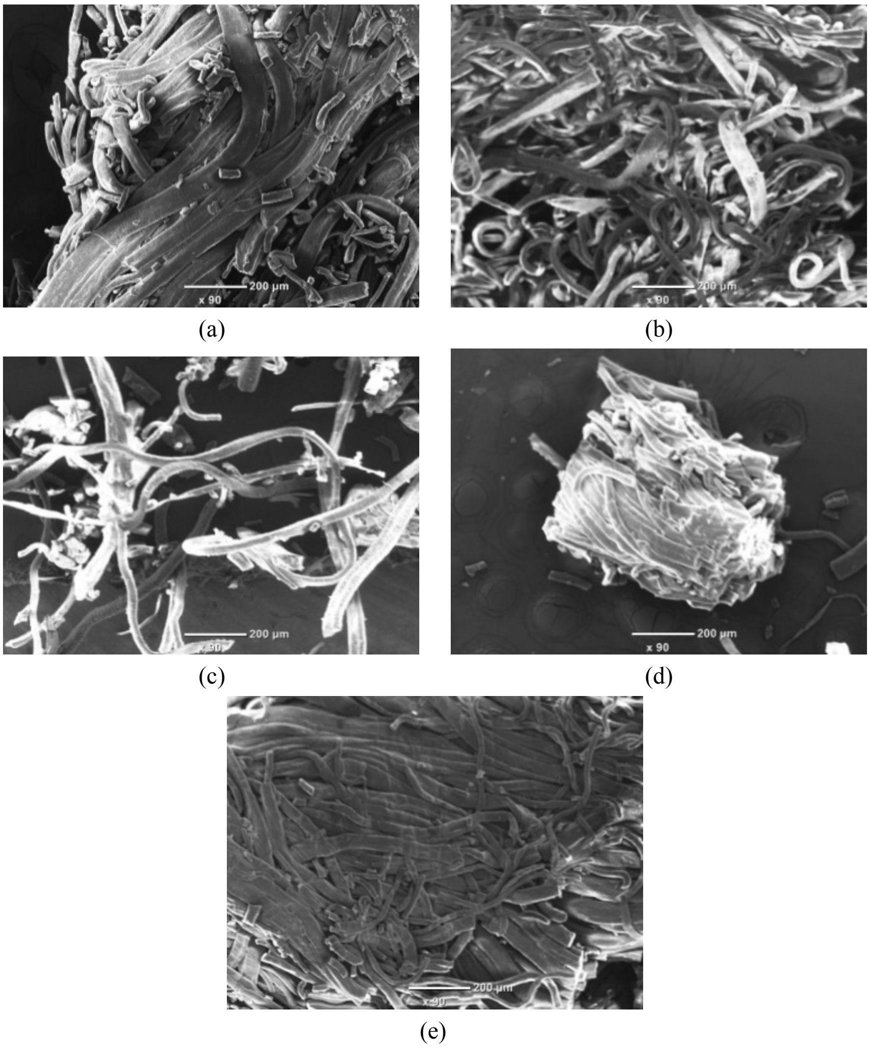


Fig. 2 SEM image of wool, modified at 65 °C (a), 70 °C (b), 75 °C (c), 80 °C (d) and 85 °C (e).

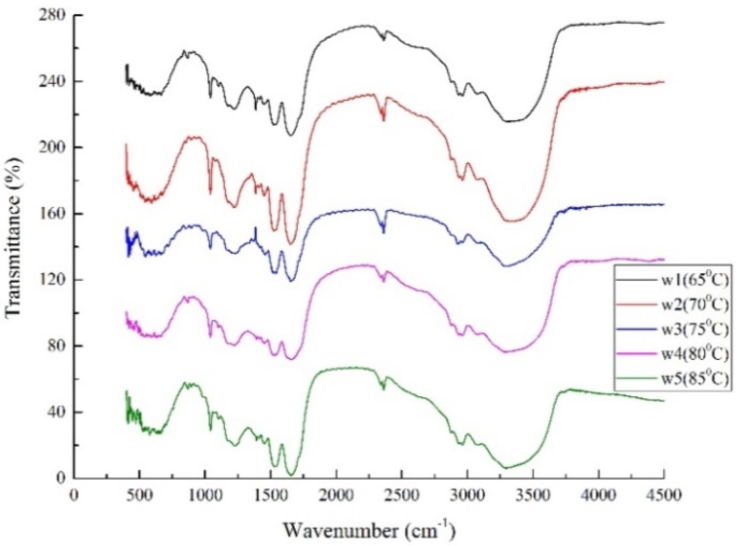


Fig. 3 FT-IR spectra of wool, modified at 65 °C (w1), 70 °C (w2), 75 °C (w3), 80 °C (w4) and 85 °C (w5).

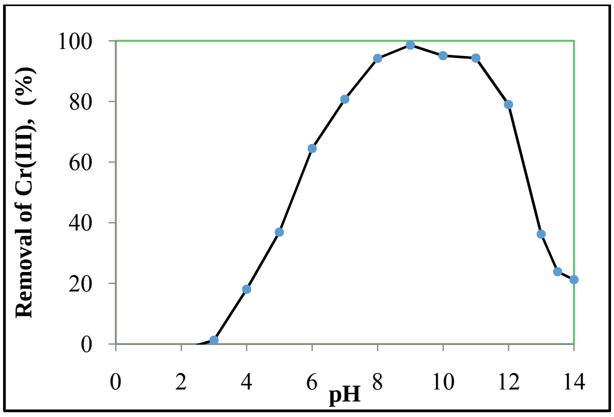


Fig. 4 Effect of pH on percentage removal of Cr(III) adsorption (T = 25 °C, C_0 = 5 mg/L, t = 60 min).

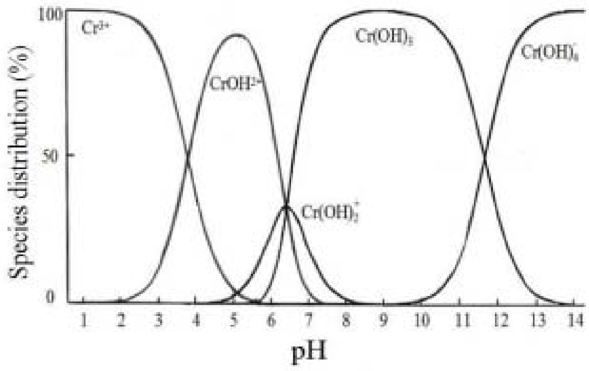


Fig. 5 Species distribution curves of Cr(III) in environmental water.

From Fig. 5, Cr(III) exists predominantly as Cr^{3+} at pH 1-3, whereas it exists predominantly as $CrOH^{2+}$ at pH 4-6, Cr(III) predominantly as $Cr(OH)_3$ at pH 8-10 [13].

In Mongolia, widely employed methods for waste water treatment are explained in two main steps:

(1) Reduction of Cr(VI) into Cr(III); (2) Hydroxide precipitation (pH 8.5). But after this treatment Cr(III) remained in water.

Based on this, pH 11 was chosen as adsorption condition for further experiments.

3.3 Effect of Contact Time

The effect of contact time on percentage removal of Cr(III) using modified wool, which were modified at different temperatures is investigated (Fig. 6). The removal percentage of Cr(III) determined as not similar to each other.

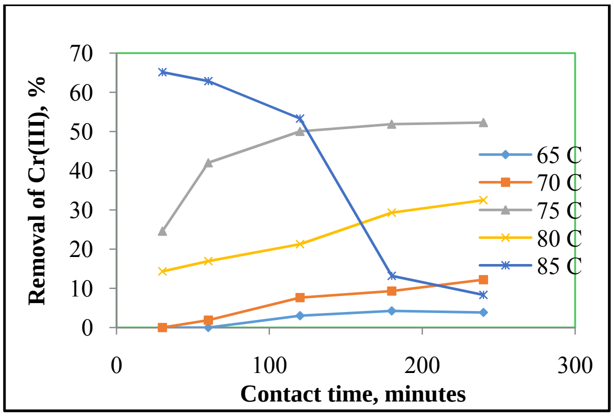


Fig. 6 Effect of contact time on percentage removal of Cr(III) (pH= 11, T = 25 °C, C_0 = 5 mg/L).

The amount of precipitation of $Cr(OH)_3$ was deducted when we calculate an exact percentage removal of Cr(III).

It is apparent from Fig. 6 that, till 180 minutes, percentage removal of Cr(III) from aqueous solution increases rapidly when used wool, modified at temperatures of 65 °C to 80 °C. However, in case of using wool, modified at temperature of 85 °C, removal is a past process that occurs in the beginning of contact time, up to 30 minutes. It is suggested that prolonging the contact time causes slight Cr(III) desorption.

And the highest percentage removal of Cr(III) was observed when using wool, modified at temperature of 75 °C. In this case, after 180 minutes, the percentage removal of Cr(III) becomes almost constant. Therefore, the contact time of 180 minutes could be considered for adsorption of Cr(III) onto wool, modified at temperature of 75 °C. Wool, modified at temperature of 75 °C is chosen as adsorbent for removal of Cr(III).

3.4 Effect of Temperature and Initial Concentration of Cr(III)

The adsorption of Cr(III) onto modified wool at different temperature shows an increase in the percentage removal of Cr(III) when the temperature is increased. The percentage removal of Cr(III) varies with temperature and initial concentration as shown in

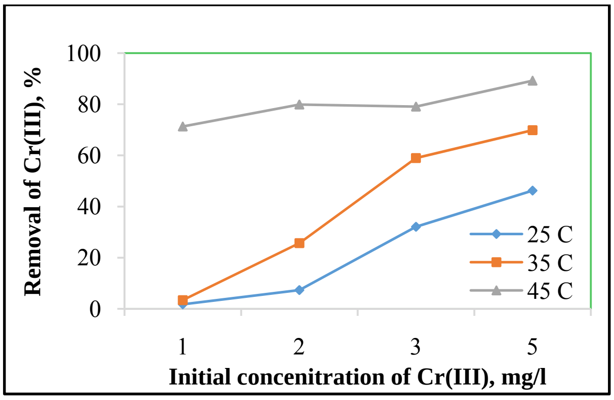


Fig. 7 Effect of temperature and initial concentration of Cr(III)on percentage removal of Cr(III) (pH = 11, t = 180 minutes, C_0 = 5 mg/L).

Fig. 7. With increase in temperature from 25 °C to 45 °C, the maximum percentage removal of Cr(III) increased 46.2% to 89.2 % for the initial concentration of 5 mg/L at pH 11. Similar trends are observed for all the other concentrations. This indicates that the adsorption reaction is endothermic in nature. Effects of increasing temperature and initial concentration of Cr(III) on the adsorption indicate that the process can be chemical adsorption. The standard Gibb's energy and the equilibrium constants K_c were calculated at each temperature using Eq. (3) for the initial concentrations 5.0 mg/L of Cr(III) (Table 1). The negative values of the free energy change (ΔG^0) at different temperatures indicate the spontaneity of the process.

The other thermodynamic parameters such as change in standard enthalpy (ΔH^0) and standard entropy (ΔS^0) were evaluated by Eq. (4). ΔH^0 and ΔS^0 were calculated from the slope and intercept of the Vant Hoff's plot of lnK_c verses $1/T$. The positive values of ΔH^0 indicate that the sorption process is endothermic. Standard entropy (ΔS^0) determines the disorderliness of the sorption at solid-liquid (adsorbent modified wool and solution containing Cr(III) interface. Table 1 summarizes the results.

3.5 Adsorption Kinetics

The adsorption kinetics describes the rate of uptake of Cr(III) ions onto modified wool and this rate controls the equilibrium time. The kinetics of Cr(III) adsorption were analyzed by pseudo first-order and pseudo second-order models at temperature of 25 °C (Eqs. (5) and (6)). The experimental data and model predicted data were compared based on the regression coefficient (R^2) shown in Table 2.

Table 1 Thermodynamic parameters.

C_0 (mg/L)	T (°C)	ΔG^0 (kJ/mol)	ΔH^0 (kJ/mol)	ΔS^0 (J/mol·K)
5	25	-10.98	113.07	415.68
	30	-12.41		
	35	-14.22		
	40	-17.48		

Table 2 Kinetic results for the adsorption process.

T (C)		25
C_0 (mg/L)		5
$q_{experience}$ (mg/g)		2.61
Pseudo I order	$K_1 \cdot 10^{-2}$ (min^{-1})	1.26
	q_q (mg/g)	15.2
	R^2	0.607
Pseudo II order	$K_2 \cdot 10^{-2}$ (g/mg·min)	1.01
	q_q (mg/g)	3.03
	R^2	0.986

From Table 2, the correlation coefficient of the second-order reaction model in this case was 0.986 which is better than the first-order reaction model and an experimental adsorption capacity is similar to calculate adsorption capacity for the second-order reaction model. The kinetics plots were made for adsorption of Cr(III) onto modified wool at temperature of 25 °C, indicating that adsorption reaction can be approximated with the second-order kinetics model.

4. Conclusion

Wool modified at 75 °C shows a better adsorption selectivity for chromium (III) in the higher pH range and higher temperature. Positive values of the standard enthalpy (ΔH^0) and entropy (ΔS^0) indicate that the sorption process is endothermic and the disorderliness of the sorption at solid-liquid interface. Negative values of ΔG^0 confirm the feasibility of adsorption. The pseudo-second-order appears to be the most convenient to describe the adsorption kinetic of Cr(III) adsorption on modified wool.

Thus, the results show that the modified wool can be used for the removal of chromium (III) from wastewater. Further research is needed to analyze the influence of common anions and cations in real wastewater-adsorbent systems.

Acknowledgments

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