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Wool powders used as sorbents to remove Co^{2+} ions from aqueous solution

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ABSTRACT

The Co^{2+} sorption of two wool powders was investigated using its radioisotope ^{57}Co ($T_{1/2}=271.8$ days and $\gamma=122.1$ and 136.5 keV) as a tracer. The effects of the type of buffer, the pH value, the contact time and the initial concentration of Co^{2+} on the sorption behaviour of wool powders were studied. The Co^{2+} releasing ability of wool powders and the re-use of wool powders to sorb Co^{2+} were also examined. The optimum sorption of Co^{2+} by the powders occurred at pH 8 in phosphate buffer and pH 10 in ammonium sulphate buffer. Fourier-transform infrared spectroscopy (FTIR) was used to study the changes in chemical structure of the wool after exposure to both buffer solutions. Compared to the untreated wool fibre, the fine wool powders showed rapid sorption rates and high sorption capacities for Co^{2+}. Co^{2+} ions were recovered after exposing the Co^{2+} loaded wool to HCl (0.1 M) and buffer at pH 3 (glycine/sodium chloride). After releasing Co^{2+} ions from wool powders, the efficiency of wool powders re-used to sorb Co^{2+} was 80% of that of the fresh wool powders. It is concluded from this study that wool powder can be used as an efficient sorbent to remove and release Co^{2+} from solution.

1. Introduction

Wool is a reactive material because of its main functional groups, including peptide bonds, side chains of amino acid residues and disulphide crosslinks [1]. Wool is known to bind a wide range of metal ions, such as mercury, copper, aluminium, nickel, zinc, cobalt, chromium, silver and gold [2–8]. There have been many reports where native wool fibres [9], chemically-modified wool fibres [10,11] and regenerated wool protein [12] have been used to remove metal ions from industrial effluent and/or recover precious metal ions from solution.

Recent studies show that the reactivity of wool can be enhanced greatly by converting the fibre into fine powder [13–16]. For example, the dye uptake of wool powder was found to be rapid, even at room temperature, while no dye was taken by wool fibre under the same condition. The rate and extent of dye uptake by fine wool powder was comparable to that obtained by activated charcoal, even when the surface area of activated charcoal was 100 times greater than that of the wool powder [15]. Naik *el at* also found that the sorption capacities of fine wool powder for Co^{2+} and Cu^{2+} were up to 10 times higher than those of commercial resins [13].

It is well established that the pH of a metal solution plays an important role in the binding of metal ions to wool [8,17,18]. Some researchers have studied metal binding in acidic and alkali conditions, using chemicals such as sulphuric acid [4], acetic acid [19,20], hydrochloric acid [10], ammonia solution [10,19–23], and also the universal buffer mixture of Teorell and Stenhagen (1938) [7] to adjust pH. Buffer systems, however, can interact with metal ions in solution. For example, the interactions of acetate and amine buffers with Cu^{2+} form copper diacetate ($Cu(CH_3CO_2)_2$) and tetra ammonium copper complexes, respectively [8]. Although the metal ion sorption by wool at various pH values has been investigated extensively, little information about the influence of buffer composition on the metal sorption behaviour of wool is documented.

Techniques used to study the binding of metal ions to wool include atomic absorption spectroscopy [5], X-ray fluorescence spectroscopy [24], inductive coupled plasma–atomic emission spectrometer (ICP–AES) [20], chelate titration [25], polarographic analysis [26], X-ray photoelectron spectroscopy [3], ATR/IR spectroscopy [21] and electron spin resonance (ESR) spectroscopy [27]. Because these techniques either require a large test sample solution, or have comparatively complex testing procedures to determine the amount of metal ions in solution, one alternative approach, using the radioisotopes (^{57}Co, ^{109}Cd and ^{64}Cu) of the stable metal ions to quantitatively track the movement of common metal ions (Co^{2+}, Cd^{2+} and Cu^{2+}) onto and off sorbents (wool powders) in solution, was employed recently by Naik *et al* [28].

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Radioisotope's decay is accompanied by emission of α, β or γ radiations. The emission of a gamma signal is ideal for tracking the movement of its natural metal ion in solution and material. The gamma emission can be easily detected using a gamma counter equipped with a scintillation crystal. The radioactivity of the radioisotope obtained can be readily correlated to the concentration of metal ion present in solution [29]. Due to its high sensitivity, accuracy and simplicity, the isotopic tracer method is widely and safely used in medicine, food preservation, agriculture, mining and archaeology [30,31].

In the present study, two wool powders with different particle sizes were utilized to sorb and recover Co^{2+} ions from solution. The effects of buffer type, pH, contact time as well as concentration of Co^{2+} ions on the sorption behaviour of wool powders were studied. The recovery of bound Co^{2+} from wool using various chemicals was examined. The efficiency of wool powders repeatedly used to sorb Co^{2+} was also investigated. Comparisons were made with the original wool fibre. The radioisotope ^{57}Co was used to track the amount of bound Co^{2+} ions on the wool samples.

2. Experimental

2.1. Materials and chemicals

Two wool powders, WP-C and WP-D, were used as sorbents, with the ‘parent’ wool fibre as control. The production of the wool powders and the characterization of all three substrates have been described previously [16], and are summarized briefly here. Wool fibres with a mean diameter of 20.4 μm, obtained from Merino wool top, were chopped into snippets, ground into fibrous material, and air-jet milled into wool powder (WP-C) with a mean particle size of 6.2 μm (on a volume basis). The same procedure was used to produce WP-D, with the exception that treatment of wool with sodium salt of dichloroisocyanuric acid (DCCA) (4% on weight of wool) was carried out at pH 4–4.5 at room temperature for 50 min, prior to air-jet milling. The mean particle size of WP-D was 4.5 μm (on a volume basis).

A cobalt standard solution (1000 mg/L), composed of cobalt nitrate (0.5%), nitric acid (2%) and water, obtained from Australian Chemical Reagents (ACR® element standard), was used as the sorbate. High specific activity radioisotope ^{57}Co (1.39E+6 CTS/10 ul/10 s, SA = 30 Mbq/mg), supplied by ANSTO Radiopharmaceuticals and Industrials, was used as the tracer.

The compositions of buffers (I and II), with pH values in the range from 2 to 10, are listed in Tables 1 and 2, respectively. The pH values were measured using a pH meter (HORIBA, D-52) calibrated with Hanna Instruments pH calibration satchels for pH 4, 7 and 10. Ethylenediaminetetraactic acid (EDTA) (purchased from Sigma-Aldrich®) solution (0.01 M) and HCl (0.1 M) were prepared with Milli-Q water. All chemicals used for this study were of analytical grade and used without purification.

Table 1
Composition of buffer I.

pH value	Composition	
	Citric acid (0.1 M) (mL)	Di-sodium hydrogen phosphate (0.2 M) (mL)
2.61	461	39
3.60	351	149
4.61	275	225
5.67	218	282
7.77	42	458
10.16	66 g ammonium sulphate and 25 mL ammonia (30%) solution in 500 mL Milli-Q water	

Table 2
Composition of buffer II.

pH value	Composition	Total volume (mL)	Chemical used to adjust pH
3	3.75 g glycine 2.92 g sodium chloride	Add Milli-Q water to 500 mL	HCl/NaOH
4	13.5 g sodium succinate		
5	9.76 g morpholino ethane sulfonic acid (MES)		
6	7.10 g di-sodium hydrogen phosphate		
8	the same as for pH 6		
9	3.75 g glycine 2.92 g sodium chloride		

2.2. Degreasing of wool fibre

Prior to binding of Co^{2+} ions, wool fibres were scoured with non-ionic detergent Hydropol TN450 (1% on weight of wool) at 60 °C for 15 min, and then rinsed twice in warm water for 5 min, and finally dried at 95 °C for 1.5 h. The cleaned wool fibre was Soxhlet extracted with ethanol (absolute, 99.5% v/v) at 60–70 °C for 8 h, and then dried in air.

2.3. Binding of Co^{2+} by wool

The procedure of binding Co^{2+} ions to wool was similar to that described elsewhere [14]. After mixing precisely-weighed wool substrate (~10 mg) with the appropriate volume of buffer, 10 uL of 3-time diluted ^{57}Co and the required volume of cobalt standard solution were added to 1 mL. The mixture was then rotated using a SLRM-2 M Intelli Mixer (MYLAB™) at 60 rpm at ambient temperature (23 °C) for the required contact time. After each appropriate time interval, the wool sample was separated from the solution by centrifuging (Brinkmann Eppendorf 5804R multipurpose centrifuge) at 5000 rpm for 15 min. Aliquots of supernatants (3×20 μL) were removed to determine the radioactivity of ^{57}Co in solution using a Wallac Wizard 1480 gamma counter. Each experiment was conducted in triplicate, and the results were averaged.

The amount of sorbed Co^{2+} on wool (q) was calculated from Eq. (1):

$$q(\mathrm{mol/mg}) = \left(1-\frac{A_t}{A_0}\right) \times \frac{C_0 \times V \times 10^{-3}}{W} \tag{1}$$

where A_0 is the radioactivity of ^{57}Co in the initial solution (counts/10 s).

A_t is the radioactivity of ^{57}Co in the final solution at contact time t (counts/10 s).

C_0 is the concentration of Co^{2+} in the initial solution (M).

V is the volume of the solution (1 mL).

W is the mass of the wool sample (mg).

2.4. Releasing of bound Co^{2+} from wool powders

Co^{2+} ions (10^{-4} M) were firstly bound to wool substrates at pH 8 (phosphate buffer) for 2 h. The Co^{2+} bound wool was then rinsed twice with Milli-Q water (1 mL) for 5 min, and dried at 105 °C.

The dried wool was then exposed to 1 mL of either EDTA (0.01 M), HCl (0.1 M) or pH 3 buffer (glycine/sodium chloride), and rotated at 60 rpm for 1 or 2 h. At the appropriate time (1 h or 2 h), the slurry was centrifuged at 5000 rpm for 15 min, and the supernatant sample (3×20 uL) counted on a gamma counter.