Adsorption and Desorption of Metals onto Reusable Adsorbent

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Abstract

This paper discusses the adsorption of metals and metalloids on modified natural material. In case of an economically valuable contaminant, such as copper or cobalt, recovering the metal provides value to the water treatment. For copper, a method is demonstrated in which the adsorbent can be recovered by the formation of a complex, leading to the regeneration of the adsorbent and recovery of the metal. After this, the metal can be hydrometallurgically recovered. The adsorbent can be used over twenty times without loss of efficiency.

Metal oxide adsorbents are an economic and easy way to lower the metal content in mine effluent. Utilizing reusable adsorbents, in case of copper, the value of the recovered metal offsets the cost of water treatment. This approach presents a win/win solution for the mining company and environment.

Keywords: adsorbent, contaminant removal, copper recovery, adsorbent recycling

Introduction

Even when operating within the concentration limits of environmental permits, small amounts of contaminants may be released into the environment or are discharged into the tailings pond or the surrounding aquifer. Large streams of mine effluents or process water result in discharging hundreds of kilograms of contaminants into the receiving water streams or ground water. For example, a 5 mg/L copper solution with a discharge of 500 m^3/h releases annually 21 900 kg of copper. With a copper price of 6,822 USD/t, the lost revenues might be up to 149,411 USD (Infomine 2018). Currently, the rising price of copper and the decreasing ore grades make the recovery of metals from secondary streams economically feasible.

The adverse effects of copper for aquatic life is dominated by the bioavailability of the copper complex (Langmuir 1997). Potentially negative effects of copper in soil are currently under scrutiny of environmental agencies, because copper is toxic for bacteria and therefore reduces the microbial activity in soil (Marques et al. 2018). This in turn leads to a poor nutrient status in the soil and to reduced yields on farmland (Adrees et al. 2015). Furthermore, copper in high concentrations is toxic to plants.

Reducing the copper emissions, therefore, has an immediate positive effect on the social acceptance of the mine by surrounding farmers. In addition, the potential revenue of copper sales assists to offset the water treatment costs.

Recovery of copper from secondary sources or and from tailings is of ecological and economical interest and has sparked research interest in this area, for which the term “precision mining” has been coined (Crane 2018). Zero valent iron on inert support has been used to selectively obtain copper from waste sources. A variety of adsorbents has been tested for metal and especially copper removal, ranging from nanotubes (Ihsanullah et al. 2016), natural and modified minerals (Uddin 2017), immobilized organic compounds (Moscatelloa et al. 2018) to biobased waste products, such as chitin (Anastopoulos et al. 2017). The high costs of many possible adsorbents prevent the use in an industrial application.

Among the cheaper options for treatment of mine or waste water is a natural modified mineral adsorbent commercialized as Aquaminerals PalPower M10. According to the manufacturer’s specification, this magnesium and iron oxides based adsorbent can be used to remove Ni, Co, Pb, Cr, Cd, Zn, Al, Cu, Fe, Mn, P, U and As contaminants from water. In this paper, we present the use of Aquaminerals Palpower M10 to remove copper from water and its subsequent recovery as CuS after hydrometallurgical treatment.

Methods

Metal and metalloid analysis was performed by an accredited laboratory (Ahma Ympäristö Oy, Oulu) using ICP-OES. Additionally, copper was analysed in house by UV-VIS spectrometry on a Specord 50 plus by AnalytikJena at 600 nm wavelength. Solid-state characterizations have been performed on a PANalytical XPert Pro diffractometer with a Copper X-ray anode and X’Celerator detector. All resulting data was handled with the Highscore plus software package. XRF spectroscopy was conducted with a PANanalytical Minipal 4 RoHS WEEE utilizing the OMNIAN function.

Laboratory scale tests were performed as batch tests in 250 mL PTEE bottles, which were agitated in an end-over-end tumbler at 20 rpm (rotations per minute). Desorption tests were performed as batch tests in an end-over-end tumbler. Filtering of occurring sludge was performed by vacuum suction, and a glass fibre filter was used for separating the copper amine complex.

Materials

A commercially available adsorbent (Aquaminerals PalPower M10) was obtained and used as is. Synthetic water solutions were prepared by dissolution of the respective salts in deionized water. Copper(II)chloride dihydrate ($CuCl_2 \cdot 2H_2O$, technical, VWR chemicals), Manganese sulfate monohydrate ($MnSO_4 \cdot H_2O$, p.A., Merck), Sodium aluminate anhydrous ($NaAlO_2$, technical, Sigma Aldrich), Ammonia (25% aqueous solution, technical, VWR chemicals) and sodium sulfate anhydrous (Na_2SO_4, >99 %, VWR chemicals) were used as received. Iron(III)sulfate ($Fe_2(SO_4)_3$, technical, Kemira) granules were grinded in a ring mill to facilitate dissolution in water.

Results and Discussion

Adsorption experiments

Copper is conveniently adsorbed on to the PalPower M10 modified mineral adsorbent. According to the XRF characterization (Table 2), the adsorbent consists of mainly MgO (58 %), SiO_2 (22 %), and Fe_2O_3 (14 %). The required contact time of M10 depends on the initial copper concentration and adsorbent dosage, between 5 minutes and 2 hours.

Two spiked copper solutions with a concentration of 100 mg/L and 5 mg/L were prepared to imitate a range of concentrations in common mining effluents. The M10 adsorbent was added as a dosage of 2 g/L and 0.3 g/L and stirred for 30 min (Table 1). After 30 min, the 100 mg/L copper solution shows a reduction of 67% at a dosage of 2 g/L. Higher dosages of the adsorbent resulted in lower copper concentrations in the solution. For a 5 mg/L copper solution, dosage was varied from 1 to 5 g/L, a 2 g/L dosage results in quantitative removal of copper of initial concentration of 5 mg/L. PalPower M10 has an adsorption capacity for copper of 33 mg/g (33 kg/t), and therefore M10 ranks among the highest copper (II) adsorbing materials known (Ahmed 2016).

Five samples of 5 mg/L solution were prepared and analyzed to alleviate the larger margins of error for small concentrations. All five samples resulted in a reduction of 99 % copper, leaving the initial 5 mg/L copper so-

Table 1 *Results of ICP-OES results of the initial solution and after adsorption to M10.*

#	initial Cu mg/L	Cu after, mg/L	removal rate, %	adsorbent dose, mg/L
1	99.5	32.9	66.9	2000
2	4.85	0.022	99.55	300
3	4.96	0.010	99.80	300
4	4.87	0.033	99.32	300
5	4.83	0.032	99.34	300
6	4.65	0.015	99.68	300

Table 2 *Fresh adsorbent, used adsorbent and extraction test results.*

	M10 new	Cu adsorbed	NH_3 12.5%	NH_3 6.25%	NH_3 3%	NH_3 1.5%
MgO	58.81	47.76	51.97	52.78	51.85	46.65
SiO_2	21.70	15.01	16.00	16.44	16.20	14.48
SO_3	1.28	0.96	0.64	0.68	0.73	0.77
Cl	--	1.42	0.06	0.12	0.16	0.18
K_2O	0.12	0.05	0.06	0.06	0.05	0.06
CaO	1.11	0.90	0.96	0.93	0.88	0.88
Cr	0.25	0.25	0.25	0.26	0.26	0.25
Mn	0.15	0.15	0.16	0.16	0.16	0.16
Fe_2O_3	13.58	14.36	15.13	15.00	14.93	15.03
Ni	0.16	0.19	0.18	0.19	0.19	0.20
Cu	--	5.73	1.46	1.94	2.73	3.81
Ag	0.17	0.16	0.17	0.17	0.16	0.17
Eu	0.06	0.13	0.12	0.12	0.12	0.11

Table 3 *ICP-OES results of leachate of some eluents from copper loaded M10 (20.00 g adsorbent, 5.00 g/LCu).*

	Leached with H_2SO_4	Leached with NH_3(aq)	Leached with H_2O
Cu mg/L	4690	3390	0.58

Table 4 *Copper concentrations of leachate from 20.00 M10 loaded with 5.00 g/L Cu at different ammonia concentrations.*

	NH_3(aq) 12.5 %	NH_3(aq) 6.25 %	NH_3(aq) 3 %	NH_3(aq) 1.5%
Cu mg/L	3520	3080	2480	1790

lution to a concentration under 0.035 mg/L copper (WHO guideline is 2 mg/L; Table 1).

The XRF results of adsorbed copper on adsorbent (1 g/L onto 20 g) in comparison to fresh PalPower M10 show that the adsorption of 1.00 g/L Cu to 20 g/L adsorbent is quantitative (Table 2). The remaining copper concentration in water is below the detection limit of the ICP-OES, and the behaviour is reflected in the 5.7 % Cu adsorbed according to XRF (Table 2).

Copper recovery

The adsorption of copper to the adsorbent PalPower M10 is a combination of surface precipitation from local lowering of the pH and adsorption onto the solid material. Copper from slags and spent adsorbents can be recovered by acid washing. 1 M HCl does not appear to be extracting copper in substantial amounts. Treatment of M10 with 2 M H_2SO_4 releases the copper, but dissolves the adsorbent M10, which can be observed by the mass loss of about 75 % and the loss of MgO in XRF. A comparison of the leaching of 2 M H_2SO_4, 12.5 % NH_3 (aq.) and H_2O gave the extraction of 4690 mg/L, 3390 mg/L, and 0.58 mg/L (Table 3; 200 mL eluent used).

Leaching of M10 with 12.5 % NH_3 (aq) mobilizes copper in form of the deep blue tetraamminecopper(II)-complex $[Cu(NH_3)_4]^{2+}$ in reasonable quantities of 3.4 g/L. In the next step the concentration of ammonia solution required was investigated.

An aqueous solution of ammonia in concentrations from 1.5 % to 12.5 % was used to extract the copper as an tetraamminecopper(II)-complex. The extracted adsorbent was characterized by XRF (Table 2) and the leachate analysed by ICP-OES (Table 4).

Table 5: Loop of adsorbent used, copper extracted and recovered CuS. Experimental setup: M10: 20.00 g; Cu: 1.00 g.

used M10, g	CuS prec., g	recovered M10, g	Yield of Cu recovered, %	comments
20.6888	1.1829	19.0628	71.9	
19.6445	1.1105	17.7348	67.5	
20.6886	0.862	18.8410	52.4	
20.7486	0.388	19.3977	23.6	
20.4808	2.0802	17.0370	126.4	fresh ammonia
20.4972	1.2011	18.8475	73.0	
20.7520	*1.3116*	*19.4793*	*79.7*	25 % *ammonia*
overall	8.1363		494.3	70,6 % average yield

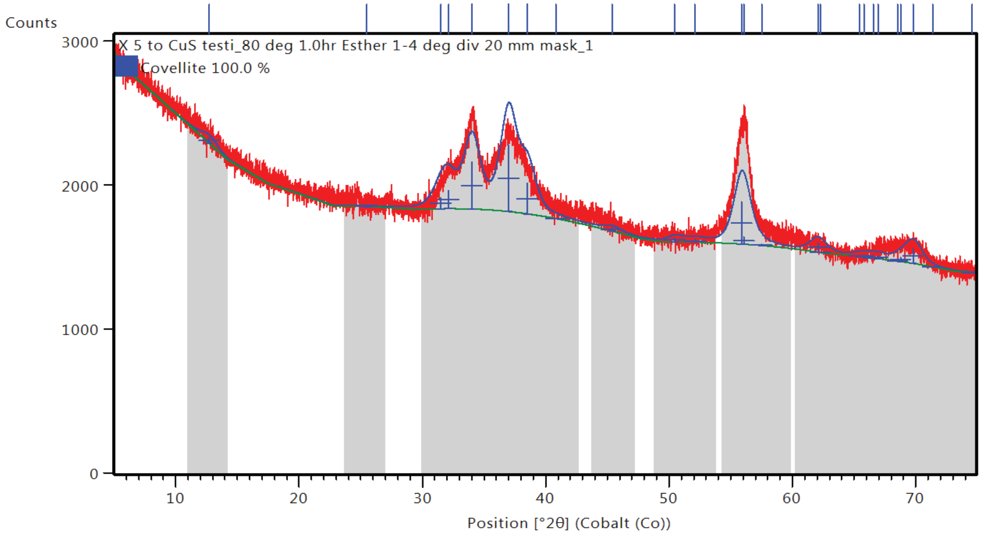

Figure 1 *X-ray diffractogram of recovered CuS.*

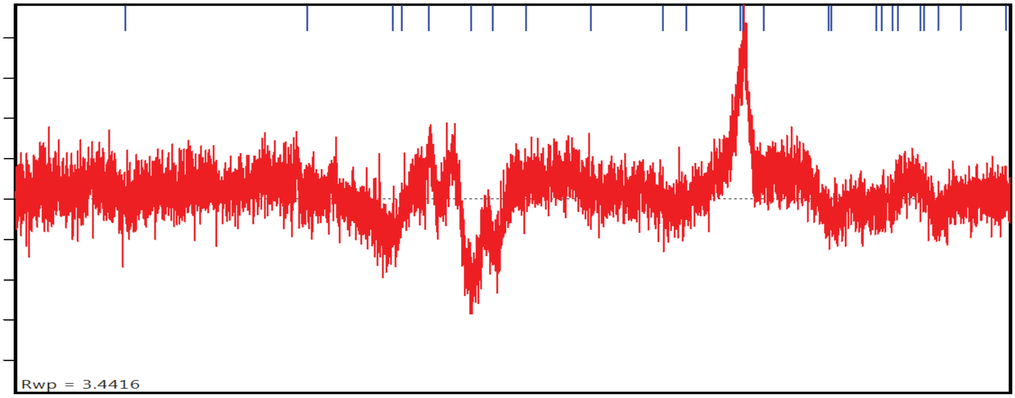

Figure 2 *Rietveld refinement of the recovered CuS.*

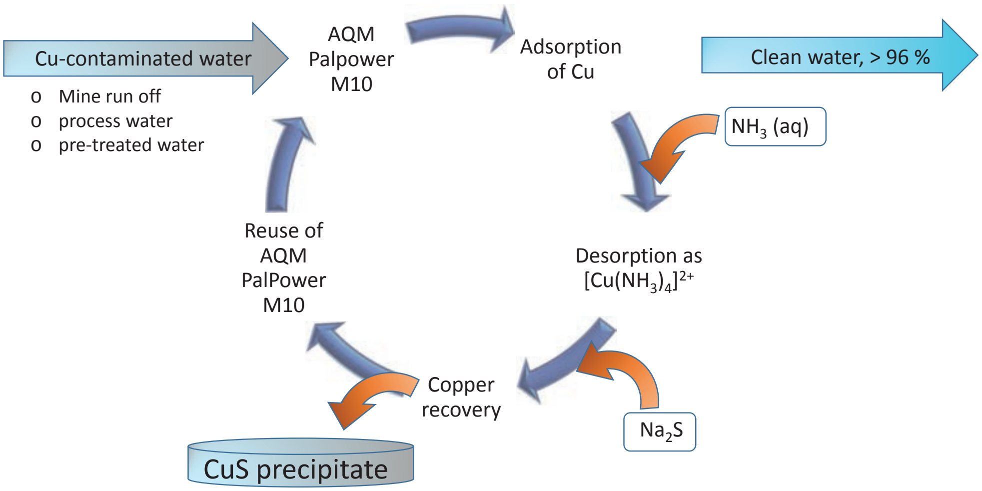

Figure 3 *Loop of copper recovery from the adsorbent.*

As can be seen, the remaining copper percentage in the extracted material correlates with the decreased extraction power of lower amine concentration. While 25 % ammonia solution has shown higher yields in copper removal, it is technically impractical to be used in large scale operations (1.3116 g, Table 5).

A loop with 20 g M10, adsorbing 1 g/L Cu from 1 L of water and subsequent recovery by ammonia and precipitation as CuS was run for 7 times (Table 3, Figure 4). About 1/20 of the M10 adsorbent was lost during handling and possible partial dissolution in water, and ammonia and was replaced by fresh M10 until 20 g initial weight was achieved. The resulting CuS was characterized by XRD (Figure 2 and Figure 3). Copper sulfide was the only phase, for which Rietveld refinement resulted in a good wRp of 3.4 %. The 12.5 % ammonia solution was recycled. A decrease in copper recovery is noticed after leaching, with simultaneous increase in copper remaining in the leached adsorbent (XRF). Using fresh ammonia leaches earlier accumulated copper. Cursive data in Table 3 indicates the use of 25 % ammonia. As expected, the percent of leached copper (80 %) is higher than for the 12.5 % ammonia solution. However, the corrosive properties and volatile characteristics of 25 % ammonia solution may make the use for industrial applications difficult. It is noteworthy, that in all cases, XRF of leached PalPower M10 showed the presence of further copper. As this did not inhibit the adsorption of further copper in the next cycle, the saturated point of the adsorbent was not reached yet, though not all Cu was recovered by leaching, no copper was lost in the process. Occasional higher concentrations of leachate could dissolve the adsorbed copper. Over time, an equilibrium of adsorbed copper and leached copper will build up.

Finally, the selectivity of the loop was verified by artificial mine water containing 1 g Cu^{2+} and 5 g Fe^{3+} as well as 100 mg Al^{3+}, 100 mg Mn^{2+} and 0.1 M Na_2SO_4 . The copper and iron were adsorbed by 20.00 g M10 adsorbent. Pure CuS (XRD) was recovered with a 63.4 % yield.

Currently piloting of the copper recovery is in planning at a suitable copper containing process water.

Conclusions

The use of PalPower M10 as adsorbent for copper and subsequent desorption via the coppertetraamine complex and copper sulfide precipitation has been demonstrated. Due to the easiness of upscale, this procedure shows economic interest for application in mine effluent or mine water. Treatment of water even with low concentrations of copper may result into better social acceptance of the mine, due to decreased contamination of soil, while revenue of recovered copper may be used to off-set parts of water treatment costs.

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