

## Removal of Heavy Metals by Plasma Cross-Linked Acrylic Acid

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**Abstract:** The heavy metal contamination of water around abandoned mines was observed in South Korea. In that assessment, the highest concentrations of 88, 5, 116 and 244  $\mu\text{g L}^{-1}$  of copper (Cu), cadmium (Cd), lead (Pb) and zinc (Zn), respectively, were found in water within 1 km from the mine. Acrylic acid was graft polymerized onto plasma-treated cellulose filter papers to develop a sorbent capable of removing the heavy metals. The ability of the grafted sorbent to remove a mixture of Cu, Cd, Pb and Zn from synthetic mine-water samples was evaluated in batch test at a starting pH of 6.5. The sorbent dosage was set at 20 g  $\text{L}^{-1}$ . The Freundlich isotherm model also explained the data. Three different grafting percentages of 42, 122 and 148 were used to evaluate the effect of percentage grafting on adsorption. The amount of metal adsorption decreased with increasing percentage graft. The solid phase adsorption for the different grafted percentages decreased in the following order:  $\text{Zn} > \text{Cu} > (\text{Cd} \sim \text{Pb})$ . Admittedly, one gram of plasma-treated acrylic acid filter paper was capable of removing approximately 111, 39, 36 and 117  $\mu\text{g}$  of Cu, Cd, Pb and Zn respectively.

**Key words:** Abandoned mine • Freundlich isotherm • Grafting • Metal removal • Oxygen plasma

### INTRODUCTION

Mining and milling operations, together with grinding, concentrating ores and disposal of tailings, provide obvious sources of contamination in the surface environment, along with mine and mill wastewater. In Korea, various mines were distributed all over the country and were actively operated until the early 1980s [1], since when, however, most have been closed, mainly due to economic reasons. After mine closure, mine waste materials, including tailings, were left without full environmental treatment, leading to the contamination of soils, plants, waters and sediments in the vicinity of the mines by potentially toxic elements from tailings by clastic movement through wind and water. The extent and degree of heavy metal contamination around the mines vary depending on the geochemical characteristics and mineralization of the tailings. For example, tailings containing large quantities of sulfide minerals could influence nearby agricultural lands and streams. Metal contamination around 44 abandoned mines in South Korea was measured and the highest concentrations of

Cu, Cd, Pb and Zn in surface water were 88, 5, 116 and 244  $\mu\text{g L}^{-1}$  respectively [1].

Sorption, utilizing low-cost filter materials, is an attractive option for small businesses, industries and municipalities to remove significant portions of the total metal concentrations to levels, which will be less detrimental to public health and environmental quality [2]. Graft copolymers of cellulosic materials have advantages such as chemical resistance, radiation stability and inexpensive production compared to conventional ion exchange [3]. Many investigators have studied the feasibility of less expensive materials such as alga [4, 5], sawdust [6], goethite [7], beech leaves [8], clays [9], waste straw [10], biosorbents [11], lignin [12, 13], groundnut husk [14], agricultural wastes [15, 16], zeolites [17-20], fly ash [21-23], red mud [24], recycled iron [25], bone char [26], biochar [27], bagasse [28] etc. for the removal of heavy metals from water. In this study, filter paper was used as a cellulose source. Oxygen ( $\text{O}_2$ ) plasma was treated to form a reactive surface on filter paper for the further reaction with acrylic acid (AA). This sort of plasma-induced graft polymerization is an attractive way

of modifying the surface chemistry and morphology of polymeric materials [29]. The main objective of the study was to form a sorbent capable of enhancing heavy metal removal from mine's surface water.

## MATERIALS AND METHODS

**Graft Polymerization:** AA underwent graft polymerization by a two-step method [29]. Cellulose filter papers were treated for 120s in an argon (Ar) plasma reactor operating at a radio frequency (RF) of 13.6MHz, gas pressure of 5mbar, argon flow rate of 50sccm and power of 100W, as described elsewhere [29]. Immediately after the treatment, O<sub>2</sub> was introduced into the chamber that was maintained at atmospheric pressure for 1hr to generate hydroperoxide as well as other functional groups on the sample surface. The operation of plasma onto cellulose filter paper, as shown in Fig. 1, was done through Plasma Enhanced Chemical Vapor Deposition (PECVD) apparatus. It had a cylindrical reactor made of stainless steel (diameter 50cm) and a parallel plate electrode configuration with an electrode spacing of 14cm. Both of the stainless steel electrodes were circular in shape; the lower grounded electrode was 30cm in diameter. The precursor gas was fed through a gas shower head built in the upper electrode. The pressure of the reaction chamber was measured through a Baratron gauge (122B, MKS Instruments). The chamber was evacuated to a base pressure of 1.6Pa using a rotary pump before plasma treatment. AA was graft polymerized onto the plasma-treated filter papers under a nitrogen atmosphere [29]. The filter papers were placed in a tube containing aqueous AA of predetermined concentration (30%) and nitrogen was bubbled through the solution. The tube equipped with a positive nitrogen pressure was subsequently placed in a constant temperature water bath for 1~5hr. After the grafting reaction, the filter papers were removed from the tube and underwent soxhlet extraction with water overnight to remove any homopolymer adhering to their surface [29]. The percentage graft was calculated from the following relation [30],

$$\text{Percentage grafting} = \frac{W_2 - W_1}{W_1} \times 100 \quad \text{Equation (1)}$$

where W<sub>1</sub> and W<sub>2</sub> are the weights of the filter paper and the grafted filter paper respectively.

**Batch Experiments:** Sorption experiments were carried out using synthetic solutions in 50 ml beakers at room temperature (28±1°C). The required concentrations of Cd, Cu, Pb and Zn were obtained by step-by-step diluting

their stock commercial solutions to the desired concentrations. The ionic strength of the water samples was controlled using 0.01M NaCl and the pH changes during the experiments were minimized using 0.003M NaHCO<sub>3</sub> [31]. Before starting the batch experiments, the pH of all solutions was adjusted to 6.5 using strong acid or base solutions. Afterwards, the dosage of plasma-treated AA-filter paper (PAAF) was set at 20g L<sup>-1</sup> [24] in the predetermined synthetic solutions. The solutions with sorbents were then mixed by gently shaking the batches in a mechanical shaker at 100 rpm for 24hr. Later, the batches were taken from the shaker and filtered through 0.45µm filter paper, after which the filtrates were acidified to pH 1.5~2 and stored at 4°C until the heavy metal measurements. One set was also run as a control batch with sorbent but without any heavy metal addition. All the chemicals used were reagent grade and were used without any further purification.

**Heavy Metal Concentrations:** In this study, we attempted to use realistic concentration ranges where the lowest values were below or about US Environmental Protection Agency's fresh water acute limits (<http://www.epa.gov/waterscience/criteria/wqcriteria.html>) and the highest values were significantly higher, as shown in Table 1. The purpose was to evaluate and compare the sorbents at both highly and slightly polluted conditions, since some sorbents are known to be effective at rather high concentrations but are less efficient at low concentration [31].

**Analyzing Sorption Data:** For PAAF, the solid phase heavy metal concentration, q<sub>e</sub> (µg g<sup>-1</sup>), was determined by analyzing the corresponding heavy metal concentration before and after the treatment using the following equation.

$$q_e = \frac{C_0 - C_e}{X} \quad \text{Equation (2)}$$

where C<sub>e</sub> is the equilibrium heavy metal concentration in the solution (µg L<sup>-1</sup>) and X the sorbent dosage (g L<sup>-1</sup>). Moreover, the equation as shown below was used as the linear form of the Freundlich isotherm to fit the sorption data.

$$\log q_e = \log K + \frac{1}{n} \log C_e \quad \text{Equation (3)}$$

where K is correlated with the quantity of sorbate associated with the sorbent and n is the Freundlich isotherm constant related to the strength of the sorption [32].

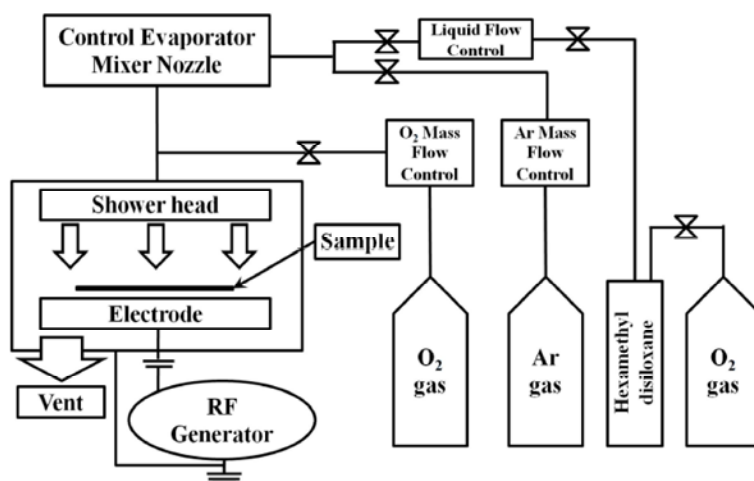


Fig. 1: Schematic diagram of PECVD system

Table 1: Initial concentrations ( $C_0$ ) of heavy metals for batch experiments

	$C_0$ ( $\mu\text{g L}^{-1}$ )			
	Cd	Cu	Pb	Zn
USEPA	2	13	65	120
Batch 1	9018	10900	9726	11020
Batch 2	4425	5242	4715	5850
Batch 3	2664	3130	2832	3287
Batch 4	892	1041	976	1192
Batch 5	438	520	516	722
Batch 6	90	120	170	323
Batch 7	3	22	73	161

## RESULTS AND DISCUSSION

**Sorption Isotherm:** Table 2 shows Freundlich isotherm constants with the  $r^2$  values for all grafting percentages investigated in this study. For Pb, at the percentage grafting of 42, the  $r^2$  values were comparatively lower. However, the  $r^2$  values  $\geq 0.5$  signify statistically significant correlation. Although  $r^2 \geq 0.5$  shows a fair correlation, using the estimated Freundlich isotherm for prediction is considered highly uncertain unless  $r^2$  is close to 1 [31]. Accordingly, most of the investigated heavy metals showed the most correlated result to fit the isotherm. Cu showed a better correlation than the others as  $0.95 \leq r^2 \leq 0.98$ .

**Influence of Percentage Grafting:** The solid phase adsorption of metal was corrected for the grafting percentages in the batches. As depicted in Fig. 2, the adsorption per dosage of adsorbent versus grafting percentage was drawn while keeping the other parameters constant. It was observed that the adsorption per dosage of the adsorbent improved with low grafting percentage

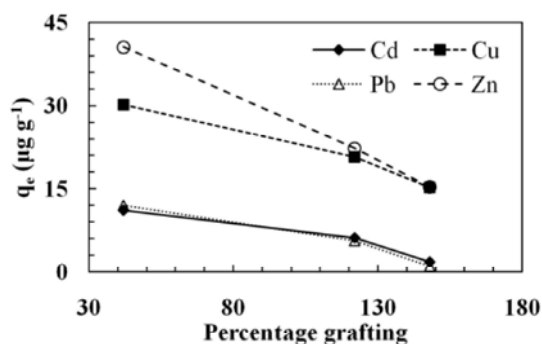


Fig. 2: Solid phase sorption of Cd, Cu, Pb and Zn at different grafting percentages

Table 2: Freundlich isotherm constants for different grafting percentages

Heavy Metal	Percentage Grafting								
	42			122			148		
	K	1/n	$r^2$	K	1/n	$r^2$	K	1/n	$r^2$
Cd	0.06	0.67	0.96	0.006	0.89	0.92	0.001	0.98	0.98
Cu	0.08	0.76	0.95	0.030	0.85	0.98	0.019	0.87	0.98
Pb	0.82	0.36	0.84	0.001	1.06	0.87	0.001	0.89	0.91
Zn	1.41	0.45	0.90	0.004	1.10	0.96	0.005	1.00	0.99

at all heavy metal concentrations. Alternatively, the amount of metal sorbed decreased with increasing percentage graft. Pb and Cd showed similar sorption criteria that were lower than those of Zn and Cu sorption. In the study, Zn was more sorbed than Cu.

**Equilibrium Concentrations:** The results of the simultaneous removal of Cd, Cu, Pb and Zn are presented in Fig. 3 on a log-log scale for batch tests. As expected, the amount of heavy metal removed increased with

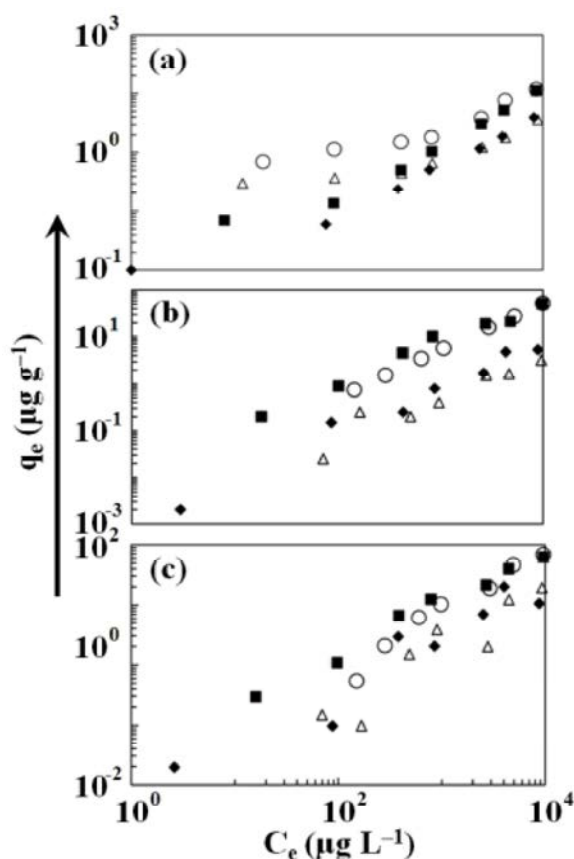


Fig. 3: Cd (◆), Cu (■), Pb (Δ) and Zn (○) removal at the following different grafting percentages: (a) 42%, (b) 122% and (c) 148%

increasing initial heavy metal concentration in all of the batches. The sorbent dosage was set at  $20\text{ g L}^{-1}$  for all the batches. All of the batches were investigated at three different grafting percentages. The highest amount of adsorbed Cu in batch 1 was  $111\mu\text{g g}^{-1}$ .

### CONCLUSION

This study has presented the effective use of PAAF to remove trace heavy metal elements in the water coming from abandoned mines. The heavy metal sorption showed satisfactory results in the batch study. The sorption of the heavy metals was dependent on the grafting percentage with a lower grafting percentage exhibiting better solid phase metal sorption. PAAF was suitable for batches with low concentrations of heavy metals. No sorbent leaching occurred during the batch tests, indicating an acceptable adsorbent quality. The effect of sorbent dosage should be investigated in future study to determine the effects on heavy metal removal.

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