



# Ethylenediamine-Modified Activated Carbon for Aqueous Lead Adsorption

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## ABSTRACT

This study is to develop a carbon-based adsorbent containing multiple functional ligands for effective removal of lead ions from aqueous media. Activated carbon (AC) was oxidized by nitric acid, followed by chlorination with thionyl chloride and reaction with ethylenediamine. Modified activated carbon (MAC) was characterized using scanning electron microscopy in conjunction of energy dispersive spectroscopy (SEM-EDS). Fourier transform infrared spectroscopy (FT-IR), and potentiometric titration. Surface characterizations confirmed that carboxyl, amine, and chlorine functional groups were effectively introduced onto the carbon surface by the treatments. The modifications lowered the pI at the point of zero charge (pI<sub>zpc</sub>) from 9.6 to 2.55 and resulted in more negatively charged surfaces. Adsorptive experiments showed that aqueous Pb removal by MAC was faster, with a 62% higher capacity than the original AC (60.2 vs. 37.2 mg g<sup>-1</sup>).

## INTRODUCTION

Lead (Pb), a toxic metal often occurring in the environment, is of great health and environmental concerns, and it is well-known to cause a cumulative poison through water intake or food chains. Excessive Pb exposure has been reported to result in brain damage and dysfunction of kidneys, liver, and central nervous system in humans, especially in children. Lead contamination in the environment usually results from wastewaters or effluents from lead mining, battery recycling, electronics assembly plants, and military facilities, as well as landfill leachate and urban rainwater runoff. Conventional cleanup technologies that are applied for Pb removal from contaminated water include chemical precipitation, ion exchange, or adsorption, among which the adsorption technique using activated carbon has been widely used because of its simplicity and cost-effectiveness. When aqueous Pb concentration is relatively low, however, meeting the regulation requirement for the Pb ion removal by ordinary activated carbons is a great challenge. There is a demand to develop more effective carbon adsorbents for removing Pb ions from various aqueous media. It has been reported that adsorbents containing nitrogen groups would enhance metal ion adsorption through the surface chelation mechanisms.

## OBJECTIVES

- Modify activated carbon through the reactions with ethylenediamine to effectively introduce amine groups onto the surfaces.
- Characterize the surface of the modified activated carbon to evaluate the effectiveness of the modification.
- Perform batch experiments of adsorption kinetics and equilibrium isotherms to determine the efficacy of the modified carbon for aqueous Pb ion removal.

## MATERIALS AND METHODS

Fifteen (15) grams of activated carbon (NORIT Dacro 20x40L, surface area of 650 m<sup>2</sup>/g, density of 400 g/L, particle size of 0.42–1.0 mm) was oxidized with 100 mL 5M HNO<sub>3</sub> solution for 7 hrs at 40 °C. The oxidized carbons were separated by filtration, washed with deionized water until aqueous pH > 5, and then oven-dried overnight under 40 °C. Twelve (12) grams of dry oxidized carbon was subsequently activated with 40 mL of 5% thionyl chloride (Aldrich 99%) in toluene (Aldrich 98%) for 5 hrs at 70 °C, which converted surface carboxylic groups to acyl chloride functionalities. The carbons were then washed more than 3 times with ethanol and purified through the Soxhlet extraction, in which the carbons were reacted with 0.05M ethylene-diamine (Aldrich 99%), and stirred for 24 hrs at 90 °C. Upon completion of the reactions, nitrogen-containing functional groups were immobilized on the carbon surface through alkyl chains. The purified carbons were washed with ethanol in an ultrasonicator for 10 min, several times until all non-reacted chemicals were removed, and then dried under vacuum. Schematic illustration of the surface reactions is shown in Figure 1. Modified activated carbons were characterized by SEM-EDS, FT-IR, and potentiometric titration, and determined for the Pb removal kinetics and capacity through batch experiments.

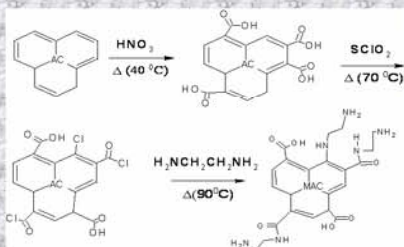


Fig. 1. Schematic illustration of activated carbon functionalization

## RESULTS AND DISCUSSION

### 1. Surface Characterization

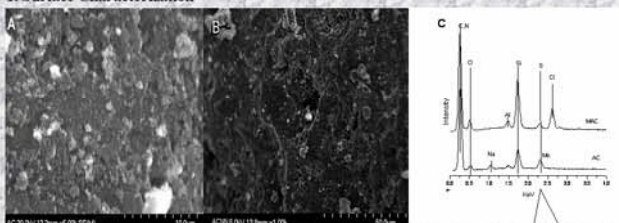


Fig. 2. SEM micrographs of AC (A), MAC (B), and EDS spectra (C)

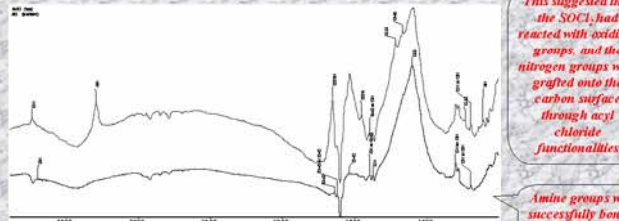


Fig. 3. FT-IR spectra of activated carbons before (bottom) and after modification (top)

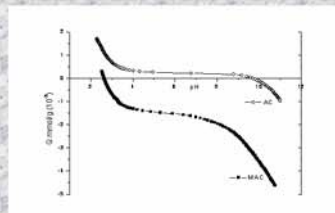


Fig. 4. H<sup>+</sup>-binding isotherm of AC and MAC (I=0.01 M NaNO<sub>3</sub>)

### 2. Lead adsorption

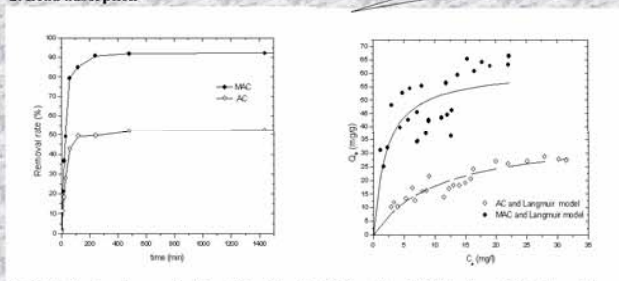


Fig. 5. The Pb adsorption as a function of time (A) at C<sub>0</sub>=21.32mg L<sup>-1</sup> and Solid loading = 0.33 g L<sup>-1</sup>, and the equilibrium isotherm (B) at buffer (acetate)=0.01M, pH=5.0(±0.2); and T=25°C

### 3. Effect of pH on Pb<sup>2+</sup> removal

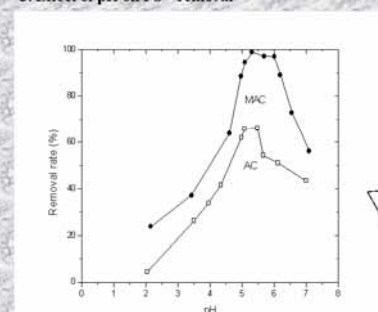
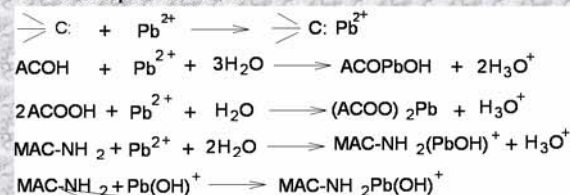


Fig. 6 Effect of solution pH on the Pb<sup>2+</sup> removal, C<sub>0</sub>=31.41mg L<sup>-1</sup>

The pH-dependent adsorption could be accounted for by the pH impacts on the association/dissociation of surface function groups of adsorbents, surface charges, formation of ion species, and the interactions between functional group and metal ions.

### 4. Lead Adsorption Mechanisms



It is believed that a combination of more negatively charged surface and presence of amine function groups as induced by the modification could be responsible for enhanced Pb adsorption by MAC.

## SUMMARY

- This study illustrates that the chemical modifications of activated carbon through the SOCl<sub>2</sub> and ethylenediamine treatments would effectively introduce amine groups on the surface as verified by the SEM-EDS and FT-IR.
- Adsorptive experiments of kinetics and equilibrium isotherm indicated that modified activated carbon showed a faster adsorption rate and a 62% higher capacity for Pb ions as compared with pre-treated activated carbon.
- Enhanced adsorption is likely caused by a combination of negative charges and presence of amine function groups on the surface as induced by the modifications through electrostatic interactions and/or surface complexation.

## ACKNOWLEDGMENT

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