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Chemical Engineering Research and Design

journal homepage: www.elsevier.com/locate/cherd

# Polyethylenimine modified activated carbon as novel magnetic adsorbent for the removal of uranium from aqueous solution

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ARTICLE INFO

*Article history:*
Received 4 August 2016
Received in revised form 14 October 2016
Accepted 17 October 2016
Available online 25 October 2016

*Keywords:*
Polyethylenimine
Activated carbon
Adsorption
U(VI) removal
Factorial design
Kinetics and thermodynamics

ABSTRACT

In this study, the polyethyleneimine modified activated carbon/Fe (PAF) was prepared and used as an effective magnetic adsorbent to remove uranium (U(VI)) ions from aqueous solution as a function of batch adsorption parameters. The developed magnetic adsorbent was investigated by FT-IR, SEM, EDX, TG/DSC and BET techniques. The effects of the adsorption parameters on the sorption amount were investigated by using factorial design. In order to study the sorption behavior for U(VI) ions, the Langmuir, and Freundlich isotherm models were applied to fit the equilibrium data. The monolayer adsorption capacity of the magnetic sorbent for U(VI) was determined to be 115.31 mg $g^{-1}$ at pH 5, 20 °C and 60 min. The kinetic results indicated that the pseudo-second-order kinetic modeling fits the equilibrium data well under employed temperature conditions. The thermodynamic examinations showed exothermic and spontaneous adsorption process. The reusability-cycling test indicated that the magnetic sorbent has good desorption performance. It was also concluded that the PAF magnetic material can be used as an effective adsorbent for the removal of U(VI) ions from wastewaters by taking into account its advantages such as being of cost effective, easy prepare and environmental friendly.



## 1. Introduction

Uranium is considered to be the most hazardous pollutant due to its chemical toxicity and radioactivity (Xie et al., 2008). Large amounts of uranium have been discharged into the environment through nuclear industry or ore mining. Uranium is responsible for a number of health problems (Raff et al., 2003). There is a great deal of work needed to monitor and remove the trace levels of radioactive contaminants of uranium due to their high toxicity and long half-life. It is present in low quantities in wash stream coming out of nuclear reactors. The maximum uranium concentration in drinking water and sea water also is reported less than 9 μg $L^{-1}$ and 1–3 ng $mL^{-1}$, respectively (WHO, 1998).

Various methods have been employed for recovery and removal of uranium from effluents and wastewater. Ion exchange (Huikuri and Salonen, 2000), biosorption (Raff et al., 2003), liquid membrane (Hayworth et al., 1983), solid phase extraction (Aydin and Soylak, 2007) and ultrafiltration (Villalobos-Rodríguez et al., 2012) are the most frequently used methods. Moreover, adsorption is one of the most effi-

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http://dx.doi.org/10.1016/j.cherd.2016.10.030

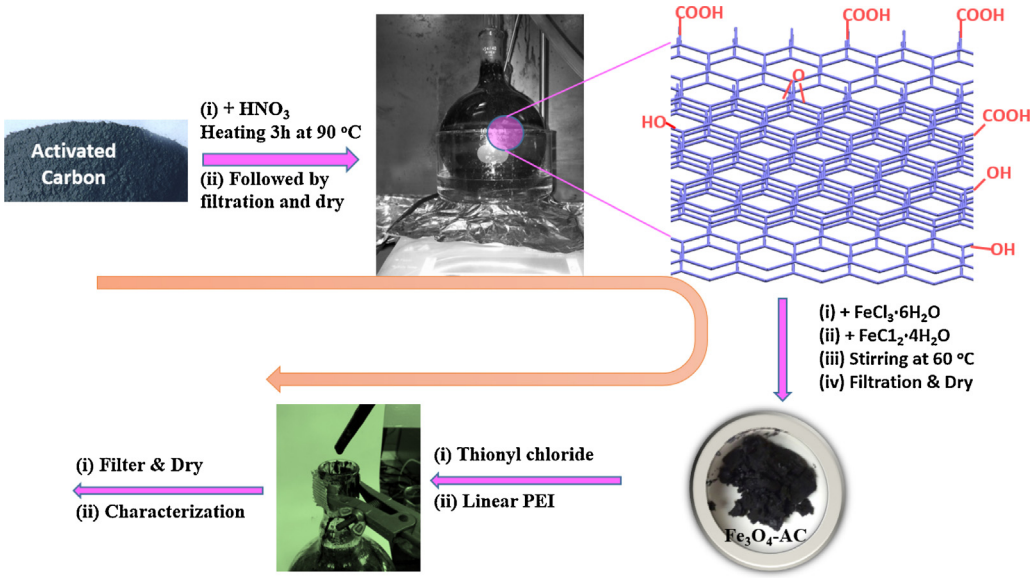


**Fig. 1 – Illustration for the preparation of PAF magnetic sorbent.**

cient, attractive and reliable processes to remove uranium ions. In this regard, different adsorbents such as graphene oxide-activated carbon felt polyhydroxyethylmethacrylate-pumice (Akkaya, 2013), coal mining waste (Mahramanlioglu et al., 2007) and activated bentonite (Aytas et al., 2011) have been used for remediation of uranium from aqueous solutions.

On the other hand, it is very important to synthesize a new adsorbent with outstanding stability and adsorptivity. Various kinds of adsorbents have been widely investigated for the sorption of pollutants (Alswat et al., 2016; Saleh, 2015; Saleh and Al-Saadi, 2015; Kraj et al., 2014; Saleh, 2013). Although the design and synthesis of adsorbents have made great progress, the cost of many synthetic adsorbents is relatively higher in comparison with the natural waste products (Misaelides et al., 1995; Moyes et al., 2000; Saleh et al., 2017; Sprynskyy et al., 2011; Sylwester et al., 2000). The composites of the different materials attracted increasing interest due to the abundance of different active sites (Salavagione et al., 2011). These materials have many micropores and also contain meso and macro-pores that are beneficial to enhance the adsorption capability of target materials (Ahmadpour and Do, 1995). These materials have also other advantages including high specific surface area, mechanical strength, and easy regeneration as compared to other sorbents. Such advantages make the adsorbents potential to be used as excellent adsorbents for extraction of organic and inorganic toxicants from real samples (Shah et al., 2013).

According to our literature survey, low cost and effective magnetic adsorbent synthesized from linear polyethyleneimine modified activated carbon for removal of uranium ions was rarely concerned. With this regard, in this study, the polyethyleneimine modified activated carbon/Fe (PAF) was prepared and used as a novel magnetic sorbent to investigate its facility in the removal of uranium ions. This work was focused on carrying out the following targets; (i) to study the structure of the magnetic adsorbent by FT-IR, SEM, EDX, BET and TG/DSC techniques; (ii) to evaluate the adsorption properties of the adsorbent for U(VI) (iii) to explore the structure/properties relation and the adsorption mechanism.

## 2. Materials and methods

### 2.1. Materials

Ferrous chloride tetrahydrate ($FeCl_2{\cdot}4H_2O$), ferric chloride hexahydrate ($FeCl_3{\cdot}6H_2O$), ammonium hydroxide 30% $NH_3$ in water, diethylene glycol, deionized water, linear polyethylenimine, average $M_n$ 2500, PDI < 1.2, formula $(CH_2CH_2NH)_n$ were obtained from Sigma–Aldrich and used in this study. $(CH_3COO)_2UO_2{\cdot}2H_2O$ was obtained from Merck, Darmstadt, Germany.

### 2.2. Preparation of the magnetic linear polyethylenimine-activated carbon (PAF)

The activated carbon (AC) prepared according to previous work (Saleh and Danmaliki, 2016a,b), was modified by $Fe_3O_4$ magnetic nanoparticles by co-precipitation of $FeCl_3{\cdot}6H_2O$ and $FeC1_2{\cdot}4H_2O$ in aqueous solution. About 7 g of the AC was dispersed in the mixture of deionized water (200 mL), ethanol (50 mL) and diethylene glycol (20 mL). The mixture was stirred for overnight. Ferric and ferrous precursor's solutions (1 M each) were added to the mixture and stirred at 50 °C for 4 h, followed by addition of ammonium hydroxide till the pH was around 9. The mixture was stirred for another 8 h at 70 °C and then separated. The obtained material was treated with $SOCl_2$. After that, the obtained material was modified with polyethylenimine by adding the linear polyethylenimine solution. The obtained mixture was stirred for 12 h at 50 °C and then cooled, filtered and dried. The preparation process for the composite was illustrated in Fig. 1.

### 2.3. Batch sorption procedure

Uranium stock solution of 1000 mg $L^{-1}$ was prepared from $(CH_3COO)_2UO_2{\cdot}2H_2O$. Sample solutions containing 10 mg $L^{-1}$ U(VI) was prepared from the stock solution with pH 5 acetate buffer solutions. A pH meter (Sartorius pp-15, Germany) was employed to measure pH values. Perkin Elmer Lambda 35 model UV–vis spectrometer (USA) was used for uranium measurement. PAF magnetic sorbent was then added and the mixture was shaken for desired contact time on a thermostatic reciprocating shaker (Selecta multimatic-55, Spain) at 120 rpm. The time required for reaching equilibrium was estimated by drawing samples at regular intervals of time until equilibrium was reached. The adsorbent can be easily separated from the mixture using a simple magnet. The concentration of U(VI) in the filtrate was analyzed by UV–vis spectrophotometer at 560 nm. The batch sorption procedure mentioned above were repeated at different experimental parameters. To ensure the accuracy, reliability, and repro-