# Kinetics, thermodynamics and surface heterogeneity assessment of uranium(VI) adsorption onto cation exchange resin derived from a lignocellulosic residue

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ABSTRACT

A new cation exchange resin (PGTFS–COOH) having a carboxylate functional group at the chain end was prepared by grafting poly(hydroxyethylmethacrylate) onto tamarind fruit shell, TFS (a lignocellulosic residue) using potassium peroxydisulphate–sodium thiosulphate redox initiator, and in the presence of N,N′-methylenebisacrylamide (MBA) as a crosslinking agent, followed by functionalisation. The adsorbent was characterized with the help of FTIR, XRD, scanning electron micrographs (SEM), and potentiometric titrations. The kinetic and isotherm data, obtained at optimum pH value 6.0 at different temperatures could be fitted with pseudo-second-order equation and Sips isotherm model, respectively. An increase in temperature induces positive effect on the adsorption process. The calculated activation energy of adsorption ($E_a$, 18.67 kJ/mol) indicates that U(VI) adsorption was largely due to diffusion-controlled process. The values of adsorption enthalpy, Gibbs free energy, and entropy were calculated using thermodynamic function relationships. The decrease in adsorption enthalpy with increasing U(VI) uploading on the adsorbent, reflects the surface energetic heterogeneity of the adsorbent. The isosteric heat of adsorption was quantitatively correlated with the fractional loading for the U(VI) ions adsorption onto PGTFS–COOH. The results showed that the PGTFS–COOH possessed heterogeneous surface with sorption sites having different activities.

## 1. Introduction

Application of plant wastes as adsorbents for removing heavy metal ions from wastewater is a well acknowledged procedure. Majority of adsorption studies have been focused on untreated plant wastes such as sago waste [1], grape stalk wastes [2], peanut hull [3], salt bush leaves [4], etc. Although these plant wastes were cheap and easily available, the application of untreated plant wastes in adsorption process also causes several problems such as high chemical oxygen demand (COD) and biological oxygen demand (BOD) as well as low adsorption capacity due to the release of soluble organic compounds contained in the plant materials [5].

It is well known that chemically modified plant wastes exhibit higher adsorption capacity than unmodified forms. Recently Wan Ngah and Hanafiah [6] reviewed the use of chemically modified plant wastes as adsorbents for the removal of heavy metal ions from wastewater. Different types of modifying agents were used for the chemical modification and the adsorption capacity of these

modified plant wastes were reported in the literature [7–13]. Among the chemical modification methods, the grafting of new functional groups on the back bone of plant wastes has frequently been regarded as an interesting process because: (a) grafting increases the density of adsorption sites, (b) grafting changes the pH range for metal adsorption and (c) grafting changes the adsorption mechanism thereby increasing the adsorption selectivity. Although crosslinking reduces the adsorption capacity of adsorbent due to the consumption of the functional groups, various crosslinking procedure may be performed along with graft copolymerization in order to reduce the swelling capacity of adsorbent and also to improve the mechanical strength. The impact of crosslinking agent in adsorption performance depends on the nature of adsorbent and when an ion exchange mechanism is involved in metal uptake, crosslinking has a significantly lower influence on metal sorption capacities [14]. Functionalisation treatments were also executed on the polymer grafted materials to improve the adsorption performance through spacer effect [15].

Although a large number of papers were devoted to the adsorption of metal ions, most of them focus on the evaluation of adsorption performances and only a few of them aim at gaining a better understanding of adsorption mechanisms. In the present work, a new cation exchanger (PGTFS–COOH) having carboxylate

functional group at the chain end is prepared by graft copolymerization of hydroxyethylmethacrylate (HEMA) onto TFS in the presence of N,N′-methylenebisacrylamide (MBA) as a crosslinking agent followed by functionalisation treatments and it is utilized for the removal of U(VI) ions from aqueous solutions. Batch adsorption kinetic studies were conducted and the data were modeled using pseudo-first-order and pseudo-second-order equations. Experimental equilibrium data were fitted to the Langmuir, Freundlich, Sips, Toth, Redlich–Peterson and Radke–Prausnitz isotherm equations to determine the best-fit isotherm model. Thermodynamic parameters revealing the adsorption mechanism were evaluated using equilibrium data. Since the variation of isosteric heat of adsorption with surface loading implies surface energy heterogeneity of adsorbent, the role of surface heterogeneity on U(VI) adsorption was investigated and quantitatively correlated with surface loading. The underlying mechanisms involved in the adsorption process were discussed in detail.

## 2. Experiment

### 2.1. Materials

TFS used for the preparation of the adsorbent was collected from a local market, washed with distilled water to remove the surface impurities and dried at 80 °C in an oven. The dried TFS was powdered and particles of 80–230 mesh size were used for chemical modification. The chemicals used throughout the study were of analytical grade. Hydroxyethylmethacrylate was obtained from Fluka (Switzerland). N,N′-methylenebisacrylamide and sodium diethyldithiocarbamate were procured from Aldrich (WI, USA). Potassium persulphate ($K_2S_2O_8$), sodium thiosulphate ($Na_2S_2O_3$), ethylenediamine (en) and 1,4-dioxane (99.9% purity) were obtained from E-Merck, India. Stock solution of U(VI) (1000 mg/L) was prepared by dissolving an accurately weighed amount of $UO_2(NO_3)_2 \cdot 6H_2O$ (Fluka) in distilled water and other working solutions with U(VI) concentrations ranging between 10 and 300 mg/L were prepared by appropriate dilution of the stock solution. The pH of the working solutions was adjusted to the desired value by the addition of 0.1 M HCl or 0.1 M NaOH solutions.

### 2.2. Preparation of adsorbent and methods of analysis

The general procedure adopted for the preparation of PGTFS–COOH is presented in Scheme 1. To 50 g of TFS powder suspended in 75 mL distilled water in a glass reactor, 0.346 M MBA, 0.134 M potassium persulphate ($K_2S_2O_8$) and 0.05 M sodium thiosulphate ($Na_2S_2O_3$) were added. Nitrogen was purged for 10 min in order to remove the dissolved oxygen. HEMA (3.21 M) was added into the reaction mixture and stirred vigorously at 70 °C for 2 h. The product was filtered, washed with hot water and dried under vacuum at 40 °C. To introduce the spacer group, the grafted

polymer was refluxed with ethylenediamine (en) at 90 °C for 6 h. The product was filtered and washed with 1,4-dioxane and dried at 80 °C. The carboxyl functional group was introduced by refluxing the material with equal part by weight of succinic anhydride (SA) in 1,4-dioxane at constant pH 4.0 and at 100 °C for about 6 h. The contents were then washed repeatedly with 1,4-dioxane and finally with ethanol, dried and powdered. The powdered PGTFS–COOH was sieved into particle size with average diameter of 0.096 mm, represented as 80–230 mesh, using standard sieves and was used for adsorption studies.

The FTIR spectra of TFS, PGTFS–COOH and U(VI)-loaded PGTFS–COOH were obtained using the pressed disc technique in a PerkinElmer IR-180 spectrophotometer. Scanning electron micrographs (SEM) were taken on a Philips XL 30 CP scanning electron microscope. The XRD patterns of the adsorbents were recorded using a Siemens D 5005 X-ray unit with Ni-filtered Cu $K_\alpha$ radiation. Thermal stability of the adsorbents was studied with a Metler Toledo Star thermo gravimetric analyzer. The surface area and total pore volume of the adsorbent were determined using a Quantasorb surface area analyzer (QS/7). A Systronic microprocessor pH meter (model 362) was used for pH measurements. A temperature controlled water bath shaker (Labline, India) was used for shaking all the solutions. The concentration of U(VI) in solutions before and after adsorption was measured using a Jasco V-530 UV–vis spectrophotometer. The total acidic and carboxylic acid groups were determined using Boehm titration method [16]. Potentiometric titration was done to determine the point of zero charge ($pH_{pzc}$) [17]. The cation exchange capacity (CEC) was determined by the column process using 1.0 M $NaNO_3$ as the eluent at a flow rate of 0.5 mL/min [18]. The apparent density of the adsorbent was measured using pycnometric method in which nitrobenzene was used as displacing liquid.

### 2.3. Adsorption experiments

Batch adsorption experiments were performed by adding 0.1 g of adsorbent to a series of Erlenmeyer flasks containing 50 mL solutions of desired U(VI) concentrations. The effect of initial solution pH on U(VI) adsorption was studied with an initial concentrations of 10 and 25 mg/L and adjusting the pH between 2.0 and 8.0 using 0.1N HCl and NaOH solutions. The effect of temperature on adsorption kinetics was studied with an initial U(VI) concentration of 100 mg/L. The flasks were agitated at 200 rpm in a temperature controlled water bath shaker set within the temperature range 30–60 °C. The solutions were withdrawn from the flasks at different time intervals and the concentration of U(VI) in the filtrate was determined using spectroscopic method [19] based on coloured complex formed with sodium diethyldithiocarbamate in aqueous medium. Equilibrium studies were also conducted within the concentration range 10–300 mg/L. After 2 h equilibrium time, the supernatants were removed by
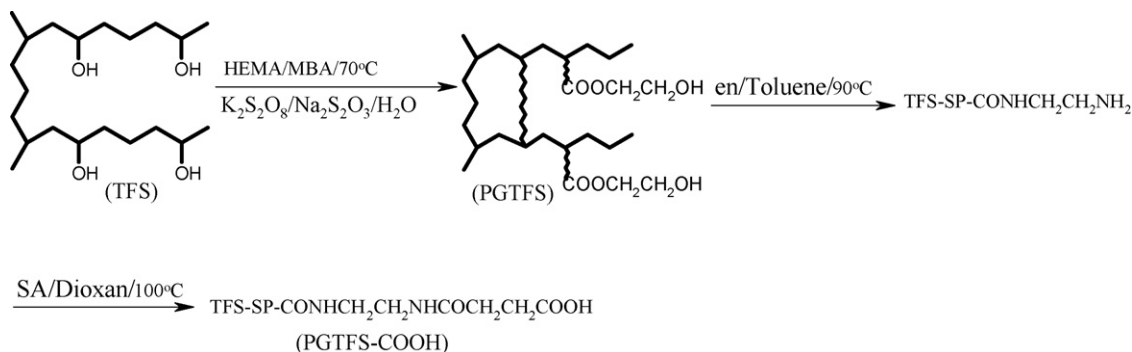


**Scheme 1.** Preparation of PGTFS–COOH.