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# Adsorption potency of imprinted Starch/PVA polymers confined ionic liquid with molecular simulation framework

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ABSTRACT

The present work evaluates sorption competency of ion imprinted starch/PVA assimilated with RTIL nanofibers and virtual molecular modelling to ascertain inter-polymer miscibility parameters and compatibility, via Materials Studio software, for effectual radioactive thorium ion exclusion. The experimental statistics suggested high sorption efficacy (87%) at ecologically optimum conditions, i.e. pH 7, 0.5 g adsorbent dose, and best compliance with Langmuir isotherm model ($R^2 = 0.975$), among 2 parameter and 3 parameter models, along with close resemblance to Pseudo second order kinetics ($R^2 = 0.968$) revealed monolayer sorption mode with chemisorption as rate restraining step. Surface topography and morphology assessed by SPIP image processing software, BET and FESEM techniques advocated superior sorption ability for imprinted nanofiber system. In addition, the interaction between Starch-PVA estimated Chi parameter and mixing energy (kcal/mol) to be 1.63 and 1.90, respectively, and revealed better compatibility for Starch-RTIL blend.



## 1. Introduction

Recondite worldwide challenges provoked by the exploitation of carcinogenic radioactive tetravalent thorium metal ions in nuclear industries have urged an emergency for the efficient attenuation of lethal content to maintain the ecological balance [1,2]. The accumulation of thorium ions in the human body over a period of time leads to neurotoxicity and noxious diseases. Hence, the removal of these elements from effluent is a topic of continued research. Several physico-chemical processes are known for the waste water treatment such as filtration, flocculation, chemical and electrochemical oxidation, ozone treatment and adsorption [3]. With the avail of cost efficiency and high competence, sorption is a best-suited technique for heavy metal ion sequestration [4]. Previous state of art depicts considerable use of myriad of efficient adsorbents such as silk fibroin [5], muscovite [6], perlite [7], activated charcoal [8], synthetic resins [9], etc. for Th (IV) ion sorption but their randomly cross-linked network structure evoked concerns associated with degree of sorption. Biomaterials have become an alternative to traditional methods of industrial wastewater treatment owing to its high sorption capacity, recyclability, and low cost. The current research work scrutinizes applicability of ion-imprinted Starch/PVA electrospun nanofibers blended with RTIL adsorbent system for expulsion of thorium ions.

Herein, biocompatible, non-toxic starch, containing abundant hydroxyl groups, has been incorporated with 1 butyl 3 methylimidazolium tetrafluoroborateionic liquid (RTIL) in order to augment the tuning of macromolecules into fibres, and hydrophilicity was enhanced by the inclusion of fibre forming biodegradable and water soluble synthetic polymer, PVA interacting strongly with starch through hydrogen bonding. Molecular imprinting technology, for selective recognizing and entrapment of ions through chemical linking in the imprinted cavity, and electrospinning technique, for high porosity and immense surface area, were employed. The inter-polymer correlation and molecular interaction has been explored via computer-aided modelling using Accelrys Materials Studio software to evaluate the miscibility factors (i.e. Chi parameter and mixing energy) of the blend system. The adsorptive exclusion of toxic thorium (IV) ions from counterfeit effluent systems using beads, with best formulation, was assayed under varied experimental factors viz. pH value, amount of adsorbent. The practicality of the Starch-PVA RTIL imprinted nanofiber system was elucidated further by evaluating the 2 parameter and 3 parameter sorption isotherms along with kinetic models and thermodynamics.

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**Nomenclature**

$a_R$ Redlich–Peterson isotherm constant (L/mg)
$a_S$ Sips isotherm model constant (L/mg)
$A_T$ Temkin isotherm equilibrium binding constant (L/g)
$b$ Langmuir isotherm constant ($dm^3$/mg)
$b_T$ Temkin isotherm constant
$C_e$ Equilibrium concentration (mg/L)
$g$ Redlich-Peterson isotherm exponent
$k_1$ Pseudo-first order adsorption rate constant ($min^{-1}$)
$k_2$ Pseudo-second order rate constant (g/ mg min)
$K_F$ Freundlich isotherm constant (mg/g) ($dm^3$/g)$^n$ related to adsorption capacity
$K_{int}$ Intra-particle diffusion rate constant (mg/ g $min^{1/2}$)
$K_L$ Langmuir isotherm constant (L/mg)
$K_R$ Redlich–Peterson isotherm constant (L/g)
$K_S$ Sips isotherm model constant (L/g)
$n_A$ Number of repeat units of starch
$n_B$ Number of repeat units of PVA or RTIL
$q_e$ Amount of adsorbate on adsorbent surface at equilibrium (mg/g)
$q_{max}$ Maximum adsorption capacity (mg/g)
$R^2$ Correlation coefficient
$\alpha$ Initial adsorption rate
$\beta_S$ Sips isotherm model exponent
$\chi$ Chi parameter

## 2. Experimental details

### 2.1. Materials and apparatus

Starch extracted from *Solanumtuberosum*, Thorium nitrate (N4O12Th) (Kemphasol, India), Polyvinyl alcohol, HCl, Glutaraldehyde (Sigma Aldrich) were obtained for carrying out the experiments. Sterile de-ionized $H_2O$procured from Millipore-MilliQ system was expended during the overall research work. Brunauer-Emmett-Teller (BET) technique (Microtrac SAA, India) for computing specific surface area, Perkin Elmer UV–vis Spectrophotometer (Lambda-35, Germany) for quantitative determination of metal ion uptake, and Field emission scanning electron microscopy (Carl Zeiss, AG, JSM −6700F Germany) and image meterology software (SPIP) to analyse morphological characteristics of imprinted hydrogel nanofibers were employed.

### 2.2. Methods

The extraction of starch from *Solanumtuberosum* [10] was followed by preparation of a homogeneous polymer solution comprising 5 wt.% starch with 20 wt.% PVA (polyvinyl alcohol) along with 1 wt.% RTIL and 2 wt.% glutaraldehyde (crosslinker) at 45 °C temperature [11]. The thorium ion imprinted solution uniformly admixed with aforesaid solution was, hence, collected as nanofibers by electro-spinning at 11.5 kV voltage and 0.54 μL/min flow rate with tip to collector distance of 12 cm which were then dried under IR lamp and subsequently treated with HCl (37%) solution at pH 5 to collect out the thorium ion, and were neutralised with water followed by drying at room temperature [12]. Batch sorption experiment was carried out under optimized parameters like pH, adsorbent concentration using Ultraviolet Visible (UV-VIS) Spectrophotometer with Arsenazo (III) reagent at ambient temperature for 105 min to study the sorption behaviour of Th (IV) ions over the ion imprinted Starch-PVA nanofibers [13]. Furthermore, time-dependency for Th (IV) ion sorption from aqueous media was inspected at all standardized conditions i.e. pH 7, 0.5 g adsorbent in a constant volume (20 mL) of each solution using stock solution of 1000 ppm Th $(NO_3)_4$ in D.I water. The flasks containing adsorbate and adsorbent were agitated on mechanical shaker at 600 rpm and supernatant was filtered after regular time interval of 15 min to evaluate the residual Th (IV) ion concentration. Data processing to study the sorption isotherms and kinetics was carried out by the ORIGIN-PRO 8.0 software (OriginLab Corporation, MA, U.S.A). The sorption potency (%Ad) and sorption efficacy ($q_e$) were evaluated as:

$$\%Ad = \left(\frac{C_o - C_e}{C_o}\right) \times 100 \quad (1)$$

$$q_e = \frac{C_o - C_e}{M} V \quad (2)$$

where,$C_o$ and $C_e$ are respectively the initial and equilibrium concentrations of metal ion (mg/L); M is the mass of the adsorbent (g); V is the volume of Th (IV) solution (mL).

## 3. Results and discussion

### 3.1. Interaction study

The molecular simulation analysis,at 298 K reference temperature, on Starch-PVA blend and Starch-RTIL blend, by Accelrys Materials Studio associating modified Florry Huggins model [14], employed geometrically optimized monomer units of Starch, PVA

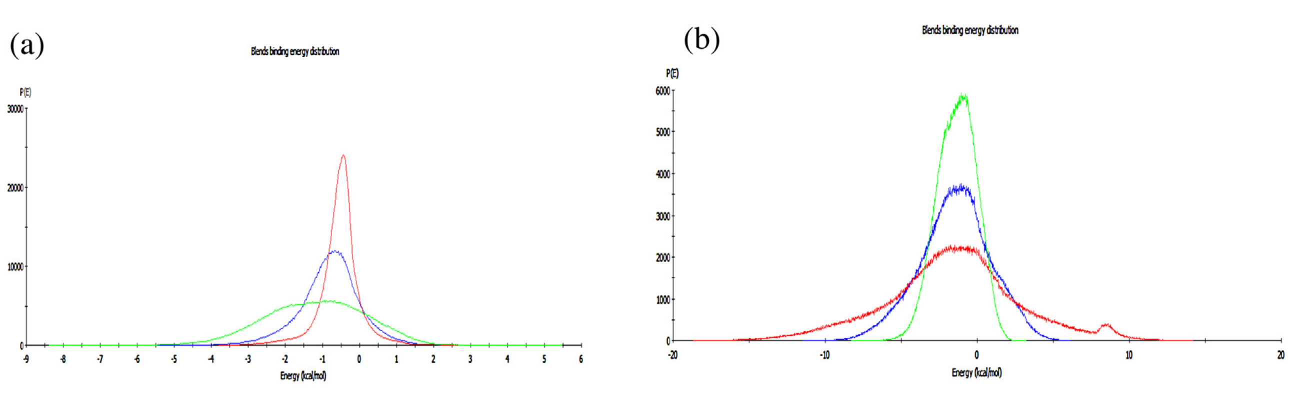


**Fig. 1.** Binding energy curves for (a) Starch-PVA, (b) Starch-RTIL (more similar distribution resembles more compatible system).