PHYSICAL CHEMISTRY 2014

12th International Conference
on Fundamental and Applied Aspects of
Physical Chemistry

The Conference is dedicated to the
25. Anniversary of the Society of Physical Chemists of Serbia

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September 22-26, 2014
Belgrade, Serbia

ISBN 978-86-82475-30-9
Title: PHYSICAL CHEMISTRY 2014 (Proceedings)
Editors: Ž. Čupić and S. Anić
Published by: Society of Physical Chemists of Serbia, Studenski trg 12-16, 11158, Belgrade, Serbia
Publisher: Society of Physical Chemists of Serbia
For Publisher: S. Anić, President of Society of Physical Chemists of Serbia
Printed by: “Jovan” Priting and Publishing Company; 200 Copies;
Number of pages: 6+ 441; **Format**: B5; Printing finished in September 2014.

Text an Layout: “Jovan”

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12th International Conference on Fundamental and Applied Aspects of Physical Chemistry

Organized by
The Society of Physical Chemists of Serbia

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EFFICIENT SEPARATION OF Tc-99 FROM AQUEOUS SOLUTION USING PINECONE ACTIVATED CARBON

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ABSTRACT

Sorption of radioactive ^{99}Tc-pertechnetate onto activated carbon prepared from pinecones was investigated. The parameters of contact time and Tc-99 concentration were varied. It was established that the sorption half-life, $t^{1/2}$, was very short ~ 2.2 min, thus making this sorbent an excellent candidate for immediate pollution remediation, which is very important in the case of nuclear accidents. The kinetic data were found to follow closely the pseudo-second-order (PSO) kinetic model. Boyd model established the sorption dependence only on film diffusion. The partitioning/distribution coefficient, K_d, attained was 2729 cm^3 g^{-1}. The equilibration time was 3 h at room temperature (T=298 K).

INTRODUCTION

High surface area, remarkable sorption capacity and efficient regeneration are among the most important characteristics of the non-hazardous porous activated carbon sorbent [1]. Diverse surface organic functional groups (ionized in solution depending on pH) are responsible for surface reactivity of activated carbon.

Tc-99 is among many hazardous radioisotopes often detected in the environment, being a long life (2.13 x 10^5 years) pure ß-emitter and has a specific activity of 629.0 MBq g^{-1}**.** It is produced in large amounts by nuclear fission of ^{235}U or ^{239}Pu in nuclear reactors**.** The predominant form of Tc-99 under oxic conditions in surface and ground waters is pertechnetate oxyanion ($^{99}TcO_4^-$), which is poorly sorbed by natural materials, highly soluble in water, and thus readily mobile in the environment [2]. Activated carbon has been demonstrated to retain $^{99}TcO_4^-$ efficiently in deionized water and the solutions of various electrolytes [3,4]. The high cost of commercially produced activated carbon prompted research on novel, more efficient, low-cost, locally available and renewable activated carbonaceous materials. In this paper, pinecone-activated carbon was tested as sorbent for $^{99}TcO_4^-$, using an easily measurable metastable nuclear isomer Tc-99m, rapidly decaying to Tc-99. Kinetic data for Tc(VII) removal was collected and fitted to kinetic models, and K_d was evaluated.

EXPERIMENTAL

Powdered activated carbon was derived by thermal–chemical process from the ground pinecones collected from Čair Park in Niš, Serbia; the BET surface area (S_{BET}) measurement of the sample was made by nitrogen adsorption at 77 K using Sorptomatic 1990 (Thermo Fisher Scientific, USA), the surface functional groups and pH_{PZC} were determined using the procedures described previously [1]. $^{99m}TcO_4^-$ sodium solution was eluted from $^{99}Mo/^{99m}Tc$ generator (Vinča Institute of Nuclear Sciences). $^{99m}TcO_4^-$ uptake from aqueous solutions was monitored at room temperature (T=298 K) in static experiments. 10 mg of sorbent was contacted with 4 cm^3 of ^{99m}Tc-pertechnetate aqueous solution at unadjusted pH. A blank experiment (no sorbent) was prepared in the same manner. At predetermined time intervals, solid phase was separated from the solutions by centrifugation: 5 min 3000 rpm (Heraeus-Christ Labofuge III Centrifuge, 6000 Max RPM, American Laboratory Trading, Inc.). From each vial (blank and sorbent containing), 100 mm^3 aliquots were taken and residual radioactivity was measured in supernatant solution. The specific activity of pertechnetate eluate was determined by a Capintec CRC-15β dose calibrator and adjusted by adding saline solution to 4.35 GBq dm^{-3}. All ^{99m}Tc supernatant analyses were carried out using a 2πγ-solid-state scintillation detector (LKB Wallac 1282 Compugamma, Finland) with autosampler. Relative measurements of sorbed radioactivity were obtained using the following equation (R-sorbed pertechnetate activity (%), R_b-measured activity of reference or blank aliquot (cpm), R_s-activity of the supernatant aliquot (cpm)):

$$R = \frac{R_b - R_s}{R_b} \cdot 100\%$$

The sorption isotherms were measured by mixing 10 mg of activated carbon with 4 cm^3 sodium pertechnetate solution with the specific activity ranging from 11.9 to 95.6 GBq dm^{-3}. The equilibration time was 3 h.

RESULTS AND DISCUSSION

The characteristics of pinecone-activated carbon are given in Table 1. As known, predicting the rate at which sorption takes place in a given system is one of the critical factors in sorption system design. To the best of our knowledge, there is an obvious lack of literature regarding modeling the kinetics of ^{99}Tc removal. Here, the kinetics of $^{99m}TcO_4^-$ sorption on pinecone activated carbon was examined using two kinetic models: PSO [5] and Boyd model with Reichenberg approximation [6] (Table 2), where Q_{eq} and Q_t denote the amounts of sorbed pertechnetate anions at equilibrium and at time t, respectively, k_2 - the rate constant of PSO sorption, $h=k_2Q^2_{eq}$ - the initial rate constant, F - the fractional attainment of equilibrium at time t, n - an integer defining infinite series solution and Bt - a mathematical function of F.

The correlation coefficient (R^2) for PSO model was equal to 0.999 suggesting that the $^{99m}TcO_4^-$ sorption on activated carbon obeyed PSO model (Table 3), indicating chemisorption involving valence forces through sharing or exchange of electrons between activated carbon functional groups and $^{99m}TcO_4^-$ [5].

Table 1. Relevant characteristics of pinecone activated carbon [1].

pH_{PZC}	3.06
S_{BET}, $m^2\ g^{-1}$	1094
Surface functional groups, mmol g^{-1}	
Carboxylic	1.742
Lactonic	0.723
Phenolic	0.493

Q_e and Q_e^{calc} values obtained for PSO model fit showed excellent agreement confirming this assumption. The very short $t_{1/2}$ as well as very high h and Q_e values suggest that this activated carbon can be regarded as a highly efficient sorbent for ^{99}Tc. The Boyd plot does not pass through the origin in the shape of a straight line, thus implying that the process is film-diffusion controlled [6].

Table 2 Kinetic models.

Kinetic model	Equation	Ref.
PSO	$\frac{t}{Q}=\frac{1}{k_2Q_e{}^2}+\frac{1}{Q_e}t \qquad h=k_2Q_e^2$	[5]
Boyd equation	$F=1-\frac{6}{\pi^2}\sum_{n=1}^{\infty}\frac{1}{n^2}\exp\left(-n^2Bt\right)$	[6]

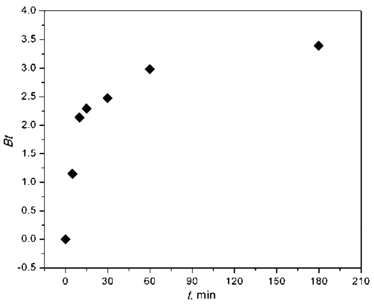

Figure 1. Boyd model.

In an attempt to avoid toxic radiation doses, the equilibrium investigation was limited to the linear isotherm part [4]. K_d (cm^3 per g) was calculated according to the equation $S = K_dC$, where S represents the sorbed Tc activity on sorbent surface (GBq per g of activated carbon) and C is the equilibrium specific Tc activity (GBq per dm^3 of solution). The Oak Ridge National Laboratory investigated several synthetic resins for $^{99}TcO_4^-$ removal from contaminated wastewater and also found linear adsorption isotherms, with

K_d values ranging from 902 cm^3 g^{-1} to 2370 cm^3 g^{-1} [7]. Holm et al. found the maximum K_d in the order of 10^6 cm^3 g^{-1} at pH 2±4 for activated carbon; the equilibrium time was ca. 5 h, at room temperature, from deionized water [3]. Gu and associates found that K_d of $^{99}TcO_4^-$ exceeded 27000 cm^3 g^{-1} when actual groundwater was used, as well as 12000 cm^3 g^{-1} when background solutions of 0.01 M $CaCl_2$ and Na_2SO_4 were treated, after overnight equilibration [4].

Table 3. PSO kinetic model parameters.

Q_e, GB g^{-1}	1.71
$t_{1/2}$, min	2.2
Q_e^{calc}, GB g^{-1}	1.71
k_2, g GB $^{-1}$ min^{-1}	0.351
h, GB g^{-1} min^{-1}	1.024
R^2	0.999

CONCLUSION

Activated carbon prepared from pinecones was investigated as a sorbent of radioactive $^{99}TcO_4^-$. Very short $t^{1/2}$ (~ 2.2 min) indicated that this sorbent can be an excellent candidate for immediate pollution remediation. The kinetic data adhered closely to PSO kinetic model, suggesting chemisorption. Boyd model verified the sorption dependence only on film diffusion. The partitioning/distribution coefficient K_d, found was 2729 cm^3 g^{-1}, after 3 h equilibration time at room temperature (T=298 K).

ACKNOWLEDGEMENT

This work was supported by the Ministry of Education, Science and Technological Development Republic of Serbia (Grants no. TR 37021 and III 43009).

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