# 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

---

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"



200 - *Coppy priting*

PHYSICAL CHEMISTRY 2014

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

*Organized by*
*The Society of Physical Chemists of*
*Serbia*

*in co-operation*
*with*

*Institute of Catalysis Bulgarian Academy of Sciences*

*Boreskov Institute of Catalysis of Siberian Branch of the Russian Academy of Sciences*

*Faculty of Physical Chemistry, University of Belgrade, Serbia*

*Institute of Chemistry Technology and Metallurgy,*
*University of Belgrade, Serbia*

*Vinča Institute, University of Belgrade, Serbia*

*Institute of General and Physical Chemistry, Serbia*

*Faculty of Pharmacy, University of Belgrade, Serbia*

**International Organizing Committee**

*Chairman:* *S. Anić (Serbia)*
*Vice-chairman:* *M. Gabrovska (Bulgaria)*
*V. A. Sadykov (Russia)*

*Members:*
*N. Cvjetičanin (Serbia), S. N. Blagojević (Serbia), M. Daković (Serbia), T. Grozdić (Serbia), D. Jovanović (Serbia), M. Kuzmanović (Serbia), D. Marković (Serbia), J. Marković-Dimitrić (Serbia), B. Milosavljević (USA), M. Mojović (Serbia), N. Ostrovski (Serbia), I. Pašti (Serbia), M. Petković (Serbia), A. Popović-Bjelić (Serbia), B. Simonović (Serbia), D. Stanisavljev (Serbia), B. Šljukić (Serbia), N. Vukelić (Serbia), V. Vukojević (Sweden)*

**International Scientific Committee**

*Chairman:* *Ž. Čupić (Serbia)*
*Vice-chairmans:* *V. N. Parmon (Russia)*
*S. Rakovsky (Bulgaria)*

*Members:*
*B. Adnađević (Serbia), S. Anić (Serbia), A. Antić-Jovanović (Serbia), G. Bačić (Serbia), A. Kelarakis (Greece), R. Cervellati (Italy), V. Dondur (Serbia), Ivan Gutman (Serbia), S. D. Furrow (USA), K. Hedrih (Serbia), M. Jeremić (Serbia), A. V. Knyazev (Russia), Lj. Kolar-Anić (Serbia), V. Kuntić (Serbia), Z. Marković (Serbia), S. Mentus (Serbia), Š. Miljanić (Serbia), M. Perić (Serbia), M. Plavšić (Serbia), D. M. F. Santos (Portugal), G. Schmitz (Belgium), I. Schreiber (Czech), P. Sevčik (Slovakia), B. C. Simionescu (Romania), N. Stepanov (Russia), D. Todorović (Serbia), M. Trtica (Serbia), V. Vasić (Serbia), D. Veselinović (Serbia)*

**Local Executive Committee**

*Chairman:* *S. Blagojević*
*Vice-chairmans:* *A. Ivanović-Šašić*

*Members:*
*P. Banković, N. Bošnjaković, J. Dostanić, A. Đerić, A. Ignjatović, A. Jović, N. Jović-Jovičić, D. Lončarević, J. Krstić, J. Maksimović, V. Marković, M. Milenković, S. Maćešić, V. Marković, B. Nedić, N. Potkonjak, D. Ranković, M. Stević, M. Žunić, M. Ristić,*

# RESEARCH ON TREATMENT OF LIQUID RADIOACTIVE WASTE CONTAINING COBALT BY ADSORPTION ON POLY(ACRILIC ACID) HYDROGEL

N. Lazarević[1], J. Jovanović[2] and B. Adnadjević[2]

[1]*Nuclear Facilities of Serbia, Mike Petrovica Alasa 12–14, 11351 Belgrade, Vinca, Serbia*
[2]*Faculty of Physical Chemistry, Studentski trg 12-16, 11001 Belgrade, Serbia (bora@ffh.bg.ac.rs)*

## ABSTRACT
The poly(acrylic acid) hydrogel (PAA) has been suggested as adsorbent material to treat cobalt-60 in radioactive liquid waste. The kinetics of isothermal adsorption of cobalt ions from an aqueous solution onto PAA hydrogel was investigated in the temperature range from 298K to 315 K. The kinetic model of $Co^{2+}$ adsorption $[1-(1-\alpha)^{1/3}]^2=kt$, was established by using the model-fitting method. The kinetic parameters of $Co^{2+}$ adsorption ($E_a$ = 41 kJ $mol^{-1}$, $ln$ [$A$/$min^{-1}$]=12) were determined. It was found that cobalt adsorption was kinetically controlled process which is determined by the rate of three-dimensional diffusion $Co^{2+}$ ions (D3).

## INTRODUCTION
Increased operation of nuclear power plants and nuclear laboratory are the source of radioactive wastes relased into environment. Enormous amounts of low-level liquid radioactive wastes (LLRW) are being produced as a results of operation, repair and disposal at those facilities. All of these LLRW were composed of different chemical and radiochemical composition [1]. The adsorption technologies using different adsorbents may be used for removal radioactive ions very successfully. The radioactive cobalt-60 with half-life ($t_{1/2}$ = 5.27 y) in the liquid waste came from neutron activation for corrosion products. Adsorption cobalt ions by different types of adsorbents have been the subject of several studies [2-4]. As an adsorbent, hydrogels are successfully applied for the removal of pollutants from aqueous solution as they are easily applicable, have high removal capacity and can be regenerated [5]. The cobalt ion ($Co^{2+}$) removal capacities by hydrogel N,N-dimethylaminopropyl methacrylamide (DMAPMAm) homopolymer and DMAPMAm/itaconic acid (DMAPMAm/IA) copolymers were investigated by taking into account of the initial metal ion concentration and pH of aqueous medium [6].

The aim of this research is to investigate the performance of PAA hydrogel in the treatment of radioactive liquid waste contained cobalt-60. Because of that, the kinetics of isothermal adsorption of cobalt ions from an aqueous solution onto PAA was investigated.

## EXPERIMENTAL

In this research, the PAA hydrogel was synthesized by the procedure described in our previous work [7]. Adsorption of $Co^{2+}$ on PAA hydrogel was carried by the batch method. Hydrogel powder ($m$ ~ 0.1 g) was added to 200g aqueous solution of $CoSO_4$ (with $Co^{2+}$ concentration 100 mg/L) and the adsorption vessel was placed in the thermostat at pre-determined temperature (298 K, 300 K, 308 K and 315 K). During the adsorption process, the adsorption system was homogenized by stirring at 600 rpm. Samples were taken from this adsorption system at regular time intervals. After centrifugation, concentration of $Co^{2+}$ remaining in supernatant was determined by measuring the absorbance at 625 nm. The determination of $Co^{2+}$ ions as Co-(thiocyanate) was carried out according to the published procedure in literature [8]. For that measurement a UV-Visible spectrometer (Cintra 10e, GBC Scientific equipment) was used.

The specific adsorption capacity of PAA hydrogel for $Co^{2+}$ at a given temperature after certain adsorption period can be calculated from the equation: $x_s = (c_0 - c_i)m_s/m$, where: $c_0$ is the initial concentration of the $Co^{2+}$ solution before adsorption (mg/L), $c_i$ is the concentration of the $Co^{2+}$ solution after a certain adsorption time (mg/L) and $m_s$ is the mass of aqueous solution of $CoSO_4$ (g). The adsorption degree of $Co^{2+}$ ions, $\alpha$, is calculated from the equation $\alpha = x_s / x_{\max}$, where: $x_{max}$ is the maximum specific adsorption capacity of PAA hydrogel for $Co^{2+}$ at a given temperature and is determined from experimental kinetic curves.

Kinetic model of $Co^{2+}$ adsorption onto PAA hydrogel was examined by the so-called “model-fitting procedure”[9].

## RESULTS AND DISCUSSION

The isothermal dependence of specific adsorption capacity of the PAA hydrogel for $Co^{2+}$ *vs.* adsorption time (kinetic curves) is shown in Figure 1.

Applying the model fitting method we obtain that kinetics of $Co^{2+}$ adsorption on PAA hydrogel can be described by theoretical kinetic model: $[1-(1-\alpha)^{1/3}]^2=kt$, where $k$ is the rate constant of adsorption of $Co^{2+}$ on PAA hydrogel. This model is characteristic for the physicochemical processes whose kinetic is determined by the rate of three-dimensional diffusion (D3).

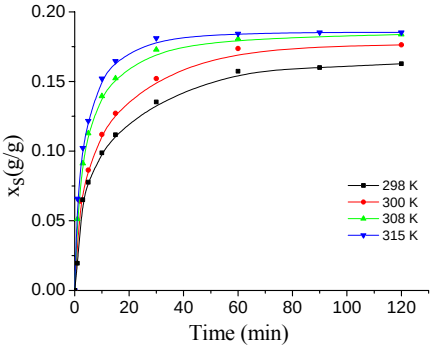


**Figure 1.** The isothermal kinetic curves of adsorption $Co^{2+}$ ions on PAA hydrogel

If model D3 describes the kinetics of the isothermal adsorption of $Co^{2+}$ on PAA, then the dependence $[1-(1-\alpha)^{1/3}]^2$ on the adsorption time should be a straight line and from slopes of these straight lines the values of model constants has been determined. Since the increase of the model constant with temperature is obtained, the kinetic parameters were determined by applying the Arrhenius equation (Table I). The change of the model constant with temperatures and kinetics parameters, activation energy ($E_a$) and pre-exponent factor ($\ln A$) for the $Co^{2+}$ adsorption is given in Table I.

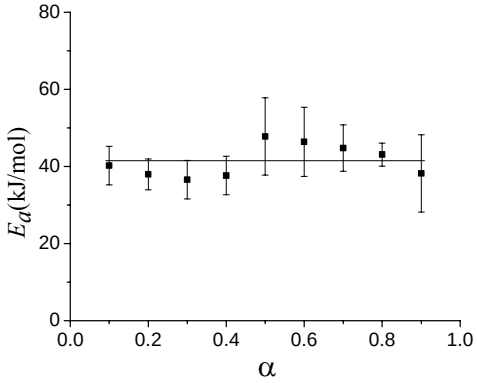


**Figure 2.** The dependence of $E_a$ *vs.* adsorption degree

With aim to investigate kinetic complexity, Friedman iso-conversional method [10] was applied to determine the dependence of the activation energy of the $Co^{2+}$ adsorption on the PAA hydrogel on the degree of adsorbed $Co^{2+}$ ions.

**Table 1.** The model constant of $Co^{2+}$ adsorption and kinetic parameters

| $T$ (K) | $k \cdot 10^{-3}$ ($min^{-1}$) | $R$ | Kinetic parameters |
|---|---|---|---|
| 298 | 7.4 ± 0.2 | 0.996 | |
| 300 | 8.31 ± 0.04 | 0.9999 | $E_a$ (kJ $mol^{-1}$) = 41 ± 4 |
| 308 | 14.1 ± 0.5 | 0.991 | ln [$A$/$min^{-1}$]= 12 ± 2 |
| 315 | 17.5 ± 0.2 | 0.999 | $R$ = 0.968 |

As can be seen from the results presented in Figure 2, the values of the activation energy are practically independent of the adsorption degree, and in accordance with the model value $E_a$ = 41 kJ $mol^{-1}$. This implies that $Co^{2+}$ adsorption on the PAA hydrogel is probably elementary process.

## CONCLUSION

The PAA hydrogel is very efficient adsorbent for removal cobalt-60 from radioactive liquid waste. The adsorption of $Co^{2+}$ions onto the PAA hydrogel is a probably kinetically elementary process, which can be modeled with the theoretical kinetic model D3 described by the equation: $[1-(1-\alpha)^{1/3}]^2=kt$.

## ACKNOWLEDGEMENT

This investigation was supported by the Ministry of Science and Technical Development of the Republic of Serbia, through Project No.142025G.

## REFERENCES

[1] Y. Park, Y.C. Lee, W. S. Shin, S.J. Choi, Chem. Eng. J., 2010, 162, 685–695.
[2] Y. A. Mustafa, M. J. Zaiter, J. Hazard. Mater., 2011, 196, 228– 233.
[3] S. Triantafyllou, E. Christodoulou, P. Neou-Syngourna, Clays Clay Miner., 1999, 47, No. 5, 567–572.
[4] S. Rengaraj, Seung-Hyeon Moon, Water Res., 2002, 36, 1783–1793.
[5] V. Behiari., M. Sotiropoulou, G. Bokias, P. Lianos, Colloids Surf. A, 2008, 312, 214–218.
[6] N. Bas, A. Yakar, N. P. Bayramgil, J. Appl. Polym. Sci., 2014, 131, DOI: 10.1002/app.39569.
[7] B. Adnadjevic, J. Jovanovic, N. Lazarevic, J. Appl. Polym. Sci., 2011 119, (3), 1805–1812.
[8] A. F. Hussain, Nat. J. Chem., 2008, 30, 229–250.
[9] S. Vyazovkin, C.A. Wight, Thermochim. Acta., 1999, 340/341, 53–68.
[10] H. Friedman, J. Polym. Sci., 1964, C 6, 183–195.