UNIVERSITY OF BELGRADE

TECHNICAL FACULTY BOR

52nd International October Conference on Mining and Metallurgy

PROCEEDINGS

Edited by

Saša Stojadinović

and

Dejan Petrović

November 29th – 30th 2021

Bor, Serbia

52nd International October Conference on Mining and Metallurgy, IOC 2021

PUBLISHER:
UNIVERSITY OF BELGRADE - TECHNICAL FACULTY IN BOR, BOR, NOVEMBER 2021

FOR THE PUBLISHER:
DEAN: Prof. dr Nada Štrbac

EDITORS:
Prof. dr Saša Stojadinović
Doc. dr Dejan Petrović

TECHNICAL EDITOR
Pavle Stojković, MSc.

PRINTED BY:
»Štamparija Atlantis d.o.o.« Niš

CIRCULATION: 100 Copies

CIP – Каталогизација у публикацији –

Народна библиотека Србије, Београд

622(082)
669(082)

INTERNATIONAL October Conference on Mining and Metallurgy (52 ; 2021 ; Bor)
Proceedings / 52nd International October Conference on Mining and Metallurgy - IOC 2021, November 29th - 30th 2021 Bor, Serbia ; [organizer] University of Belgrade, Technical Faculty in Bor ; [co-organizer Institute for Mining and Metallurgy Bor] ; edited by Saša Stojadinović and Dejan Petrović. - Bor : University of Belgrade, Technical Faculty, 2021 (Niš : Atlantis). - V, 228 str. : ilustr. ; 25 cm

Tiraž 100. - Bibliografija uz svaki rad.

ISBN 978-86-6305-119-5

а) Рударство -- Зборници б) Металургија -- Зборници

COBISS.SR-ID 52072201

ORGANIZER:

UNIVERSITY OF BELGRADE – TECHNICAL FACULTY IN BOR

Co-ORGANIZER:

INSTITUTE FOR MINING AND METALLURGY BOR

Under the Auspice of:

The Ministry of Education, Science and Technological Development of the Republic of Serbia

COMMITTEES

52^{nd} International October Conference on Mining and Metallurgy, IOC 2021

SCIENTIFIC COMMITTEE

Prof. dr Nada Štrbac, (UB TF Bor, Serbia)

Prof. dr Iwao Katayama, (Osaka University, Osaka, Japan)

Prof. dr Rodoljub Stanojlović, (UB TF Bor, Serbia)

Prof. dr Radoje Pantović, (UB TF Bor, Serbia)

Prof. dr Jakob Lamut, (ULj FNT Ljubljana, Slovenia)

Prof. dr Sanda Krausz, (University of Petroşani, Romania)

Prof. dr Grozdanka Bogdanović, (UB TF Bor, Serbia)

Prof. dr Jelena Penavin Škundrić, (TF Banja Luka, B&H)

Prof. dr Seshadri Seetharaman, (Royal Institute of Technology, Stockholm, Sweden)

Prof. dr Dragoslav Gusković, (UB TF Bor, Serbia)

Prof. dr Jožef Medved, (ULj FNT Ljubljana, Slovenia)

Dr Slavomir Hredzak, (SAS Kosice, Slovakia)

Prof. dr Aleksandar Dimitrov, (FTM Skopje, FYR Macedonia)

Prof. dr Karlo Raić, (UB TMF, Serbia)

Prof. dr Snežana Šerbula, (UB TF Bor, Serbia)

Dr Ana Kostov, (IRM Bor, Serbia)

Prof. dr Kemal Delijić, (MTF Podgorica, Montenegro)

Prof. dr Stoyan Groudev, (UMG "Saint Ivan Rilski" Sofia, Bulgaria)

Dr Andrei Rotaru, (Facultatea de Mecanica, Romania)

Prof. dr Krzystof Fitzner, (AGH University, Krakow, Poland)

Prof. dr Sulejman Muhamedagić, (FMM Zenica, B&H)

Prof. dr Anđelka Mihajlov, (Educons University, Serbia)

Prof. dr Luis Filipe Malheiros, (FEUP, Porto, Portugal)

Prof. dr Svetlana Ivanov, (UB TF Bor, Serbia)

Prof. dr Batrić Pešić, (Materials Science Faculty, Idaho, USA)

Prof. dr Ljubica Ivanić, (UB TF Bor, Serbia)

Dr Srećko Stopić, (RWTH Aachen, IME Aachen, Germany)

Prof. dr Boštjan Markoli, (ULj FNT Ljubljana, Slovenia)

Dr Magnus Ericsson, (Lulea Technical University, Stockholm, Sweden)

Prof. dr Tamara Holjevac Grgurić, (MF Sisak, Croatia)

Prof. dr Boyan Boyanov, (University Paisiy Hilendarski, Plovdiv, Bulgaria)

Prof. dr Milan Antonijević, (UB TF Bor, Serbia)

Prof. dr Tatjana Volkov-Husović, (UB TMF, Serbia)

Prof. dr Branka Jordović, (TF Čačak, Serbia)

Prof. dr Milan Trumić, (UB TF Bor, Serbia)

Prof. dr Tomaš Havlik, (TUKE, Slovakia)

Prof. dr Carl Heinz Spitzer, (TU Clausthal, Germany)

Dr Mile Bugarin, (IRM Bor, Serbia)

Prof. dr Velizar Stanković, (UB TF Bor, Serbia)

Prof. dr Costas Matis, (AU Thessaloniki, Greece)

Dr Milenko Ljubojev, (IRM Bor, Serbia)

Prof. dr Velimir Radmilović, (University of California at Berkeley, USA)

Prof. dr Dejan Tanikić, (UB TF Bor, Serbia)

Dr Mirjam Jan-Blažić, (Slovenian Foundryen Society, Slovenia)

Prof. dr Vitomir Milić, (UB TF Bor, Serbia)

ORGANIZING COMMITTEE

EVALUATION OF ADSORPTION PERFORMANCE OF PHOSPHATES REMOVAL USING CELL-MG HYBRID ADSORBENT

Jovana Bošnjaković[1], Nataša Knežević[2], Natalija Čutović[2], Mladen Bugarčić[3], Aleksandar Jovanović[2], ZlateVeličković[4], Srećko Manasijević[1]

[1]Research and Development Institute Lola L.T.D., K. V. 70A, 11030 Belgrade, Serbia

[2]Faculty of Technology and Metallurgy, University of Belgrade, K. 4, 11000 Belgrade, Serbia

[3]Institute for Technology of Nuclear and Other Raw Materials, B. F. d'E. 86, 11000Belgrade, Serbia

[4]University of Defense, Military Academy,G. P. J. Š. 33, Belgrade 11040, Serbia

Abstract

Due to the high accumulation of nutrients in water (primarily phosphates) because of increased use of fertilizers and plant protection products, it is necessary to apply various techniques for their detection, and then removal. Adsorption is one of the promising techniques to removing them. Magnetite (MG) modified cellulose membrane (Cell-MG), obtained by reaction of 3-aminosilane and subsequently with diethylenetriaminepentaacetic acid dianhydride functionalized waste Cell fibers (Cell-NH_2 and Cell-DTPA, respectively), and amino-modified diatomite was used for phosphate ionsremovalfrom water. Cell-MG membrane was structurally and morphologically characterized using SEM and TEM techniques. The influences of operational parameters, i.e. pH, contact time, temperature, and the mass of adsorbent on adsorption and kinetics were studied in a batch system. The calculated capacities of 79.08 mg g^{-1} at 45°Cfor phosphate ions were obtained from non-linear Langmuir model fitting. The reusability of adsorbent and results from wastewater purification showed that Cell-MG could be used as general-purpose adsorbent. Based on the kinetic studies the adsorption process followsthe pseudo second-order model. Thermodynamic parameters showed that the adsorption process is endothermic and spontaneous.

Keywords*: phosphates, adsorption isotherm, kinetics, activation energy.*

1. INTRODUCTION

Nowadays, there is a great demand for an efficient adsorbent that is able to simultaneously remove both anions and cations, as well as organic pollutants from water. The presence of different anions in wastewater poses a great danger to the environment. The adsorption process, as a promising, cheap and efficient technique, is most often used in the removal of pollutants (in this case PO_4^{3-}ions) from aqueous solutions [1,2].

Cellulose, a natural, widespread, fibrous and eco-friendly polymer can be used as a sorbent in various forms in order to eliminate pollutants from water. It can be used as a sorbent in natural and modified form, but due to its small sorption capacity, its modification is desirable [3]. Due to easy chemical modification, non-toxicity, good mechanical properties, cellulose shows potential as a sorbent [3]. Iron oxides, magnetite and hematite, have given good results in the removal of oxyanions and cations. The incorporation of hematite and magnetite into waste cellulose, as an adsorbent, improves the sorption capacity due to the improvement of magnetic properties.

The aim of this study was to remove PO_4^{3-} ions using modified Cell-MG membranes. The membrane was obtained by combining modified cellulose with 3-aminopropyltriethoxysilane (Cell-NH_2) and diethylenetriaminepentacetic acid dianhydride (Cell-DTPA) with magnetite and hematite, using it to remove ions.

2. EXPERIMENTAL

Cell-MG hybrid membranes and D-APTES (Diatomite modified with 3-aminopropylsilane, i.e. APTES) were prepared by the procedure described in Perendija*et al*. [4]. Magnetite was synthesized according to the method described in the literature [5].

3. RESULTS AND DISCUSSION

3.1 SURFACE MORPHOLOGY ANALYSIS

The results of the morphological analysis of the Cell-MG membrane and Fe_3O_4 particles, using SEM and TEM techniques, respectively, are given on Figures 1 and 2[4].

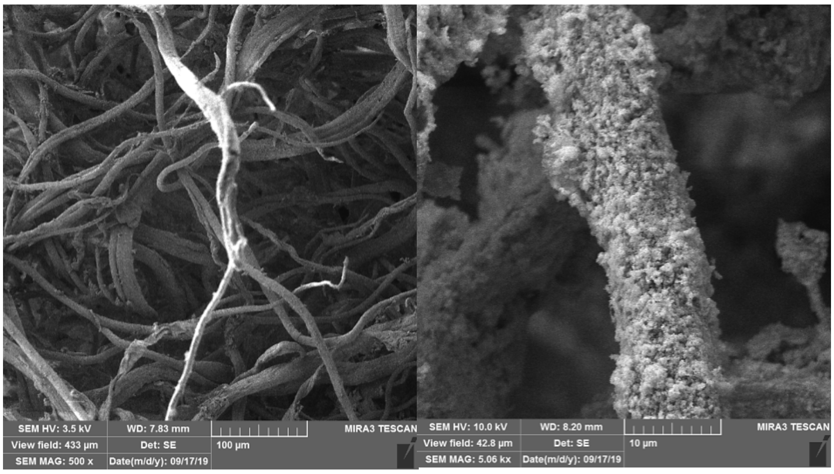

Figure 1.SEM images of Cell based membrane (left) and Cell-MG hybrid membrane (right)

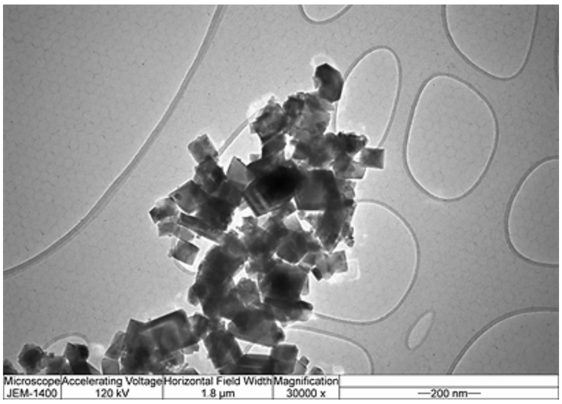

Figure 2.TEM image of Fe_3O_4 particles

The applied optimized procedure, which is used for the deposition of MG on the Cell-COOH membrane, provides a uniform distribution of MG nanoparticles, which contributes to increasing the surface area of the adsorbent and the active Fe-OH site capable of removing pollutants. As can be seen in Figure 1, there are no changes in the structure of cellulose fibers, while the surface morphology of the hybrid adsorbent is significantly changed due to the precipitation of MG. 7.8% by weight of iron and ~ 10.8% by weight of 14% were evenly distributed in the Cell-MG hybrid membrane [4].

3.2 ADSORPTION STUDY

Adsorption capacities were determined at the optimal pH value of 6, C_i = 9.1 mg L^{-1}, t = 90 min. Adsorption results are presented using Langmuir, Freundlich and Dubinin-Radushkevich adsorption isotherms.

Table 1. The results of non-linear fitting using Langmuir isotherm model for PO_4^{3-}adsorption onto Cell-MG hybrid membrane

Ion	*Temperature*	q_m(mg g^{-1})	K(dm^3 mg^{-1})	K_L(dm^3 mol^{-1})	R^2
PO_4^{3-}	25□	69.51	0.406	38524,623	0.989
	35□	71.51	0.546	51903,707	0.996
	45□	79.08	0.799	75946,905	0.992

Table 2.Non-linear Freundlich and Dubinin-Radushkevich isotherm parameters for PO_4^{3-}on Cell-MG membrane

	Parameters	*25°C*	*35°C*	*45°C*
Freundlich isotherm	K_F(mg g^{-1})(dm^{3}mg^{-1})$^{1/n}$	46.21	70.58	126.5
	1/n	1.309	1.313	1.299
	R^2	0.989	0.991	0.994
Dubinin-Radushkevich isotherm	q_m (mg g^{-1})	57.18	65.42	79.66
	K_{ad} (mol^2 KJ^{-2})	7.420	7.280	7.080
	E_a (KJ mol^{-1})	8.212	8.287	8.401
	R^2	0.898	0.917	0.943

The good adsorption capacities (q_m), obtained using the Langmuir isothermal model (Table I), are slightly increased with temperature increase, which indicates the chemical type of the binding of PO_4^{3-} ions. Also, the high values of the Langmuir constant (K_L) reflect the pronounced sorption affinity of the adsorbate towards the adsorbent surface. This means that the adsorption produced is caused by the high affinity of the adsorbent surface for ions by creating a weak interaction with the surface functionality.

3.3 THERMODYNAMIC PARAMETERS OF ADSORPTION

Table 3. Calculated Gibbs free energy, enthalpy and entropy for the PO_4^{3-} adsorption on Cell-MG hybrid membrane

Ion	ΔG° (kJ mol^{-1})			ΔH° (kJ mol^{-1})	ΔS° (J mol^{-1} K^{-1})	R^2
PO_4^{3-}	298 K	308 K	318 K			
	-36.13	-38.11	-40.35	26.72	210.7	0.992

A gradual increase in ΔG° in relation to the increase in temperature indicates more favourable processes of desolvation and diffusion at a higher temperature. Based on the literature values for Δ*G*° and the obtained values of Δ*G*° in the range -36.13 to -40.35 kJ mol^{-1}, a spontaneous process is clearly indicated, in which both physisorption and hemisorption processes participate.

A high Δ*S*° indicates increased randomness at the adsorbent/solution interface. The progress of the adsorption process is accompanied by the formation of a surface structure with the adsorbed pesticide by the formation of different interactions.

3.4 ADSORPTION KINETICS

Table 4. Pseudo-first, pseudo-second and second order reaction kinetic parameters for the PO_4^{3-}adsorption using Cell-MG adsorbent

Ion/order of kinetic law		*Pseudo-first*	*Pseudo-second*	*Second order*
PO_4^{3-}	q_e	51.67	66.44	66.44
	k (k_1, k_2)	0.062	0.003	0.008
	R^2	0.930	0.984	0.934

Determination of PSO rate constants at 25, 35, and 45 °C provides data for determining activation energy. The obtained value of 14,797 KJ mol^{-1}indicates the importance of the structural characteristics of the studied pollutants and adsorbent: geometry, spatial arrangement, atomic/surface functionalities charges,dipolarity/polarity, and proton donating/accepting properties that contribute to the efficiency of molecule diffusivity, the extent of solvent-sorbate and sorbate-surface functionalities interactions.

4. CONCLUSION

Magnetite-synthesized (MG) modified cross-linked carboxy functionalized cellulose membrane showed good efficacy for removing phosphate ions from water. The obtained results indicate that both the properties of phosphate ions and hybrid membrane adsorbent affect the manner and extent of sorbate-surface functionalities interactions. Based on kinetic and thermodynamic studies, it was confirmed that Cell-MG membranes as adsorbents have a high potential. The obtained results and applied methods are in line with the current trend in environmental protection where understanding the molecular interaction helps to design a new adsorbent with better performance.

ACKNOWLEDGEMENTS

This work was supported by the Ministry of Education, Science and Technological Development of the Republic of Serbia (Contract Nos. 451-03-9/2021-14/200066; 451-03-9/2021-14/200023; 451-03-9/2021-14/200135; 213-1/21-08-03-2021).

REFERENCES

[1] T. Sumathi, G. Alagumuthu, International Journal of Chemical Engineering, 2014, pp 1-7.
[2] A.E. Burakov, E.V. Galunin, I.V. Burakova, A.E. Kucherova, S. Agarwal, A.G. Tkachev, V.K.Gupta, Ecotoxicology and Environmental Safety, 2018, pp 702-712.
[3] Suhas, V.K. Gupta, P.J.M. Carrott, R. Singh, M. Chaudhary, S.Chaudhary, S.Kushwaha, Bioresource Technology, 2016, 1066-1076.
[4] J. Perendija, Z.S. Veličković, I. Cvijetić, J.D. Rusmirović, V. Ugrinović, A.D. Marinković, A. Onjia, Cellulose., 27 (2020) 8215–8235.
[5] U. Schwertmann, R.M. Cornell, Iron Oxides in the Laboratory (Second Edition), WILEYVCH Verlag GmbH, Weinheim, 2001.