

Alternative adsorbent materials used to remove phosphates from water

ANA-MARIA NICOLETA CODREANU^{1,2}, ALINA MIRELA CONSTANTIN¹, GEORGIANA CERNICA^{1,2}, IRINA DUMITRESCU¹

¹ National Research and Development Institute for Industrial Ecology - ECOIND, 57-73 Drumul Podu Dambovitei Street, 060652, Bucharest, Romania

² Faculty of Applied Chemistry and Materials Science, University Politehnica of Bucharest, Department of Analytical Chemistry and Environmental Engineering, No 1-7, Polizu Street, 011061 Bucharest, Romania

*Corresponding author: anamaria.codreanu@ecoind.ro

Received:
09.08.2023

Accepted:
06.12.2023

Published:
20.12.2023

Abstract

The aim of the study was to develop alternative adsorbent materials based on pyritic ash, with high iron content, in order to retain phosphates from wastewater.

Experimental studies of phosphate removal efficiency have shown that the phosphates removal from water using pyritic ash adsorbent materials is strongly influenced by some parameters such as: contact time, stirring speed, amount of adsorbent material or iron content. An increase of phosphate removal efficiency up to 53% could be observed for iron-rich adsorbent materials (PA1) by increasing the contact time to 6 hours and the stirring speed to 100 rpm. An increase of phosphate removal efficiency was also observed by increasing the amount of adsorbent material from 0.1 g to 0.5 g for all three adsorbent materials studied (PA1, PA2, PA3). The best efficiency was shown for PA1 (53.13%), while PA3 showed the lowest efficiency (19.74%).

Keywords: *adsorbent materials, pyritic ash, valorization, phosphates removal*

INTRODUCTION

Water is an essential and important planet resource, but in spite of this the phenomenon of water pollution is very high nowadays. Water pollution affects both aquatic life and human health, so it must be properly treated before it is discharged [1]. Industrial effluents represent one of the major sources of water pollution. Industrial effluents loaded with phosphates and nitrates from the leather industry, fertilizer industry, pharmaceutical industry, and mining industry lead to eutrophication [2]. The main classes of phosphates found in wastewater composition are orthophosphates occur in H_3PO_4 , $H_2PO_4^-$, HPO_4^{2-} and PO_4^{3-} forms, condensed phosphates and organic phosphates [3÷5]. To prevent eutrophication, the concentration of phosphates in water should not exceed 50 $\mu\text{g/L}$. When the phosphates concentration in water exceeds 0.02 mg/L eutrophication begins by decreasing the amount of dissolved oxygen and algae growth [6, 7]. Phosphates removal techniques include chemical and physical methods [8÷11], biological methods [12, 13], adsorption techniques [14, 15] and nano-techniques [16÷18].

On the other hand, management of the large quantities of pyritic ash produced is an environmental challenge for the whole world [19]. Pyritic ash is a by-product of pyrite ores combustion process to produce sulphuric acid [20]. Which after cleaning and cooling do burning pyrite ores at temperatures between 600 °C-1000 °C, metallic oxides are obtained, mainly iron oxides (hematite) [21] and gaseous sulphur dioxides process processed to sulphuric acid [22]. Sulphuric acid produced is widely used in the fertilizer industry [20]. Countries such as: China, US, Russia, India

and Morocco are in the top five sulphuric acid producing countries [23]. Approximately 15 million tons of pyritic ash are produced annually [24].

Unfortunately, this waste presents a low or non-existent management, being stored in open spaces [25]. The environmental effects of pyritic ash include acidification, acid drainages, water and wind erosion, loss of vegetation or particles air dispersion [26, 27]. Pyritic ashes can also have negative effects for human health, producing cancer, anemia, fatigue or cardiovascular diseases, because they can enter into the human body through inhalation, dermal adsorption or dietary intake [28, 29].

Starting from the chemical composition of this waste, research has focused by valorization of this waste through different methods based on the circular economy principles [30]. The most current methods for pyritic ash valorization include: metals recovery [31÷37], chemical lopping combustion [38÷40] or valorization in order to obtain value added products (pigments, catalysts, adsorbent materials) [41÷44].

In order to develop a new pyritic ash valorization and to solve the phosphate contaminated wastewater problem, the present study attempted the valorization of pyritic ash wastes as adsorbent materials for retaining phosphates from water.

MATERIALS AND METHODS

Chemical reagents and apparatus

The pyrite ash (PA), used in our studies, was collected from a sulphuric acid production enterprise in Southern Romania.

Nobertherm provided the compact muffle furnace used for calcining the samples. Determination of the metal content of adsorbent materials was carried out using ICP-MS 7900 provided by Agilent Technologies. pH measurements were performed using inoLab_IDS multiparameter 9430. The Mastersizer 2000 particle size analyzer was used to determine specific surface area and particle size distribution. The grinding mill ZM 200 provided by Retsch was used for grinding de sample.

Preparation of adsorbent materials

Sample preparation of adsorbent materials is described in figure 1.

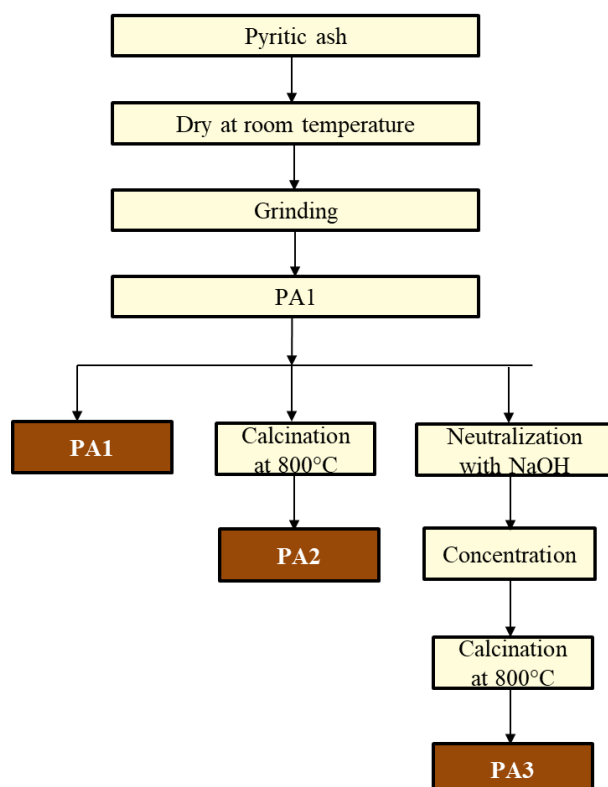


Fig. 1. Sample preparation of adsorbent materials based on pyritic ash

The collected pyritic ash sample was dried at room temperature until it reached constant mass. The dry sample was ground using the grinding mill (Pyrite ash sample no.1 - PA1). The pyrite ash sample no. 2 (PA2) was prepared by calcining a quantity of sample PA₁ at 800 °C for 2 hours, while pyrite ash sample no. 3 (PA3) was prepared by neutralization with a certain volume of 10% NaOH by stirring, until pH 9 was reached, followed by calcination at 800 °C for 2 hours. The final adsorbent materials based on pyritic ash were shown in figure 2.

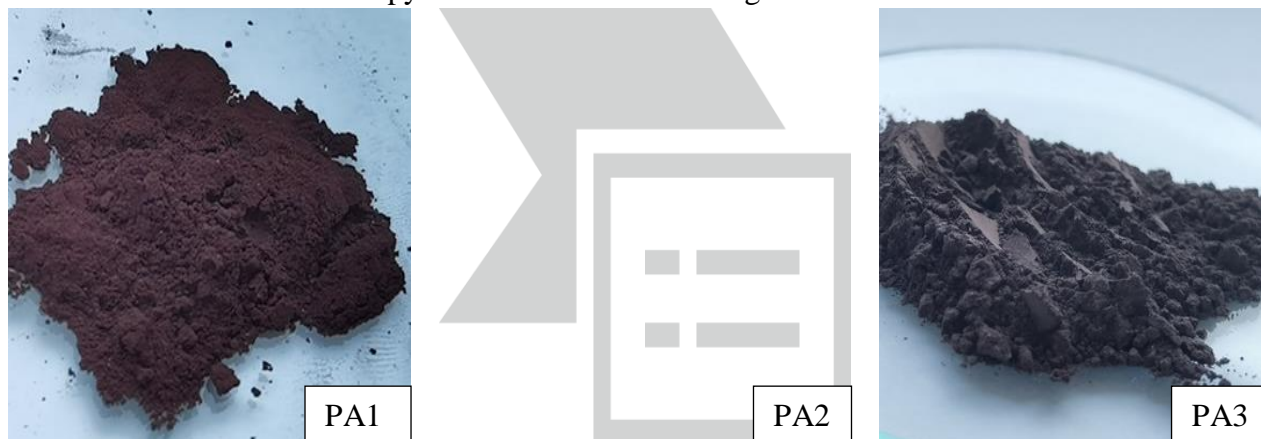


Fig. 2. Aspect of adsorbent materials based on pyritic ash (PA1, PA2, PA3)

Characterization of adsorbent materials

Adsorbent materials based on pyritic ash (PA1, PA2, PA3) were characterized in terms of pH, specific surface area, particle size distribution and also compositionally by determining the content of metals.

The L/S ratio for the pH measurement was 5:1 (volume: weight). Following pH measurements (Table 1) it could be observed that PA1 shows an acid pH (2.82), PA2 shows a weak acid pH (5.4), while PA3 shows a pH close to neutral (6.68). Particle size distribution analyses showed that all three adsorbent materials had particle sizes smaller than 1.9 μm for 90% mass, while specific surface area analyses (Figure 3; Table 1) showed that the PA3 adsorbent material had the smallest specific surface area (1.03 m^2/g) for 90% mass.

Table 1. Characterization of PA1, PA2, PA3 in terms of pH, specific surface area and particle size distribution

Parameter	PA1	PA2	PA3
pH	2.82	5.40	6.68
Specific area (m^2/g)	1.42	1.23	1.03
Particle size distribution (μm)	≤ 1.64	≤ 1.75	≤ 1.90

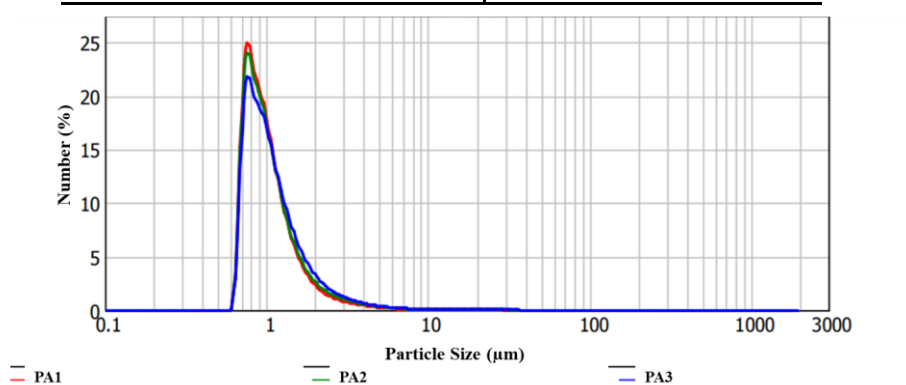


Fig 3. Particle size distribution of PA1, PA2, PA3

The results of the ICP-MS metal content analysis (Table 2) revealed the presence of iron in the composition of all three pyritic ash adsorbents. Adsorbent material PA1 has the highest iron content (49.77%), while adsorbent material PA3 has the lowest iron content (46.02%). The results also showed the presence of significant amounts of calcium and aluminium in the composition of the three adsorbent materials, while metals such as cadmium, phosphorus, copper, cobalt are found in small amounts.

Table 2. Metal content of PA1, PA2, PA3

Sample	Metal content (%)									
	Fe	Ca	As	P	Cd	Co	Pb	Zn	Cu	Al
PA1	49.8	1.77	0.15	0.04	0.0009	0.014	0.28	0.43	0.058	0.40
PA2	48.8	1.72	0.13	0.03	0.0009	0.013	0.27	0.32	0.054	0.40
PA3	46.0	1.78	0.13	0.03	0.0009	0.013	0.24	0.33	0.053	0.39

Metals leaching from adsorbent materials based on pyritic ashes in water

In order to observe the leaching tendency of metals present in the composition of adsorbent materials PA1, PA2, PA3 in water over a well-defined period of time, different amounts of each adsorbent material were placed in contact with water, ratio S/L was 1:10 (weight: volume) for 24 h, at room temperature, stirring speed 50 rpm. After filtration, the filtrate was subjected to metal content analysis. The amounts of metals leached into the water can be seen in Table 3. It can be seen that the phosphorus shows a very low leaching rate in water in the case of all three samples of pyritic ash adsorbent materials

Table 3. Results of leaching tests in water for PA1, PA2, PA3

Sample	Metal oxides content (%)									
	Fe ₂ O ₃	CaO	As ₂ O ₃	P ₂ O ₅	TiO ₂	PbO	ZnO	CuO	Al ₂ O ₃	MgO
PA1	86.8	2.55	0.28	0.20	0.19	0.38	0.75	0.09	4.19	0.93
PA2	82.2	2.99	0.25	0.19	0.21	0.38	0.67	0.08	3.99	0.77
PA3	76.4	1.00	0.22	0.14	0.17	0.30	0.64	0.07	3.25	0.68

Process of the removal of phosphate from water containing phosphate

Phosphate removal-experiments were carried out by mixing well-defined amounts of pyritic ash adsorbents (PA1, PA2, PA3) using orbital shaker with different volume of KH₂PO₄ 10 mg/L solution at room temperature 22°C ± 2°C. After a certain period of stirring, the leachate was filtered using filter paper with porosity under 0.45 µm. Phosphate content in filtrate was measured according to SR EN ISO 6878:2005 (ammonium molybdate spectrometric method) using UV-VIS spectrophotometer. All adsorption tests were done in triplicate.

RESULTS AND DISCUSSION

Effect of contact time and stirring speed on phosphate removal

In order to study the influence of contact time and stirring speed on the removal efficiency of phosphates from water using pyritic ash adsorbent materials, 0.5 g each of PA1, PA2, PA3 adsorbent material and 100 mL KH₂PO₄ 10 mg/L solution were placed in contact, by applying stirring speeds between 0 and 100 rpm, at room temperature, in time intervals of 2 h, 4 h and 6 h, respectively. The experimental results (Figures 4 to 6) showed that increasing the contact time (2h

to 6h) and increasing the stirring speed (0 rpm÷100 rpm) leads to increasing the phosphate removal efficiency on the surface of all three pyritic ash adsorbent materials.

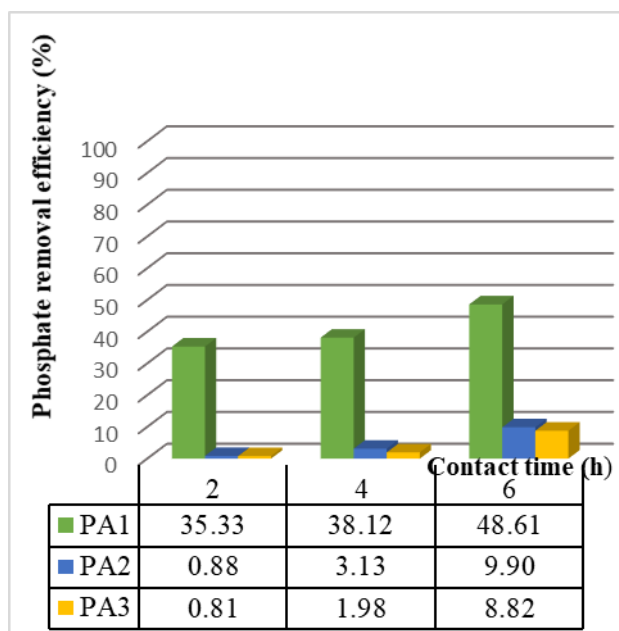


Fig. 4. Influence of contact time to phosphate removal efficiency at stirring speed (0 rpm)

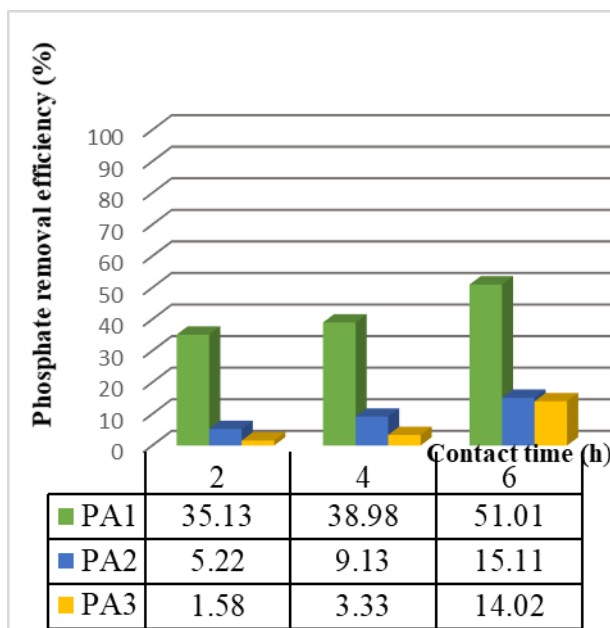


Fig. 5. Influence of contact time to phosphate removal efficiency at stirring speed (50 rpm)

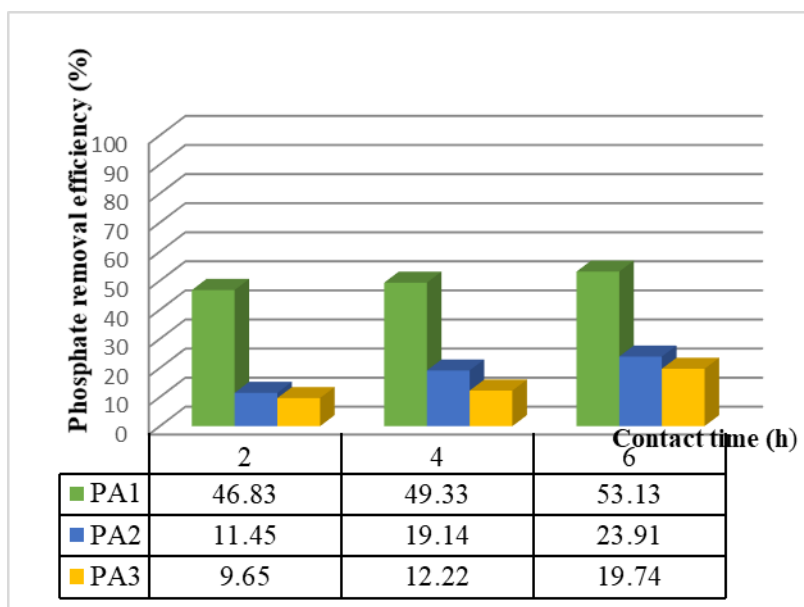


Fig. 6. Influence of contact time to phosphate removal efficiency at stirring speed (100 rpm)

It could be observed that, even if the agitation process is not applied, the efficiency of phosphate removal from water increases (figure 4), the best results were obtained for the adsorbent material PA1 (48.61%). The phosphate removal efficiency increased from 35.33% at 2 hours contact time to 48.5% at 6 hours contact time. For the adsorbent materials PA2 and PA3 a phosphate removal efficiency increases from 0.80% to 9.90% and 8.82% respectively was observed. The adsorbent material PA3 showed the lowest phosphate removal efficiency at 6 hours.

When a stirring speed of 50 rpm was applied, an increase of phosphate removal efficiency could be observed for all three adsorbents (figure 5). The experimental results showed that at 6 hours contact time of and 50 rpm stirring speed, the adsorbent material PA1 showed the best results (51.01%). Compared to the results obtained at a stirring speed of 0 rpm, in the time interval 2-6 hours, for the

adsorbent materials PA2 and PA3 an increase in phosphate removal efficiency was observed when the stirring speed was increased at 50 rpm. For the PA2 adsorbent material an increase in phosphate removal efficiency to 15.11% could be observed at contact time 6 hours, stirring speed 50 rpm, while for the PA3 adsorbent material an increase from 1.58% at 2 hours to 14.02% at 6 hours was observed.

At the same time, by increasing the stirring speed to 100 rpm and by increasing the contact time to 6 hours, were obtained the best phosphate removal efficiency results for all three pyritic ash adsorbents PA1, PA2, PA3 (figure 6). Also, in these accounts, it was observed that PA1 showed the highest phosphate removal efficiency (53.13%), while PA3 recorded the lowest phosphate removal efficiency (19.74%) from water at 6 h contact time and 100 rpm stirring speed.

Effect of amount of adsorbent material on phosphate removal

In order to study the influence of adsorbent material amount on the phosphate removal efficiency, the amounts of PA1, PA2 and PA3 adsorbent materials were varied (0.1g ÷ 0.5g) and brought into contact with 100 mL KH₂PO₄ 10 mg/L solution for 6 hours, under 100 rpm stirring at room temperature. Experimental results (figure 7) demonstrated that increasing the amount of adsorbent material significantly improves the efficiency of phosphate removal from water. In the case of PA1 adsorbent material, could be observed an increase of about 6 times of the phosphate removal efficiency when the amount of adsorbent material increases from 0.1 g to 0.5 g. In the case of PA2 and PA3 adsorbent materials, a tripling of the phosphate removal efficiency from 8.58% to 23.91% could be observed for PA2 and a doubling of the phosphate removal efficiency from 8.01% to 19.74% could be observed for PA3.

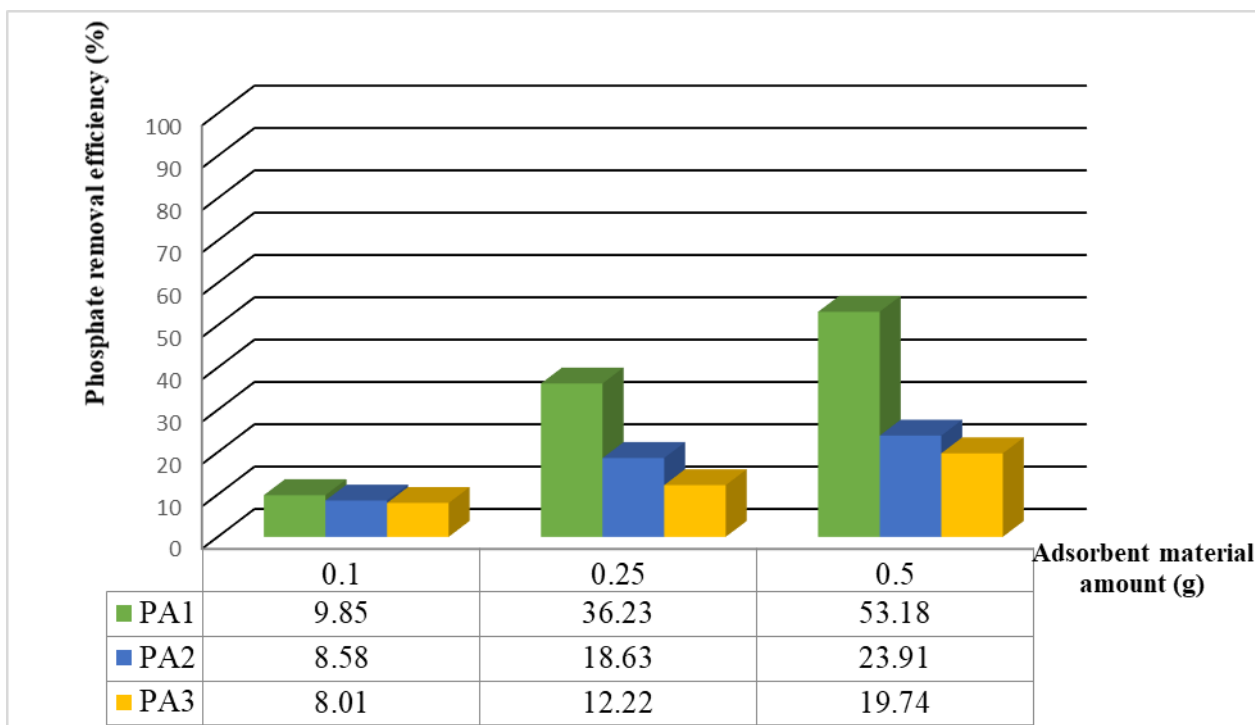


Fig. 7. Influence of adsorbent material amount

CONCLUSIONS

Experimental studies carried out on the phosphates removal efficiency from water by the three pyritic ash adsorbents (PA1, PA2 and PA3) showed that this indicator is strongly influenced by the variation of some indicators, such as contact time, stirring speed and amount of adsorbent material.

The obtained results demonstrated that by increasing the contact time between adsorbent materials and the KH_2PO_4 10 mg/L solution from 2 h to 6 h and also, by increasing the stirring speed (0 rpm÷100 rpm) is improving phosphates removal efficiency from phosphates contaminated water. At the same time, following the studies carried out, an increase of phosphates adsorption capacity was observed on the surface of all three pyritic ash adsorbent materials by increasing the amount of adsorbent material.

All the experimental results obtained demonstrated that the iron content found in the all three adsorbent materials (PA1, PA2, PA3) composition also represents an important factor for phosphates removing process from contaminated water. Thus, it could be observed that the adsorbent material PA1, which presented the highest iron content, was the best material used in the process of removing phosphates from water.

ACKNOWLEDGEMENTS

This work was carried out through the “Nucleu” Program within the National Research Development and Innovation Plan 2022-2027 with the support of Romanian Ministry of Research, Innovation and Digitalization, contract no. 3N/2022, project no. PN 23 22 04 01.

REFERENCES

- [1] ALAGHA, O., MANZAR, M. S., ZUBAIR, M., ANIL, I., MUAZU, N. D., QURESHI, A., J. Nanomaterials., **10**, no. 1361, 2020, p.1, <https://doi.org/10.3390/nano10071361>.
- [2] VELUSAMY, K., PERIYASAMY, S., KUMAR, P. S., NGUYEN D. V., SINDHU, J., SHEKA, D., SUBHASHINI, B., Environ. Chem. Lett., **19**, no. 4, 2021, p. 3165, <https://doi.org/10.1007/s10311-021-01239-2>.
- [3] YOUSEFI, M., NEBIZADEH, R., ALIMOHAMMADI, M., MOHAMMADI, A. A., MAHVI, A. H., Desalin. Water Treat., **158**, 2019, p. 290, <https://doi.org/10.5004/dwt.2019.24281>.
- [4] BACELO, H., PINTOR, A., SANTOS, S., BOAVENTURA, R., BOTELHO, C., Chem. Eng. J., **381**, 2020, p. 122566, <https://doi.org/10.1016/j.cej.2019.122566>.
- [5] YIN, Q., Wang, R., Zhao, Z., J. Clean. Prod., **176**, 2018, p. 230, <https://doi.org/10.1016/j.jclepro.2017.12.117>
- [6] KILPIMAA, S., RUNTTI, H., KANGAS, T., KOUKKANEN, T., Chem. Eng. Res. Des., **92**, no. 10, 2014, p. 1923, <https://doi.org/10.1016/j.cherd.2014.03.019>.
- [7] WANG, B., LIAN, G., LEE, X., GAO, B., LI, L., LIU, T., ZHANG, X., ZHENG, Y., Chemosphere, **238**, 2020, p. 124684, <https://doi.org/10.1016/j.chemosphere.2019.124684>.
- [8] RUZHITSKAYA, O., GOGINA, E., MATEC Web of Conf., 2017.
- [9] KUMAR, I. A., VISWANATHAN, N., Arab. J. Chem., **13**, no. 2, 2020, p. 4111, <https://doi.org/10.1016/j.arabjc.2019.06.006>.
- [10] MANIKAM, M. K., HALIM, A. A., HANAFIAH, M. M., KRISHNAMOORTHY, R. R., Desalin. Water Treat., **149**, 2019, p. 23, <https://doi.org/10.5004/dwt.2019.23842>.
- [11] KUMAR, I. A., JEYAPRABHA, C., MEENAKSHI, S., VISWANATHAN, N., Int. J. Biol. Macromol., **130**, 2019, p. 527, <https://doi.org/10.1016/j.ijbiomac.2019.02.106>.
- [12] RAJESH BANU, J., MERRYLIN, J., KAVITHA, S., YUKESH KANNAH, R., SELVAKUMAR, P., GOPIKUMAR, S., SIVASHANMUGAM, P., KUMAR, G., Curr. Pollut. Rep., **7**, 2021, p. 1, <https://doi.org/10.1007/s40726-020-00169-x>.
- [13] PAN, J., GAO, B., SONG, W., XU, X., YUE, Q., J. Hazard. Mater., **382**, 2020, <https://doi.org/10.1016/j.jhazmat.2019.121073>.
- [14] ZHENG, Y., ZINMERMAN, A. R., GAO, B., Sci. Total Environ., **747**, 2020, <https://doi.org/10.1016/j.scitotenv.2020.141277>.
- [15] JI, J., PENG, Y., WANG, B., LI, X., ZHANG, Environ. Sci. Technol., **54**, no. 6, 2020, p. 3702, <https://doi.org/10.1021/acs.est.9b07928>.
- [16] HE, Y., LIN, H., DONG, Y., WANG, L., CHU, S., LUO, M., LIU, J., Chem. Eng. J., **347**, 2018, p. 669.

- [17] MAECELO, L. R., DE GOIS, J. S., DA SILVA, A. A., CESAR, D. V., *Environ. Chem. Lett.*, **19**, no. 2, 2020, p. 1229, <https://doi.org/10.1007/s10311-020-01134-2>.
- [18] MADHURA, L., SINGH, S., KANCHI, S., SABELA, M., *Environ. Chem. Lett.*, **17**, no. 4, 2018, p. 65, <https://doi.org/10.1007/s10311-018-0778-8>.
- [19] SORIANO-DISLA, M., SPILLE, U., GABARRON, M., FAZ, A., ACOSTA, J., *J. Environ. Manage.*, **217**, 2018, p. 403, <https://doi.org/10.1016/j.jenvman.2018.03.104>.
- [20] GABARRON, M., BABUR, O., SORIANO-DISLA, J. M., FAZ, A., ACOSTA, J. A., *Chemosphere*, **209**, 2018, p. 277, <https://doi.org/10.1016/j.chemosphere.2018.06.109>.
- [21] PEREZ-LOPEZ, R., SAREZ, R., ALVAREZ-VALERO, A. M., NIETO, J. M., PACE, G., *Sci. Total. Environ.*, **407**, no. 21, 2009, p. 5761, <https://doi.org/10.1016/j.scitotenv.2009.07.031>.
- [22] RUNKEL, M., STURM, P., *J. S. Afr. Inst. Min. Metall.*, **109**, no. 8, 2009, p. 491.
- [23] <https://mcgroup.co.uk/news/20130906/global-sulfuricacid-production-surpassed-2307-million-tonnes.html>
- [24] YANAN, L., DONG, C., JIANGUO, T., JUN, L., DONGRUN, Y., BUXIN, C., *Trans. Indian Inst. Met.*, **72**, no. 2, 2019, p. 501, <https://doi.org/10.1007/s12666-018-1502-x>.
- [25] DEMENECH, C., CAMALS, A., SOLER, A., SABANES, A., DUMESTRE, A., *Procedia Earth Planet. Sci.*, **17**, 2017, p. 432, <https://doi.org/10.1016/j.proeps.2016.12.109>.
- [26] KONG, S., LU, B., JI, Y., ZHAO, X., CHEN, L., LI, Z., HAN, B., BAI, Z., *Microchem. J.*, **98**, no. 2, 2011, p. 280, <https://doi.org/10.1016/j.microc.2011.02.012>.
- [27] VASILACHE N., DIACU E., MODROGAN C., CHIRIAC, F.L., PAUN, I.C., TENEA, A.G., PIRVU, F., VASILE, G.G., *Water*, **14**, 2022, <https://doi.org/10.3390/w14132022>.
- [28] ABBAS, M. H. H., ABDELHAFEZ, A. A., *Chemosphere*, **90**, no. 2, 2013, p. 588, <https://doi.org/10.1016/j.chemosphere.2012.08.042>.
- [29] WILSON, B., PYATT, F. B., *Ecotoxicol. Environ. Safe.*, **66**, no. 2, 2007, p. 224, <https://doi.org/10.1016/j.ecoenv.2006.02.015>.
- [30] CODREANU, A. M. N., CONSTANTIN, A., KIM, L., GASNAC, M. G., *Rom. J. Ecol. Environ. Chem.*, **4**, no. 2, 2022, p. 96, <https://doi.org/10.21698/rjeec.2022.209>.
- [31] CHU, Y. C., KO, T. H., *J. Chem. Hindawi*, **2018**, 2018, p. 1, <https://doi.org/10.1155/2018/5036581>.
- [32] HE, B., TIAN, X., SUN, Y., YANG, C., ZENG, Y., WANG, Y., ZHANG, S., PI, Z., *Hidrometallurgy*, **104**, no. 2, 2010, p. 241, <https://doi.org/10.1016/j.hydromet.2010.06.009>.
- [32] CHEN, D., GUO, H., XU, J., LV, Y., XU, Z., HUO, H., *Metall. Mater. Trans. B-Proc. Metall. Mater. Proc. Sci. B*, **48**, no. 2, 2017, p. 933, <https://doi.org/10.1007/s11663-017-0913-0>.
- [34] ZHANG, H., CHEN, G., CAI, X., FU, J., LIU, M., ZHANG, P., YU, H., *J. Hazard. Mater.*, **420**, 2021, p. 156.
- [35]. JIANG, T., TU, Y., SU, Z., LU, M., LIU, S., LIU, J., GU, F., ZHANG, Y., *Hydrometallurgy*, **193**, 2020, p. 105314, <https://doi.org/10.1016/j.hydromet.2020.105314>.
- [36] WANG, Y., XIAO, L., QUIN, P., YE, S., CHEN, Y., *Hydrometallurgy*, **179**, 2018, p. 192, <https://doi.org/10.1016/j.hydromet.2018.06.008>.
- [37] PANDA, S., AKCIL, A., MISHRA, S., ERUST, C., *J. Hazard. Mater.*, **342**, 2018, p. 454, <https://doi.org/10.1016/j.jhazmat.2017.08.038>.
- [38] MA, Z., ZHANG, S., XIAO, R., *Chem. Eng. J.*, **395**, 2020, 125097, <https://doi.org/10.1016/j.cej.2020.125097>.
- [39] ZHANG, S., XIAO, R., *Sci. Technol.*, **8**, 2018, p. 106.
- [40] ZHANG, M., GOUFU, L., HUI, Z., SHUAI, Z., YONGGANG, L., *Energy*, **233**, 2021, p. 122.
- [41] ZHANG, J., YAN, Y., HU, Z., FAN, Z., ZHENG, Y., *J. Clean. Prod.*, **170**, 2018, p. 486, <https://doi.org/10.1016/j.jclepro.2017.09.175>.
- [42] ALP, I., DEVERCI, H., YAZICI, E. Y., TURK, T., SUNGUN, Y. H., *J. Hazard. Mater.*, **166**, no. 1, 2009, p. 144, <https://doi.org/10.1016/j.jhazmat.2008.10.129>.
- [43] YANG, L., YAN, Y., HU, Z., XIE, X., *Constr. Build. Mater.*, **38**, 2013, p. 8, <https://doi.org/10.1016/j.conbuildmat.2012.08.049>.

[44] ZHENG, Y., LIU, Z., Powder Technol., **207**, no. 1-3, 2011, p. 335, <https://doi.org/10.1016/j.powtec.2010.11.015>.

Citation: Codreanu, A.M.N., Constantin, A.M., Cernica, G., Dumitrescu, I., Alternative adsorbent materials used to remove phosphates from water, *Rom. J. Ecol. Environ. Chem.*, **2023**, 5, no. 2, pp. 59-67.



© 2023 by the authors. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<http://creativecommons.org/licenses/by/4.0/>).