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ALTERNATIVE ADSORBENT MATERIALS USED TO REMOVE PHOSPHATES FROM WATER

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Introduction

One of the major sources of water pollution is represented by industrial effluents. Industrial effluents loaded with phosphates and nitrates from the leather industry, fertilizer industry, pharmaceutical industry, mining industry lead to eutrophication. When the phosphates concentration in water exceeds 0.02 mg/L eutrophication begins by decreasing the amount of dissolved oxygen and algae growth. Phosphates removal techniques include: chemical and physical methods, biological methods, adsorption techniques and nano-techniques.

On the other hand, management of the large quantities of pyritic ash produced is an environmental challenge for the whole world. Approximately 15 million tonnes of pyritic ash are produced annually. Unfortunately, this waste presents a low or non-existent management, being stored in open spaces. Starting from the chemical composition of this waste, research has focused by valorisation of this waste through different methods based on the circular economy principles [29]. The most current methods for pyritic ash valorization include: metals recovery, chemical lopping combustion or valorization in order to obtain value added products (pigments, catalysts, adsorbent materials).

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

Materials and methods

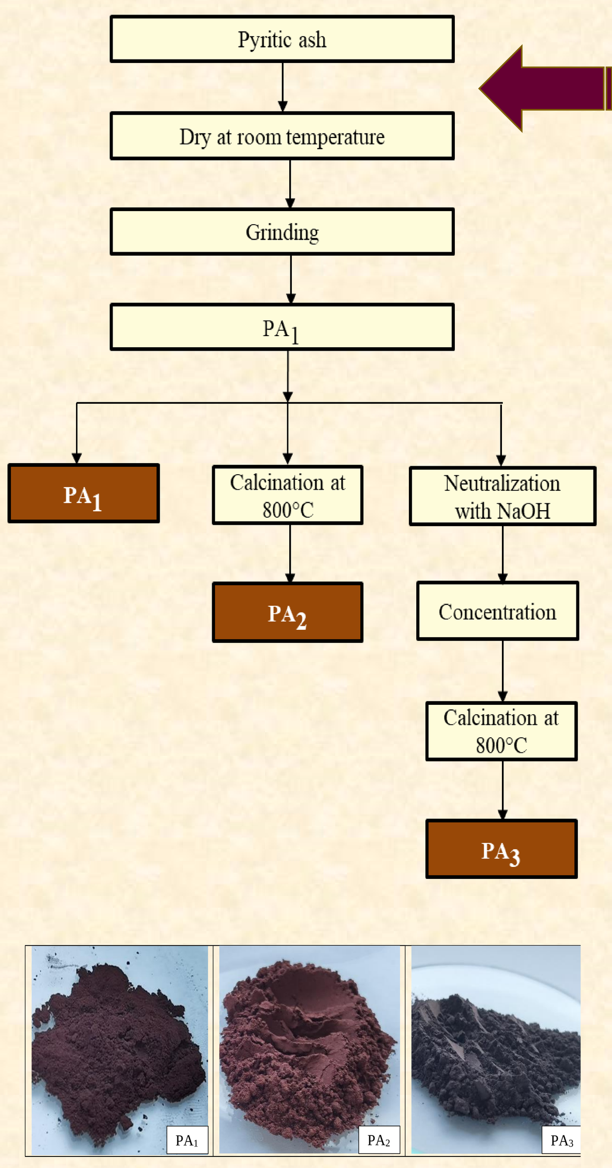

Figure 1. Sample preparation of adsorbent materials

Samples preparation

The pyrite ash (PA), used in our studies, was collected from a sulphuric acid production enterprise in Southern Romania. Samples preparation of adsorbent materials is described in Figure 1.

Samples characterization

Adsorbent materials based on pyritic ash (PA_1, PA_2, PA_3) 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. Following pH measurements (Table 1) it could be observed that PA_1 shows an acid pH (2.82), PA_2 shows a weak acid pH (5.4), while PA_3 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 2; Table 1) showed that the PA_3 adsorbent material had the smallest specific surface area (1.03 m^2/g) for 90% mass. 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 PA_1 has the highest iron content (49.77%), while adsorbent material PA_3 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.

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 (PA_1, PA_2, PA_3) using orbital shaker with 100 mL volume of KH_2PO_4 10 mg/L solution at room temperature 22 (+/-) 2 ^oC. 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.

	PA_1	PA_2	PA_3
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

Tabel 1. Characterization of PA_1, PA_2, PA_3 in terms of pH, specific surface area and particle size distribution

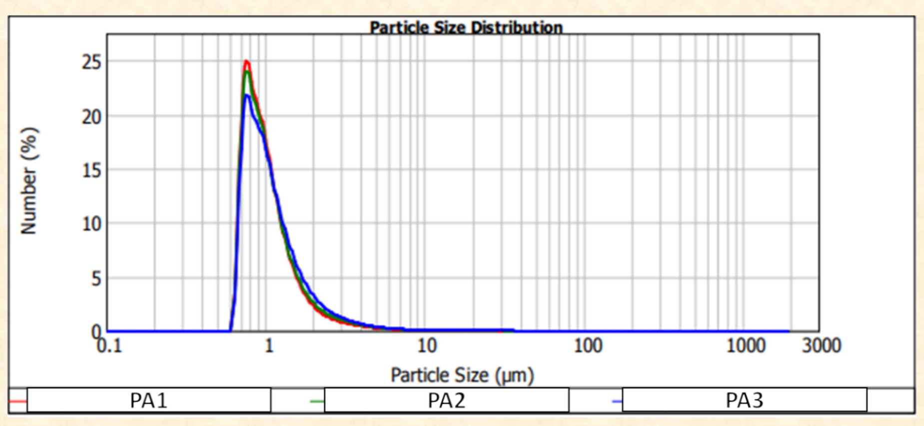

Figure 2. Particle size distribution of PA_1, PA_2, PA

Metal content (%)	Fe	Ca	As	P	Cd	Co	Pb	Zn	Cu	Al
PA_1	49.77	1.77	0.15	0.04	0.0009	0.014	0.28	0.43	0.058	0.40
PA_2	48.79	1.72	0.13	0.03	0.0009	0.013	0.27	0.32	0.054	0.40
PA_3	46.02	1.78	0.13	0.03	0.0009	0.013	0.24	0.33	0.053	0.39

Table 2. Metals content of PA_1, PA_2, PA_3

Results

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..

Effect of contact time and stirring speed on phosphate removal

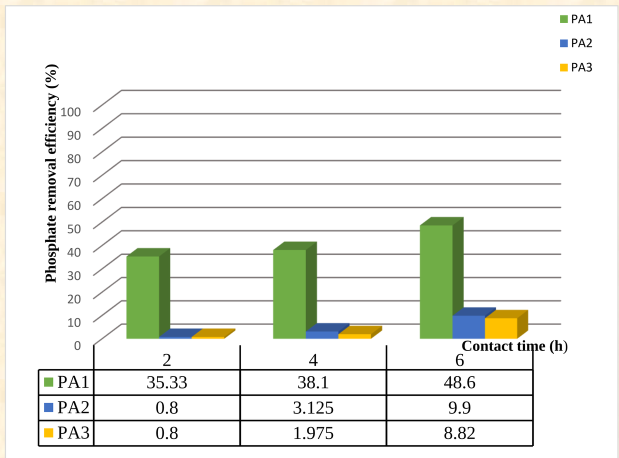

Figure 3a. Influence of contact time at stirring speed (0 rpm)

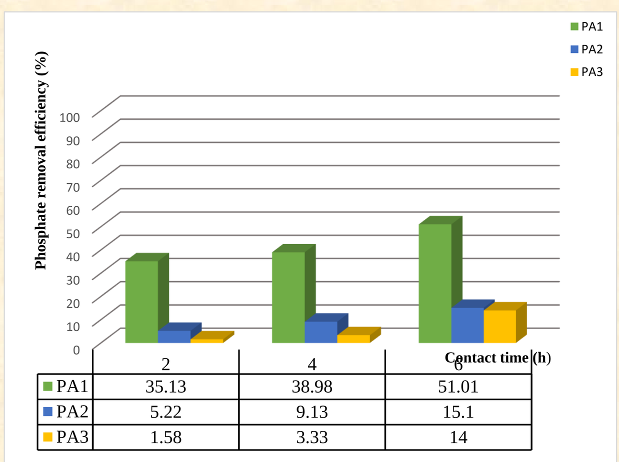

Figure 3b. Influence of contact time at stirring speed (50 rpm)

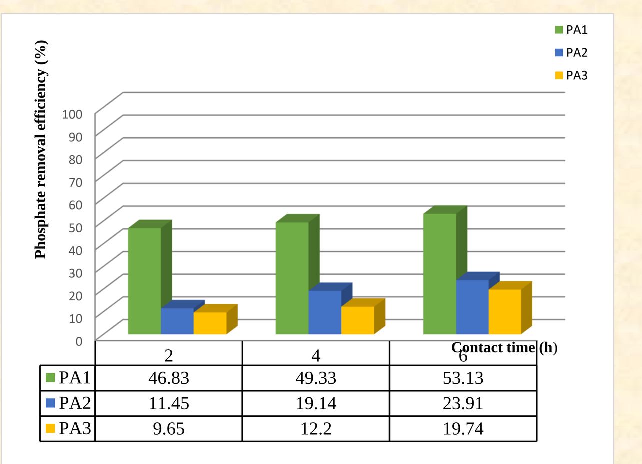

Figure 3b. Influence of contact time at stirring speed (100 rpm)

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 PA_1, PA_2, PA_3 adsorbent material and 100 mL KH_2PO_4 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 3a-3c) showed that increasing the contact time (2h-6h) and also 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.
It could be observed that 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 PA_1, PA_2, PA_3 (figure 3c). Also, in these accounts, it was observed that PA_1 showed the highest phosphate removal efficiency (53.13%), while PA_3 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

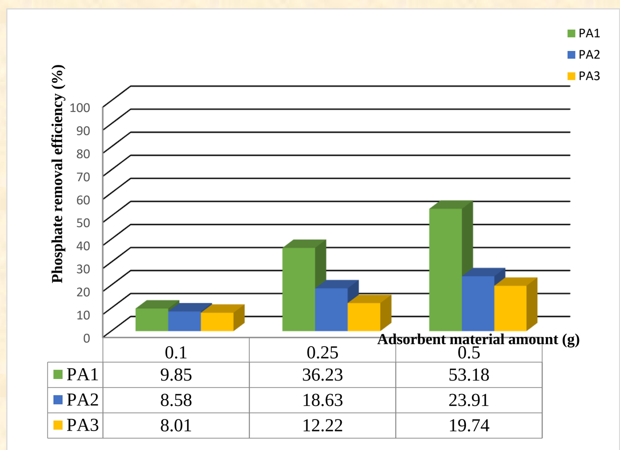

Figure 4. Influence of adsorbent material amount

Experimental results demonstrated that increasing the amount of adsorbent material (0.1 g - 0.5 g) significantly improves the efficiency of phosphate removal from water. In the case of PA_1 adsorbent material, could be observed an increase of about 6 times of the phosphate removal efficiency when the adsorbent material increases from 0.1 g to 0.5 g. In the case of PA_2 and PA_3 adsorbent materials, a tripling of the phosphate removal efficiency from 8.58% to 23.9% could be observed for PA_2 and a doubling of the phosphate removal efficiency from 8.01% to 19.74% could be observed for PA_3. The best efficiency was shown for PA_1 (53.13%), while PA_3 showed the lowest efficiency (19.74%).

Conclusions

- Experimental studies carried out on the phosphates removal efficiency from water by the three pyritic ash adsorbents (PA_1, PA_2 and PA_3) 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.

Acknowledgments

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