**Phosphorous removal and recovery from wastewater by adsorption using an innovative calcined pyroaurite**

Dario Frascari1\*, Carla Maggetti1, Tommaso Tabanelli2, Davide Pinelli1

*1 Dept. of Civil, Chemical, Environmental and Materials Engineering, University of Bologna, Via Terracini 28, 40131 Bologna; 2 Dept. of Industrial Chemistry “Toso Montanari”, University of Bologna, Viale Risorgimento 4, 40136 Bologna.*

*\*Corresponding author E-Mail: dario.frascari@unibo.it*

**1.Introduction**

Approximately 90% of phosphate rock is used for food production: 82% for fertilizers, 5% for animal feed, and 2–3% for food additives [1]. Furthermore, in current agricultural P utilization, nearly 90% of P is lost to the environment. Such losses enrich the P concentration in local streams, leading to environmental problems such as red tide and eutrophication. Municipal wastewaters (MWW) may contain from 5 to 20 mg/l of total phosphorous [2], making them an interesting source of P because of the possibility to simultaneously purify the water from P and recover it. Removal of ionic substances using the principle of adsorption by ion exchange resin has been used quite commonly in wastewater treatment. Adsorption guarantees full control of the effluent quality and allows P recovery, leading to a final product than might be used in fertilizer manufacture [3]. In comparison with alternative P recovery technologies, adsorption presents advantages such as operational simplicity, low capital and operational costs [4]. The choice of the adsorbent material must be done based on many parameters: capacity, selectivity, ease of regeneration, but also it must be able to bind phosphate at low concentration. This is fundamental since the MWW usually shows P concentrations around 7 mg/L, a very low concentration compared to those of other anions, such as sulfate and chloride, but with relatively high valence and weight. The consequence is that traditional ion exchange processes are not effective in removing phosphate anions. Various adsorbents and anion exchangers were found to show high adsorption capacity for phosphate ion, including metal oxides/hydroxides, hybrid anion exchangers HAIX and double-layered hydroxides LDH [5]. LDH are intensively studied due to their favorable properties such as high surface area, basicity, anion exchange properties and positive surface charge. In this work pyroaurite (used after calcination at 350°C for 5 hours), an LDH belonging to the group of hydrotalcite, has been studied as adsorbent material for the removal and recovery of P from a MWW from the purification plant of the municipality of Bologna (HERA). In particular, the research focused on (i) assessing the performances of calcined pyroaurite regarding P adsorption and desorption in batch and continuous flow tests with an actual MWW and (ii) evaluating the sorbent structure stability during 6 repeated breakthrough tests.

**2. Methods**

The performance of the material in terms of P adsorption has been estimated by adsorption isotherm tests, and continuous flow adsorption/desorption breakthrough tests, in a fixed-bed column packed with calcined pyroaurite. Cations analyses were performed with an HPIC method. All the procedures and methods followed are extensively described by Pinelli et al. [6]. The continuous tests were performed in a small-scale laboratory PVC column (0.40 m length, 0.013 m of diameter) packed with the adsorbent material for a height of 0.20 m.

**3. Results and discussion**

*3.1 Adsorption Isotherm*

A 9-points isotherm was performed with a real MWW effluent to investigate the performance of calcined pyroaurite in presence of competing anions. The results of the isotherm test are shown in Figure 1 in terms of P sorbed concentration versus P the residual equilibrium concentration in the liquid. The experimental data were interpolated with the Langmuir and Freundlich models, with regression coefficient closer to 1. The experimental data showed a favorable isotherm: high solute adsorbed can be obtained even at low concentrations in the fluid. Indeed, the estimated P operating capacity at saturation resulted to be 13.1 mgP gdry resin-1.

**Figure 1**. 9-point adsorption isotherm of calcined pyroaurite with HERA MWWT.

*3.2 Continuous flow adsorption/desorption breakthrough tests*

The adsorption/desorption breakthrough tests were conducted in a packed-bed column fed with the HERA WWTP effluent at 24-25°C. The adsorption phase was performed with an empty bed contact time (EBCT) of 5 min. The results obtained (Figure 2) show an excellent phosphate selectivity: all the other anions finish eluting even before the phosphate starts coming out: all the competing anions start to exit the column from 8 to 12 hours of operation (100 to 150 BVs) and their concentration became equal to the inlet one around hour 29 (350 BVs). Phosphate anions started to exit the column after about 40 h (500 BVs), meaning that large volumes of wastewater can be treated in a single adsorption cycle. The half saturation P concentration (3.5 mgP/L) has been reached after 77.5 h (928 BVs). The desorption/regeneration procedure was performed eluting the NaOH 2% with EBCT 10 min to regenerate the resin and recover the P rich product. The curves obtained (Figure 3) are partially overlapped, and this means that purity in P of the final desorbed solution cannot be expected.

**Figure 2.** P adsorption continuous flow test conducted with calcined pyroaurite. Breakthrough curves of phosphorous and the competing cations obtained with P-spiked HERA WWTP effluent.

**Figure 3.** P desorption continuous flow test conducted with calcined pyroaurite. Breakthrough curves of phosphorous and the competing cations obtained with NaOH 2%.

To verify the repeatability of the adsorption/desorption process and the stability of the actual active phase after that the calcined pyroaurite is rehydrated, a set of 5 breakthrough tests has been conducted with the same operational conditions: the performances were similar, indicating a reproducible behavior of the process. Moreover, after the test, there was no sign of mechanical degradation of the resin, so mechanical stability and structural integrity have been preserved, even if more tests are necessary to confirm the durability and regeneration capability of the material.

Calcined pyroaurite after 5 BTs shows very good average performances: for the adsorption phase 665 BVs of MWW effluent were treated at breakpoint BP (1mgP/L as law limits for P concentration in MWW), with an adsorption yield (Yads,P) of 95% and an operating capacity at BP (ƞP) of 7.5 mgP/gdry resin. The mean concentrations CL at BP in the desorbed product were: 70 mgP/L for P, 81 mg/L for Cl-, 8 mg/L for NO3- and 257 mg/L for SO42-. The concentration factors (the ratio between the concentration in the desorbed product and that in the fresh MWW) were 32, 0.38, 0.49 and 2.99 for P, Cl-, for NO3- and SO42- respectively confirming that the sorbent is very selective for P (only sulphate was partially concentrated in the desorbed product).

**4. Conclusions**

Calcined pyroaurite seems to be a very interesting material for P removal and recovery from MWW. The data collected after 5 breakthrough tests confirm that the process is reproducible and that, therefore, the adsorbent phase and structure is preserved after each test. The process seems to work well on a small scale with an EBCT of 5 min. BT curves of the other competing anions are well separated from the P one and the adsorbed amounts of the other anions are low, showing that the material is very selective toward P. The concentrations of the desorbed product confirm that the process leads to concentrate P by 30-70 times, sulphate by only 2-5 times, while nitrate and especially chloride dilute to less than half of the initial concentration of MWW. These are all promising results, but further tests in a pilot plant with a greater high resin bed are needed to optimize the process.

**References**

[1] D. Cordell, S. White, «Life’s Bottleneck: Sustaining the World’s Phosphorus for a Food Secure Future», *Annu. Rev. Environ. Resour.*, vol. 39, n. 1, pp. 161–188, 2014, doi: 10.1146/annurev-environ-010213-113300.

[2] M. Henze, *Biological wastewater treatment: principles, modelling and design*. London: IWA Pub., 2008.

[3] S. Sengupta, A. Pandit, «Selective removal of phosphorus from wastewater combined with its recovery as a solid-phase fertilizer», *Water Res.*, vol. 45, n. 11, pp. 3318–3330, 2011, doi: 10.1016/j.watres.2011.03.044.

[4] L. M. Blaney, S. Cinar, A. K. SenGupta, «Hybrid anion exchanger for trace phosphate removal from water and wastewater», *Water Res.*, vol. 41, n. 7, pp. 1603–1613, 2007, doi: 10.1016/j.watres.2007.01.008.

[5] S. Gubernat, A. Masłoń, J. Czarnota, P. Koszelnik, «Reactive Materials in the Removal of Phosphorus Compounds from Wastewater—A Review», *Materials*, vol. 13, n. 15, 2020, doi: 10.3390/ma13153377.

[6] D. Pinelli, S. Bovina, G. Rubertelli, A. Martinelli, S. Guida, A. Soares, D. Frascari, «Regeneration and modelling of a phosphorous removal and recovery hybrid ion exchange resin after long term operation with municipal wastewater». Chemosphere 286:131581, 2022, doi: 10.1016/j.chemosphere.2021.131581