

„Wet-process phosphoric acid decadmiation using ion-exchange method”

K. Borowik, P. Rusek, S.Schab, A. Bińczak

Fertilizer Research Group, Lukaszewicz Research Network – New Chemical Syntheses Institute, Al.Tysiąclecia Państwa Polskiego 13a, 24-100, Puławy, Poland

Keywords: wet process phosphoric acid, cadmium removal, phosphorous fertilizer.

Presenting author email: krzysztof.borowik@ins.lukasiewicz.gov.pl

Cadmium is a toxic element that poses a threat to human and animal health due to its presence in phosphorus raw materials used to produce mineral fertilizers. Wet-process phosphoric acid (WPA) is used primarily for the production of mineral fertilizers. WPA purification methods used in industry conditions are based on precipitation methods, solvent extraction, and ion exchange. Currently, effective and low-cost solutions to purify acid from contamination with magnesium, iron, aluminum, and cadmium compounds are still being sought. However, purification of phosphoric acid increases production cost of mineral fertilizers. The basic problem related to the use of WPA for the production of P-fertilizers is the content of highly toxic cadmium, which is a limited element in mineral fertilizers (Kouzbour 2019). This paper present results of cadmium sorption from technical-grade WPA by means of Amberlite 200 ion exchanger.

Experimental procedure

The aim of the work was to remove cadmium from WPA using ion-exchange method in a dynamic condition. The objective of the research was wet-process phosphoric acid obtained from an industrial phosphoric acid plant of the Grupa Azoty Zakłady Chemiczne Police S.A. . Typical composition of tested acid is presented in table. 1. A few commercial ion-exchangers were primarily tested in a static conditions to select the most perspective one for removal of cadmium. The tested ion-exchangers were: Purolite S957, Amberlite 200, Amberlite IRA910, Amberlite IRA458, Amberlite IRA900, Lewatite TP260, Purolite RSC, and Amberlite 958. Among them, Amberlite 200 exhibit the highest affinity towards Cd(II) sorption, so that it was selected for the further experiments.

Table 1. Chemical compounds of WPA - Chemical Plants Police S.A.

Compound	Value
P ₂ O ₅	49.5 %
S	1.14 %
CaO	0.008%
SiO ₂	0.02 %
MgO	1.68 %
Fe ₂ O ₃	1.12 %
Al ₂ O ₃	2.32 %
K ₂ O	0.0004 %
Na	0.036 %
Cd	34.1 mg/kg

Cadmium separation was carried out on Amberlite 200 cation exchanger in a dynamic conditions using laboratory set presented in Fig.1. WPA was diluted with water prior the experiment to 15% P₂O₅ (d=1,122 g/cm³) to make acid density lower than ion exchanger. Due to the long duration of a single test, a special sample collector was designed and manufactured to enable continuous operation for many days, automatically collecting up to 24 samples of the eluate in standard laboratory plastic tubes V=50 cm³. The autosampler is made of material resistant to phosphoric acid (PTFE). The device controller allows to set the standstill time and rotation time with an accuracy of 0.01 seconds, The ion exchange column was immersed in a glycerin-based liquid in a glass cylinder, connected to ultra thermostat by tubes for precise temperature control.

The ion exchange column was continuously fed with the acid solution at a regulated selected speed using a peristaltic pump. The purified acid was passed through the column, eluate samples were collected and the cadmium content was analyzed using the GF-AAS method (VARIAN AA240Z/GTA120). Cadmium was determined at the wavelength $\lambda=228.8$ nm, using 1% NH₄H₂PO₄ solution as a matrix modifier.

Cadmium sorption experiments were repeated in three loading-unloading cycles. Sorption of cadmium ions was carried out until total breakthrough, then the bed was regenerated with 4M HCl, washed with water and two further cycles of loading and regeneration of the bed were performed. A total of three loading cycles and three regeneration

cycles were performed on the same ion exchange bed in the described manner. The total experiment time was 45 days.

Experiment conditions:

- ion-exchange column dimensions: $L=320$ mm, $\varnothing = 20$ mm, batch volume $BV= 70$ cm³
- flow rate, $V= 0,206$ cm³/min = 0,176 BV/h
- temperature, $t= 40^{\circ}\text{C}$
- single collected fraction volume, $V= 50$ cm³
- bath loading time: 13 days

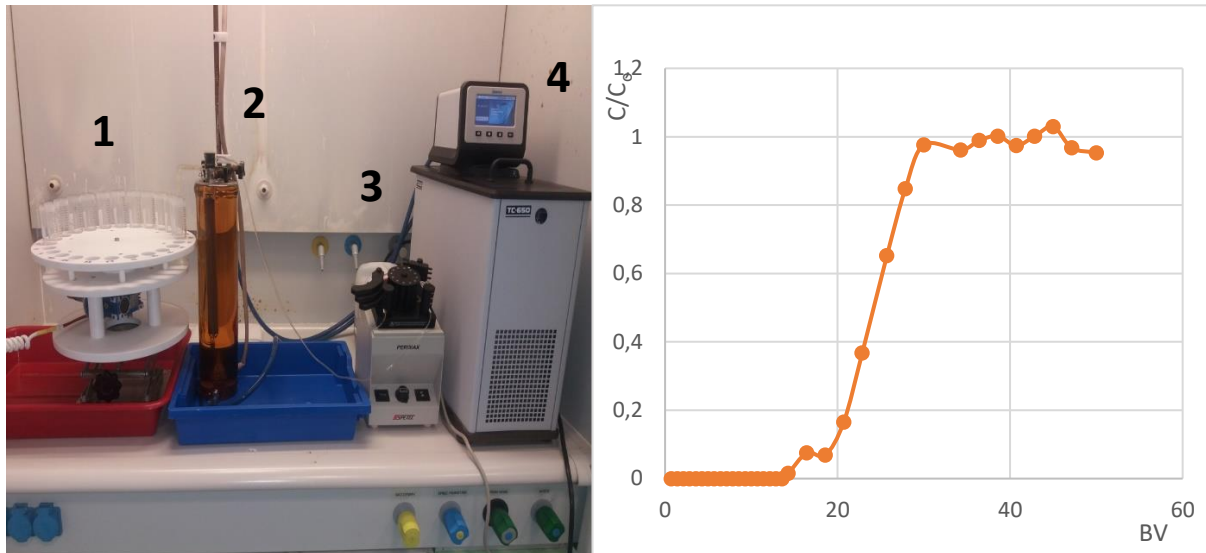


Fig.1. Laboratory set for ion-exchange cadmium removal from WPA. 1- automatic sample collector, 2- glass column filled with ion-exchanger, immersed in thermostatic liquid, 3-peristaltic pump SPETEC Perimax 12/4, 4- ultra thermostat Brookfield TC-640

Fig.2. Break-through curve of Cd(II) in WPA on Amberlit 200 – Run 2.

Results

Calculated cadmium concentration in each sample was used to plot the break-through curve, presented in Fig. 1. which represents the ratio of cadmium concentration in a specific eluate sample C , to initial Cd(II) concentration C_0 , as a function of the volume of purified WPA, expressed in bed volume (BV). After the elution is done, the ion-exchanger was regenerated, using 4M HCl, and the solution was collected for cadmium content determination.

Conclusions

The conducted research indicates, that Amberlit 200 can be used for purification of phosphoric acid. This ion exchanger shows no tendency to lose working capacity under the experimental conditions, i.e. using phosphoric acid 15% P_2O_5 at $t = 40^{\circ}\text{C}$ for 45 days, using 4M r-ru HCl for bed regeneration. Using a volumetric flow rate of 0.176 BV/h, twenty times the volume of phosphoric acid can be purified with an efficiency of $>80\%$.

Calculating the volume of the ion exchanger bed and the volume of the purified acid for industrial conditions, it can be seen that the required volume of the ion exchanger bed is very large due to the insufficient selectivity of the ion exchanger towards cadmium ions and, as a result, low Cd(II) sorption capacity. Due to kinetic reasons, the use of Dowex 200 for WPA purification seems to be limited. Magnesium(II) was found to be the main interfering ion.

S.Kouzobour et al. „Comparative analysis of industrial processes for cadmium removal from phosphoric acid: A review”, Hydrometallurgy 188 (2019), 222-247.