Removal of Cd(II) ions from industrial wet phosphoric acid on strongly acidic cation exchangers

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Phosphoric acid is one of the most important intermediates of the inorganic chemical industry, which is manufactured from phosphate ores using thermal and wet processes (Gilmour, 2013). About 84% to 90% of the worldwide production of wet phosphoric acid (WPA) is used in the manufacture of phosphate fertilizers (Kouzbour et al., 2019). Demand for P-fertilizers continues to grow as the world's population increases and the amount of arable land decreases. Wet-process phosphoric acid is contaminated with heavy metals including cadmium. The presence of high concentrations of hazardous metal substantially decreases its quality and commercial value (Taha et al., 2020). During the production process, most of the Cd is transferred from WPA into the P-fertilizers (Roberts, 2014). Cd accumulates in soils, and leaches into ground and surface waters, leading to increased uptake by crops, which results in increased levels in animals and in food products (Kouzbour et al., 2022). To prevent environmental pollution and to ensure safety for human health, the use of P-fertilizers in agriculture is framed by Regulation EU 2019/1009 of 5 June 2019 laying down the rules of making fertilizing products available on the EU markets. The allowable value for the Cd depends on the P content in macronutrient inorganic fertilizer. Where fertilizer has total P content of less than 5% P_2O_5 equivalent by mass, the Cd content must not exceed 3 mg/kg, or if it has P content equivalent or more by mass 5% P_2O_5, Cd content must not exceed 60 mg/kg P_2O_5.

Ion exchange is the process of purification, separation, and decontamination of aqueous or other ion-containing solutions with solid polymeric or mineral ion exchangers. This technique is widely used in different industries, especially in heavy metal removal from wastewater due to its high exchange capacity, high removal efficiency, and fast kinetics. Moreover, ion exchange and chelating resins are characterized by the ability to reuse for several cycles of sorption/desorption, and acid and heat resistance (Elzoghby, 2021).

The purification of wet-process phosphoric acid from Cd(II) ions using commercial cation exchange resins bearing sulfonic reactive groups was investigated. The sorption characteristic of AmberLite IRC 120H and Dowex G26 relative to Cd(II) ions were tested in a batch system, taking into account the influence of various parameters, such as the resin dose (0.1–6 g), phase contact time (1–30 min), and phosphoric acid concentration (1-5 mol/dm^3) to estimate the optimal parameters of the removal process. The concentration of Cd was analyzed by an inductively coupled plasma optical emission spectrometry (ICP-OES) at the wavelength 214.439 nm. The selected physicochemical properties of AmberLite IRC 120H and Dowex G26 are detailed in Table 1.

Table 1. Physicochemical properties of AmberLite IRC 120H and Dowex G26.

	AmberLite IRC 120H	**Dowex G26**
Manufacturer	DuPont	Dow Chemical Company
Polymer structure	Styrene-DVB	Styrene-DVB
Matrix	Gel	Gel
Type	Strong acid cation	Strong acid cation
Functional group	Sulfonic acid	Sulfonic acid
Ionic form	H^+	H^+
Physical form and appearance	Amber, translucent, spherical beads	Brown, spherical beads
Particle size range	300-1180 μm	600 -700 μm
Maximum working temperature	120 °C	130 °C
pH range	0-14	0-14

It was found out that as both resin's mass increases, the sorption efficiency significantly increases. This is related to the increased surface area and resin active sites. Therefore, an ion exchanger dose of 5.0 g has been selected for the other experiments for Amberlite IRC 120H and Dowex G26. Moreover, the increase in phosphoric acid molarity gradually reduces the sorption efficiency of Cd(II) ions, from 98.6 to 65.9% on Amberlite IRC 120H, and from 98.8 to 72.3% on Dowex G26 resin by varying phosphoric acid molarity from 1.0 to 5.0 mol/dm^3. This behavior suggests that Cd(II) sorption mechanism obeys to ion exchange type mechanism at low phosphoric acid concentration.

Kinetic studies of the sorption process play a key role in determining the time required for the system to establish equilibrium, which is important in industrial applications, and provide information on the mechanism and rate controlling steps of the process. Pseudo-first order (PFO), pseudo-second order (PSO), intraparticle diffusion (IPD) and Boyd models were used to describe the kinetic studies. The fitting of the kinetic model has been declared based on the agreement between the experimental data and the fitted curve, as well as the obtained R^2 coefficient. The best fit was obtained for the PSO model. Moreover, the tested sorption processes for both resins were very fast, and the equilibrium was established after 15 minutes. To acquire better knowledge about the adsorption mechanism and describe the equilibrium data the Langmuir, Freundlich, and Temkin adsorption models were used. The physicochemical properties of industrial WPA used in this study are given in Table 2.

Table 2. Physicochemical specification of industrial WPA.

	Wet phosphoric acid
H_3PO_4 molarity [mol/dm^3]	9.63
density [g/cm^3]	1.477
MER index [%]	1.77
Constituents concentration wt. [%]	
P_2O_5	46.3
F	8.14
Fe_2O_3	0.60
SiO_2	0.57
Al_2O_3	0.14
Constituents concentration [ppm]	
MgO	816
Zn	230
CaO	161
Cr	150
K_2O	146
Mn	101
U	91.5
V	88.6
Na_2O	48.6
Cd	**40.7**
Cu	26.0
Ni	18.6
As	15.2

The obtained results indicate that the removal of Cd(II) from wet phosphoric acid on Amberlite IRC 120H and Dowex G 26 proceeds with excellent efficiency. In this context, the use of ion exchangers appears to be a promising solution for WPA purification and the production of eco-friendly phosphate fertilizers as well as preventing for spread of Cd on agricultural land.

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