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

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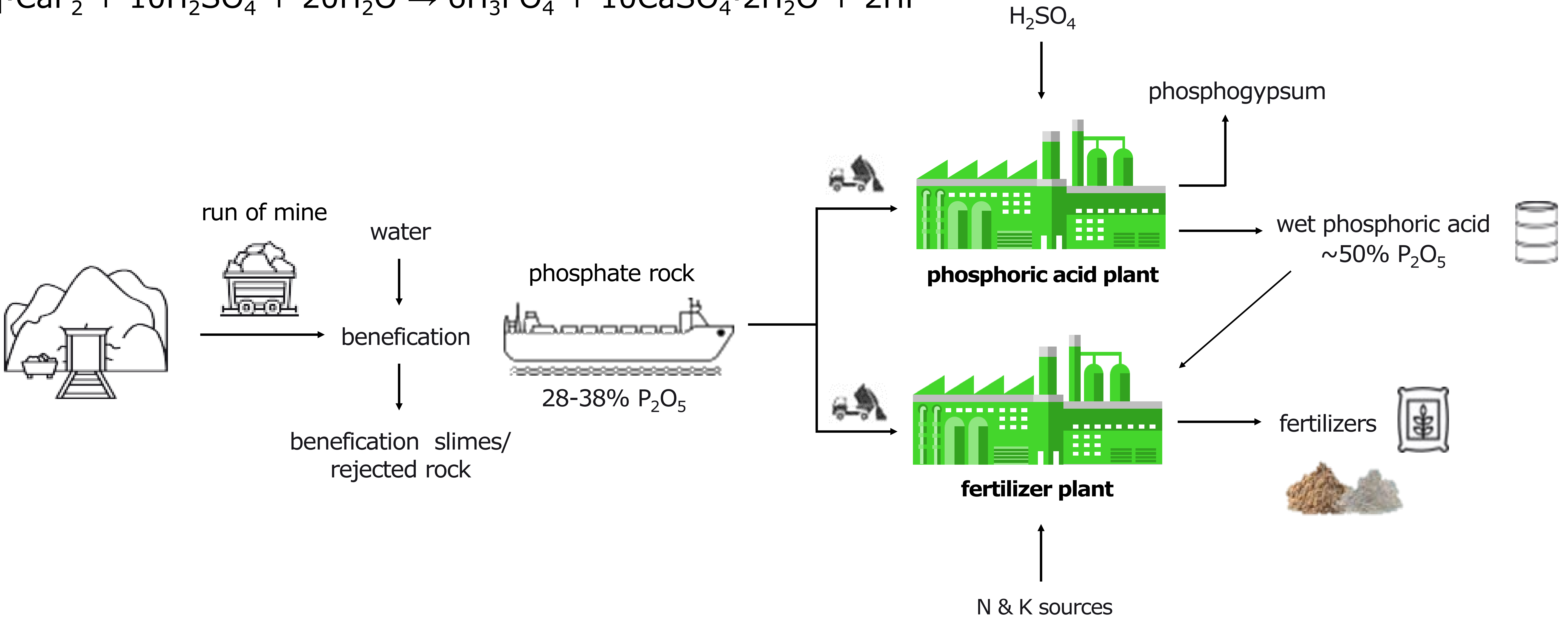
10th International Conference on Sustainable Solid Waste Management 21-24 June 2023, Chania, Crete, Greece

Phosphoric acid production
Wet process

Dihydrate process

$$[3Ca_3(PO_4)_2]\cdot CaF_2 + 10H_2SO_4 + 20H_2O \rightarrow 6H_3PO_4 + 10CaSO_4\cdot 2H_2O + 2HF$$



Wet phosphoric acid

- **84- 90%** of the worldwide production of wet phosphoric acid (WPA) is used in the manufacture of phosphate fertilizers,
- Wet-process phosphoric acid is contaminated with heavy metals including **cadmium**,
- During the production process, most of the Cd is transferred from WPA into the **P-fertilizers**,
- The presence of high concentrations of hazardous metal substantially decreases WPA quality and its commercial value,
- **Cadmium** accumulates in soils, and leaches into ground and surface waters, leading to increased crop uptake, which results in increased levels in animals and food products.

Table 1. Physicochemical specification of industrial WPA.

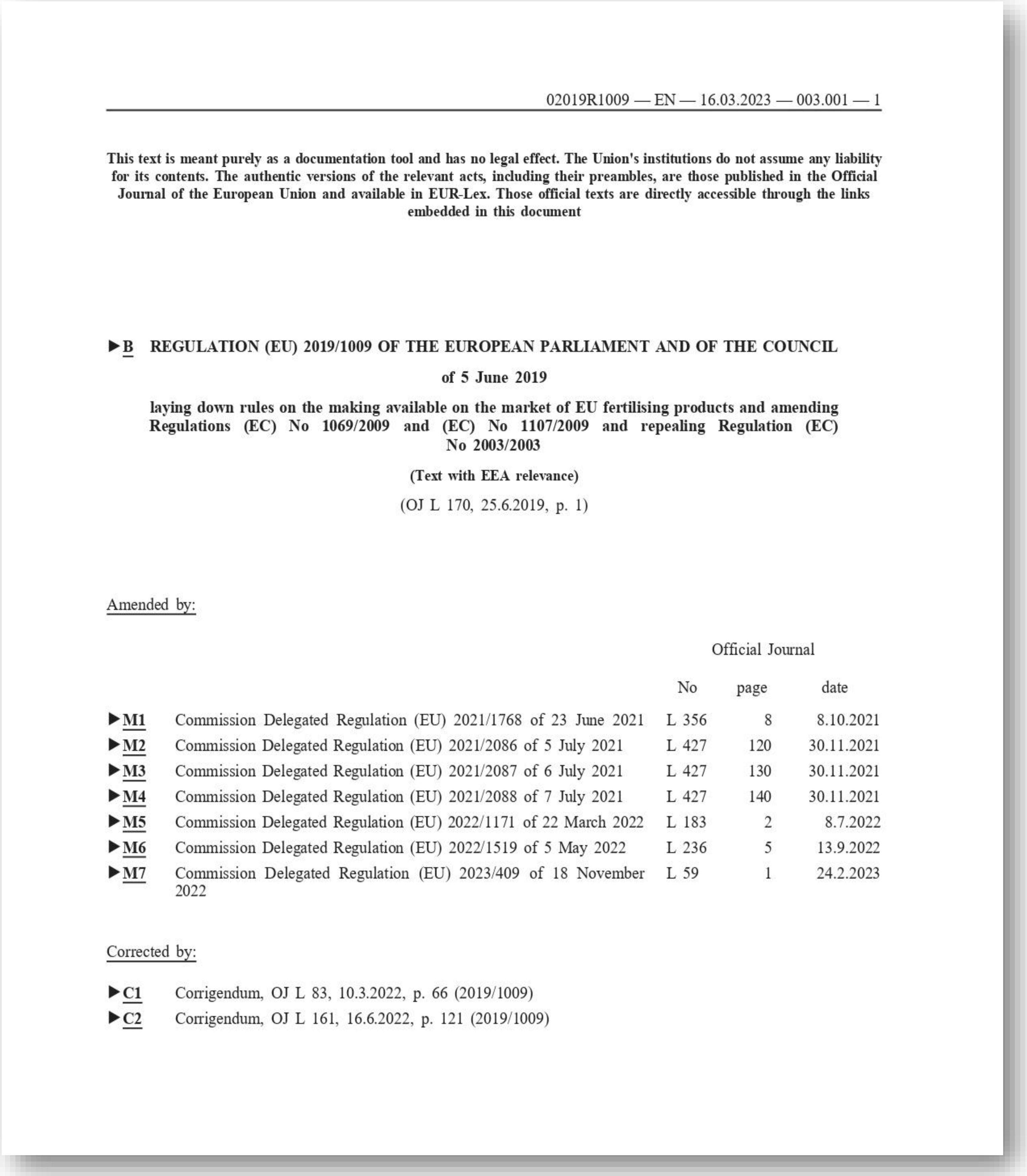
Parameter	Wet phosphoric acid
H_3PO_4 molarity [mol/dm^3]	9.63
density [g/cm^3]	1.477
Constituents concentration wt. [%]	
P_2O_5	46.3
F	8.14
Fe_2O_3	0.60
SiO_2	0.57
Al_2O_3	0.14
Constituents concentration [ppm]	
MgO	816
Zn	230
CaO	161
Cr	150
K_2O	146
Mn	101
U	91.5
V	88.6
Na_2O	48.6
Cd	**40.7**
Cu	26.0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

Cadmium in phosphate fertilizers

Limit values of cadmium

- ✓ where an inorganic macronutrient fertilizer has a total phosphorus (P) content of **less than 5%** phosphorus pentoxide (P_2O_5)-equivalent by mass: **3 mg/kg dry matter**, or
- ✓ where an inorganic macronutrient fertilizer has a total phosphorus (P) **content of 5%** phosphorus pentoxide (P_2O_5)-equivalent or more by mass („phosphate fertilizer”): **60 mg/kg phosphorus pentoxide (P_2O_5)**.

Regulation (EU) 2019/1009 of the European Parliament and of the Council of 5 June 2019 Laying down Rules on the Making Available on the Market of EU Fertilising Products.



02019R1009 — EN — 16.03.2023 — 003.001 — 1

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►B REGULATION (EU) 2019/1009 OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL

of 5 June 2019

laying down rules on the making available on the market of EU fertilising products and amending Regulations (EC) No 1069/2009 and (EC) No 1107/2009 and repealing Regulation (EC) No 2003/2003

(Text with EEA relevance)

(OJ L 170, 25.6.2019, p. 1)

Amended by:

		Official Journal		
		No	page	date
►M1	Commission Delegated Regulation (EU) 2021/1768 of 23 June 2021	L 356	8	8.10.2021
►M2	Commission Delegated Regulation (EU) 2021/2086 of 5 July 2021	L 427	120	30.11.2021
►M3	Commission Delegated Regulation (EU) 2021/2087 of 6 July 2021	L 427	130	30.11.2021
►M4	Commission Delegated Regulation (EU) 2021/2088 of 7 July 2021	L 427	140	30.11.2021
►M5	Commission Delegated Regulation (EU) 2022/1171 of 22 March 2022	L 183	2	8.7.2022
►M6	Commission Delegated Regulation (EU) 2022/1519 of 5 May 2022	L 236	5	13.9.2022
►M7	Commission Delegated Regulation (EU) 2023/409 of 18 November 2022	L 59	1	24.2.2023

Corrected by:

►C1 Corrigendum, OJ L 83, 10.3.2022, p. 66 (2019/1009)
►C2 Corrigendum, OJ L 161, 16.6.2022, p. 121 (2019/1009)

Materials and methods

Ion exchangers

Gel type strongly acidic cation exchangers with polystyrene divinylbenzene (DVB) matrix and a sulfonic acid group–AmberLite IRC 120H (DuPont) and Dowex G26 (Dow Chemical Company).

Sorption process

The sorption of Cd(II) from WPA was tested in a batch system investigating the optimal parameters of the removal process, such as the resin dosage (0.1–6 g), H_3PO_4 molarity (1–5 mol/L), phase contact time (1–15 min), initial solution concentration ($0.5 \cdot 10^{-3}$–$2.5 \cdot 10^{-3}$ M) and temperature (293-333 K).

Cd determination

The concentration of Cd was analyzed by an inductively coupled plasma optical emission spectrometry (ICP-OES) at the wavelength 214.439 nm.

Effect of ion exchanger mass

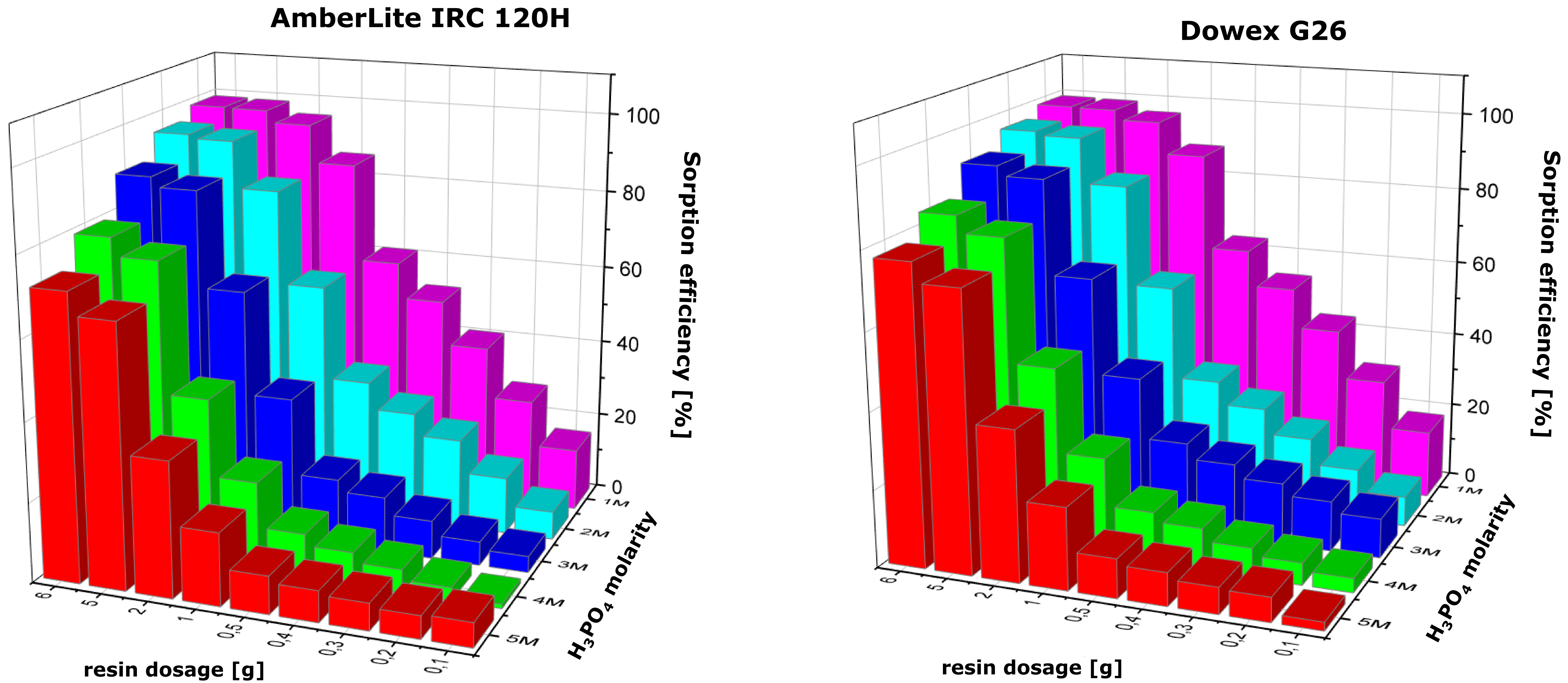
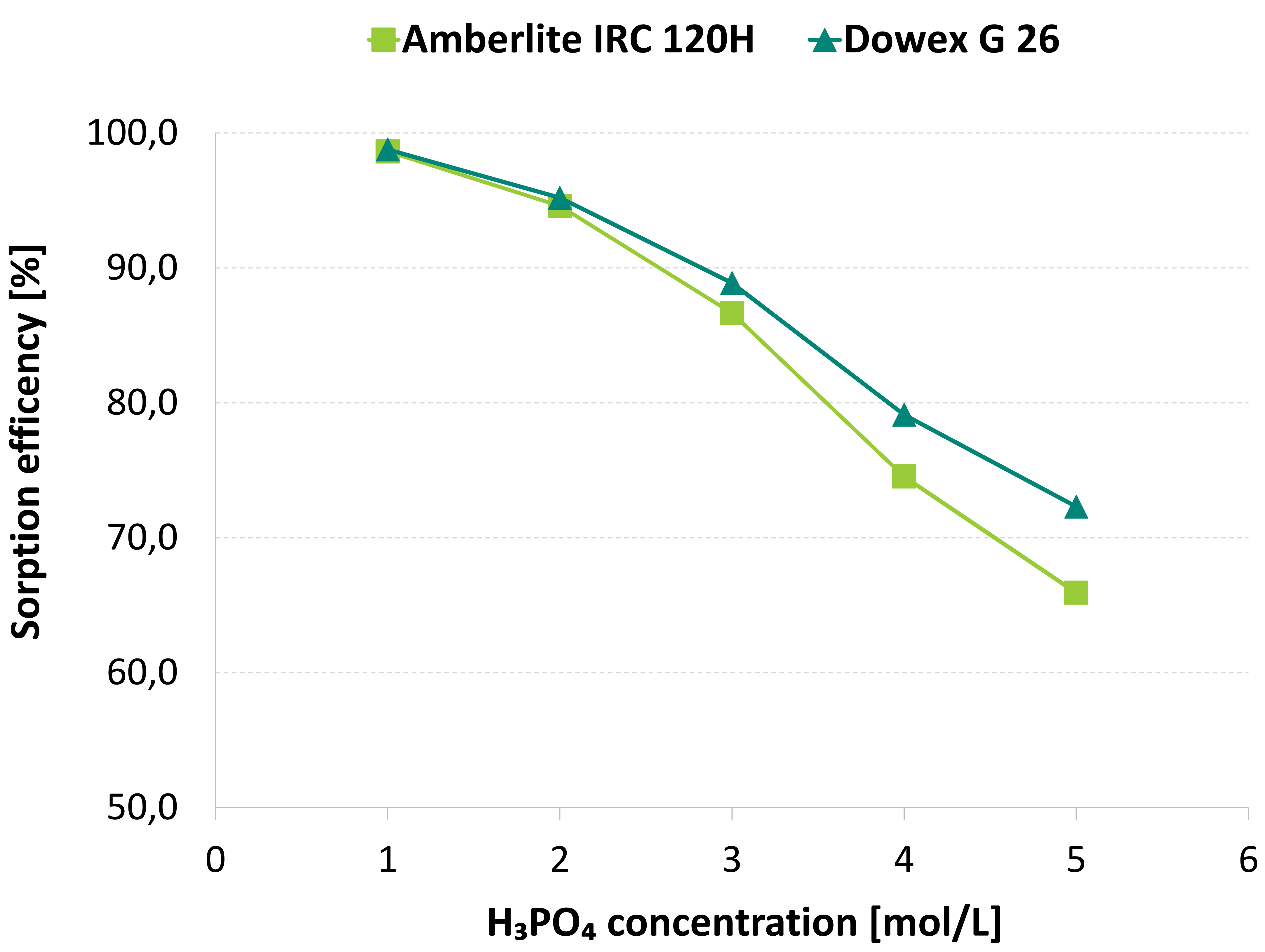


Figure 1. Effect of ion exchanger mass on Cd(II) removal from industrial WPA (t=5 h; V=30 cm^3, shaking speed 170 rpm; T=293 K).

Effect of phosphoric acid concentration



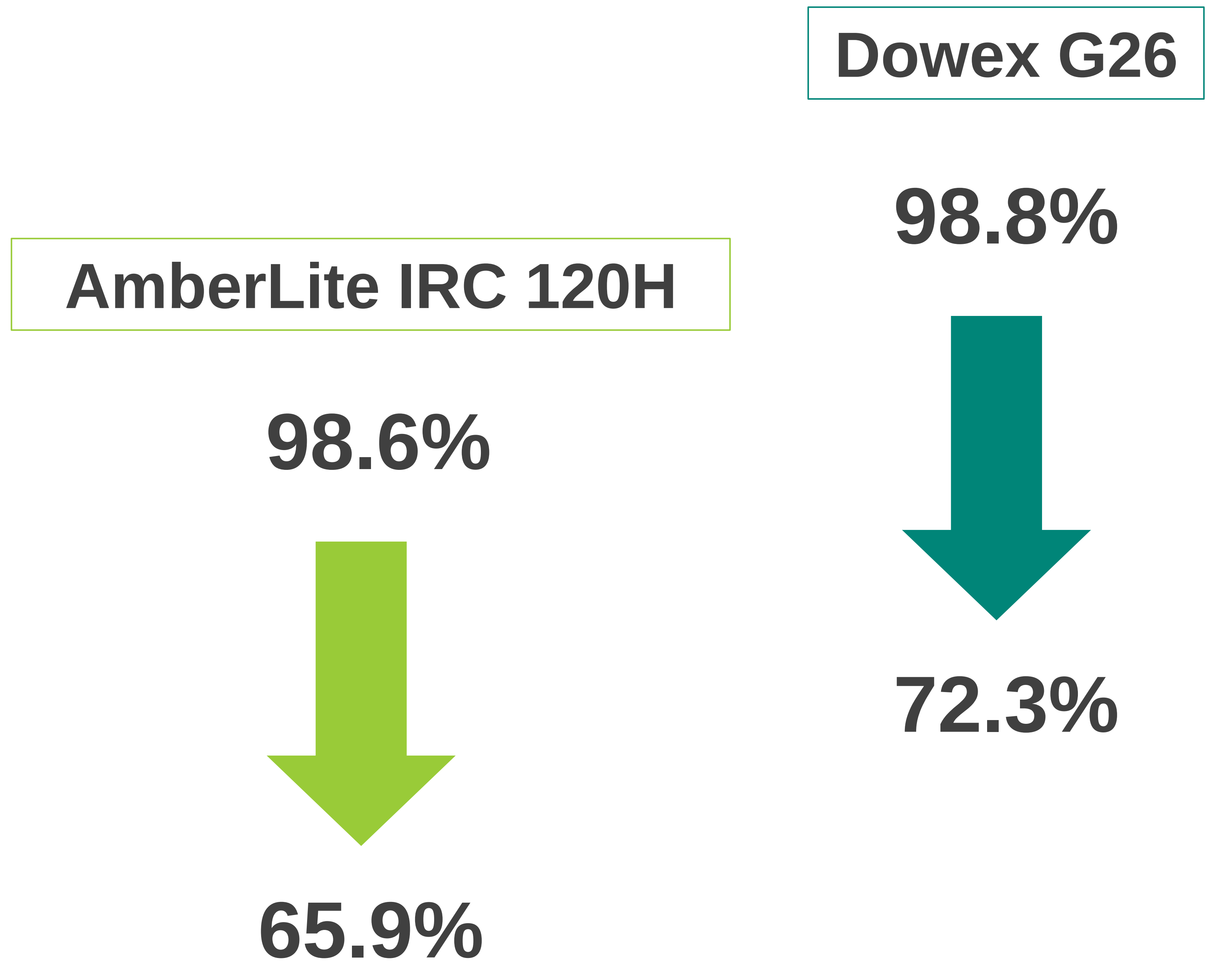


Figure 2. Effect of phosphoric acid concentration on Cd(II) removal on AmberLite IRC 120H and Dowex G26 (t=5 h; m=5g; V=30 cm^3, shaking speed 170 rpm; T=293 K).

Sorption kinetic models

$$\log(q_1 - q_t) = \log(q_1) - \frac{k_1 t}{2.303}$$

Pseudo-First Order

$$\frac{t}{q_t} = \frac{t}{q_2} + \frac{1}{k_2 q_2^2}$$

Pseudo-Second Order

$$q_t = k_i t^{1/2} + C$$

Intraparticle Diffusion

$$B_t = -0.4977 - \ln(1-F)$$

Boyd

Kinetic models

where:

q_1, q_2 and q_t – the amount of Cd(II) ions adsorbed per amount of ion exchanger at equilibrium. and at time t (mg/g),
k_1 – the rate constant of pseudo-first order equation (1/min),
k_2 – the rate constant of pseudo-second order equation (g/mg·min).

where:

k_i – the rate constant of intraparticle diffusion equation (mg/g·min$^{0.5}$),
C – the value of intercept related to the boundary layer thickness (Weber–Morris diffusion constant),
F – the fraction of solute adsorbed at time t ($F = q_t/q_e$).

Effect of phase contact time

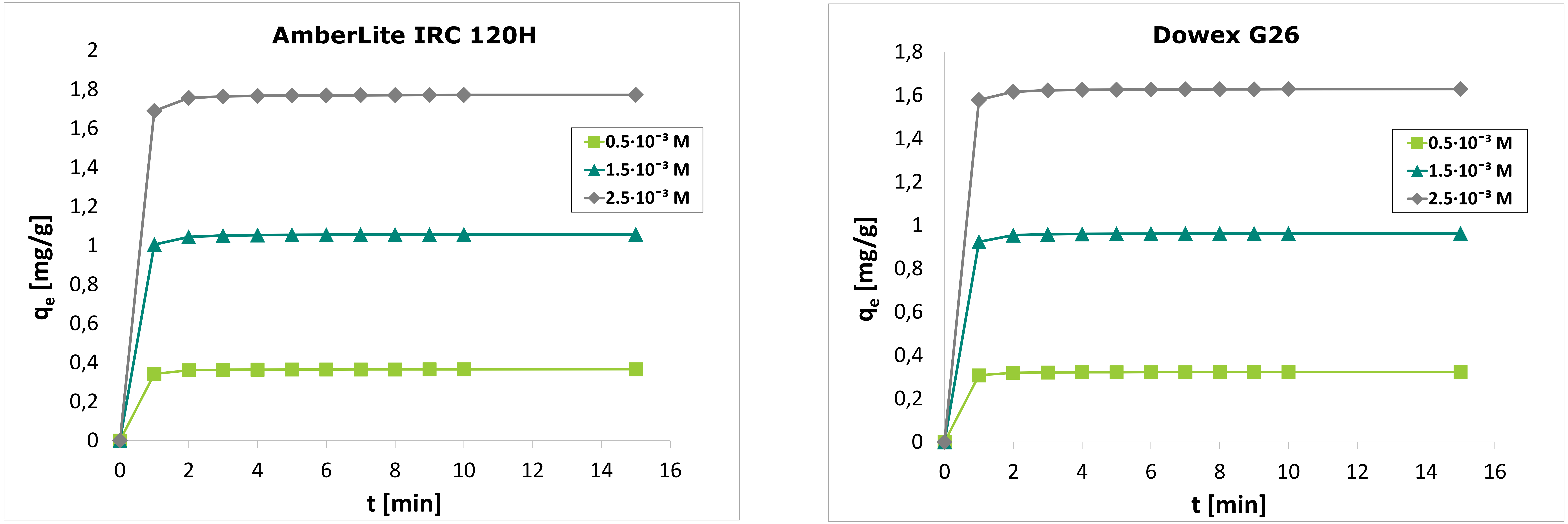


Figure 3. Effect of phase contact time and initial solution concentration on the sorption of Cd(II) on AmberLite IRC 120H and Dowex G26 (m=5g; V=30 cm^3; shaking speed 170 rpm; T=293 K).

Kinetic studies

Table 2. The kinetic parameters for the sorption of Cd(II) (C_0=0.5·10^{-3} mol/dm^3; T=273 K).

Kinetic models	Parameters	AmberLite IRC 120H	Dowex G26
	$q_{e,exp}$ [mg/g]	0.37	0.32
Pseudo-First Order (PFO)	$q_{1, cal}$ [mg/g]	0.012	0.009
	k_1 [1/min]	0.38	0.46
	R^2	**0.849**	**0.918**
Pseudo-Second Order (PSO)	$q_{2, cal}$ [mg/g]	0.37	0.32
	k_2 [g/mg·min]	61.4	95.5
	h	8.28	10.0
	R^2	**1.000**	**1.000**
Intraparticle Diffusion (IPD)	k_{i1} [mg/g·$min^{1/2}$]	0.030	0.019
	C_1	0.314	0.290
	R^2	**0.901**	**0.883**
Boyd	B_t	0.381	0.455
	R^2	**0.849**	**0.918**

Sorption isotherm models

$$\frac{C_e}{q_e} = \frac{1}{q_0 K_L} + \frac{C_0}{q_0}$$

Langmuir

$$\log q_e = \log K_F + \frac{1}{n} \log C_e$$

Freundlich

$$q_e = B \ln A + B \ln C_e$$

Temkin

Isotherm models

where:

q_e – sorption capacities at the equilibrium (mg/g),
q_0 – the maximum theoretical quantity adsorbed to provide a full monolayer (mg/g),
C_e – the equilibrium concentrations of Cd(II) in the solution (mg/L),
K_L – the Langmuir constant (L/mg),
K_F – the Freundlich constant (mg/g),
n – the Freundlich intensity parameter which denotes the surface heterogeneity or the magnitude of the adsorption driving force.

where:

A – the Temkin constant related to the maximum binding energy (L/g),
B – the constant related to the adsorption heat (J/mol) expressed as $B = RT/b_T$
R – the gas constant (8.314 J/mol·K),
T – the absolute temperature (K),
b_T – the Temkin isotherm constant.

Equilibrium studies

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Table 3. Adsorption isotherm parameters for the Cd(II) sorption from WPA (T=273 K).

Isotherm models	Parameters	AmberLite IRC 120H	Dowex G26
Langmuir	q_{exp} [mg/g]	2.73	2.40
	q_0 [mg/g]	1.84	2.00
	K_L [L/mg]	0.124	0.154
	R_L	0.018	0.016
	R^2	**0.937**	**0.956**
Freundlich	K_F [L/mg]	0.25	0.38
	n	0.70	0.73
	R^2	**0.973**	**0.982**
Temkin	A [L/g]	1.09	1.51
	B [J/mol]	1.31	1.18
	b_T [kJ/mol]	1.89	2.10
	R^2	**0.802**	**0.842**

Separation factor – R_L

$$R_L = 1/(1+K_L C_0)$$

$0 < R_L < 1$ sorption favorable

$R_L > 1$ sorption unfavorable

$R_L = 0$ sorption irreversible

Freundlich isotherms

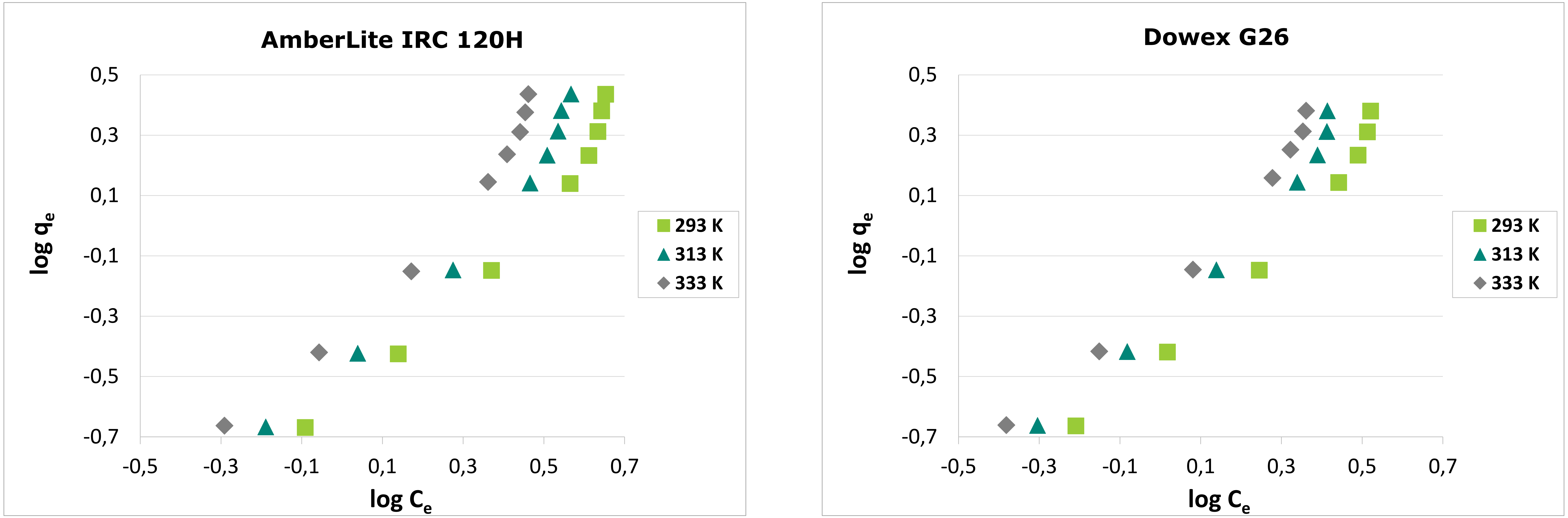

Figure 4. Adsorption isotherms for the sorption of Cd(II) on AmberLite IRC 120H and Dowex G26 at different temperatures.

Effect of temperature
Thermodynamic studies

Table 4. The thermodynamic parameters for the sorption of Cd(II).

Thermodynamic parameters		AmberLite IRC 120H	Dowex G26
ΔH^0 [kJ/mol]	-	8.92	7.56
ΔS^0 [J/mol K]	-	26.20	23.24
ΔG^0 [kJ/mol]	293 K	-15.61	-16.04
	313 K	-17.19	-17.78
	333 K	-18.96	-19.25

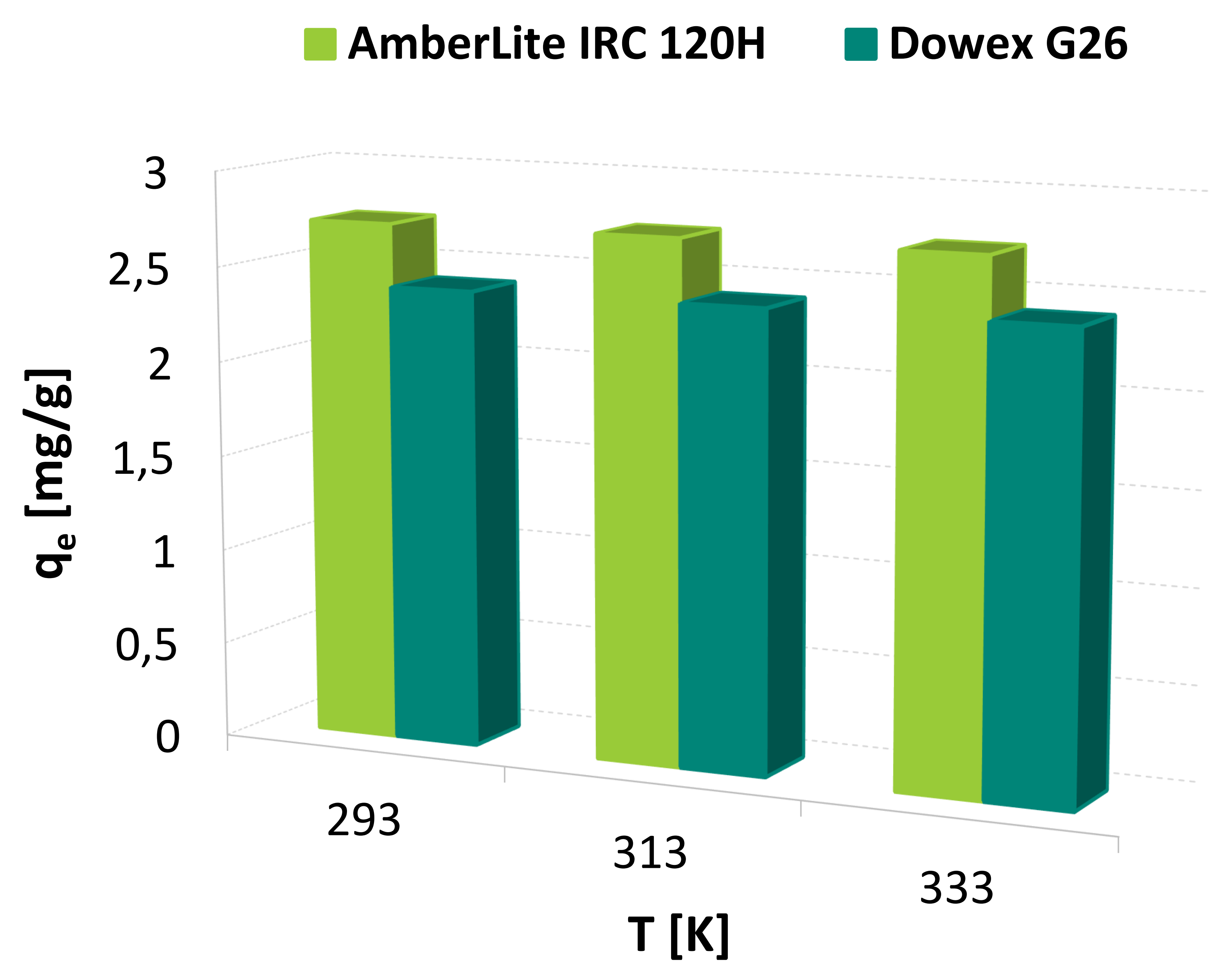

Figure 5. The comparison of the maximum sorption capacity of ion exchangers to the Cd(II) at different temperatures.

Conclusions

1. In the equilibrium state at 293 K, the maximum adsorption capacity was 2.73 mg/g for AmberLite IRC 120H and 2.40 mg/g for Dowex G26. The optimum process conditions are: the ion exchanger mass of 5g, H_3PO_4 molarity of 1 mol/L, phase contact time of 15 minutes, and temperature 333 K.

2. The tested sorption processes were very fast, and the equilibrium was established after 15 minutes. The process kinetics follows the Pseudo-Second Order kinetic model.

3. The determined adsorption isotherms allowed the fitting of isotherm models to the experimental data. Great agreement of the obtained data with the Freundlich isotherm model was observed.

4. Based on the thermodynamic parameters, it was found that the sorption processes using both ion exchangers were endothermic (positive $\Delta H°$ values), and spontaneous and thermodynamically favorable (negative $\Delta G°$ values). Moreover, obtained values of $\Delta G°$ and $\Delta H°$ parameters suggest that physical adsorption is the dominant mechanism.

5. The obtained results indicate that removal Cd(II) from industrial wet phosphoric acid on AmberLite IRC 120H and Dowex G26 proceeds with excellent efficiency. In this context, the use of strongly acidic ion exchangers appears to be a promising solution for WPA purification and the production of eco-friendly P-fertilizers, as well as preventing for spread of Cd on agricultural land.

Thank you for your attention!

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