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ADSORPTION STUDIES OF CADMIUM FROM DILUTED SOLUTIONS

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ABSTRACT. The paper presents some results of the adsorption tests of cadmium from aqueous solutions on three different substrates. The optimised conditions of the process are identified and the adsorption parameters are calculated from the Langmuir plots. Considerations about the mechanism and efficiency of the process are done.

KEYWORDS: adsorption, ion exchange, cadmium, wastewater treatment.

1. INTRODUCTION

Ionic cadmium occurs in natural waters coming from wastewater insufficiently treated. Cadmium has a chemical structure closely the one of zinc and can replace it in the enzymes, leading to a decrease in their effect as catalysts. This is the reason why cadmium is considered toxic for living organisms, including humans. The first cadmium disease was registered in 1970 in Japan under the name “Itai-Itai”. Cadmium is a cumulative poison: at birth the concentration is null and by ageing the ions deposit in leaver and kidneys leading to disturbances in the calcium metabolism and to a weak bones structure, [1,2].

Normally, cadmium appears in very low concentrations (less than 1μg/L) but industrial pollution can increase this value. The toxic dose is considered by the Romanian standard at 5μg/L and by WHO at 3 μg/L, [3].

Water treatment for cadmium removal can be easily done – as for the other metal cations, [4, 5] – using the ion exchange process. This process is effective at medium concentrations but it must be carefully developed when very low ion concentrations are involved.

Considering the concentration at which cadmium is dangerous, the ion exchange process must be optimise for obtaining high efficiency. The paper studies the adsorption of cadmium ions on two different cation exchangers and one substrate of modified anion exchanger; the optimised adsorption conditions and the isotherms that allowed to make assumptions on the mechanism of the processes are presented.

2. EXPERIMENTAL

1. *Solutions*

- Solutions of cadmium nitrate with the concentration 10^{-3}….10^{-1} Eg/L were prepared using $Cd(NO_3)_2 \cdot 4H_2O$, 99.7% (Reactivul Romania) and bi- distilled water.
- Solutions of Ethylenediaminotetraacetic acid Disodium salt Dihydrate, $C_{10}H_{14}N_2Na_2O_8 \cdot 2H_2O$), Complexon III (Reanal Budapest, Hungary), as reactive for cadmium concentration identification.

- Solid solution of NaCl - Eriochrome Black T (Chemapol, Chech Rep.) as indicator.
- Buffer solution NH_4OH – NH_4Cl (pH=9).

2. *adsorption substrates*:

Table 1.

Characteristics of the adsorption substrate

Name	Type	Exchange capacity [mE/g]	Prorsity	Manufacturer
C-100	Sulfonic cation exchanger, R-SO_3Na	2.5	Micro	VIROLITE Or. Victoria, Romania
CC-21	Carboxilate cation exchanger, R-COONa	10	Medium	
AT- VP	Surface modified anion exchanger*)	-		Laboratory

*) on the surface of the anion exchanger AT-14 there was adsorbed pyrocatechol violet (PV) from a 1% water solution, [6].

3. *Adsorption tests*

Experiments were done in a flask, by bringing in direct contact the metal solution and the substrate, at room temperature, under stirring. Concentration was evaluated before and after the process and the values were used for further calculations.

3. RESULTS AND DISCUSSIONS

Laboratory tests were done in order to optimise the adsorption conditions.

Previous studies, [7,8] proved that an adequate ratio: weight of substrate: volume of solution is 1: 10 considering the efficiency but also the technological parameters. In the same studies a contact time of 5 minutes was sufficient for the adsorption process of any transitional metal. This time was evaluated from the curve adsorption efficiency vs. contact time, at the point where any significant increase was no longer registered. In the case of cadmium, after 5 minutes of adsorption, the efficiency was higher than 90%, both for a 0.05 Eg/L and for a 0.005 Eg/L solution, on each of the ion exchangers that were investigated. Table 2 shows these results:

Table 2

Optimization of the adsorption time

No.	$C_I \times 10^3$[Eg/L]	$C_F \times 10^3$[Eg/L]	Time [min]	Efficiency [%]
1	49	2.4	1	95.1
		2.2	3	95.5
		0.48	5	99.02
2	4.98	0.153	1	96.93
		0.11	3	97.99
		0.064	5	98.71

Of course, in industrial conditions, of continuos flow, contact times lower than one minute are of no use, therefor our decision regarding 5 minute for the contact time is more the result of a technological approach.

Adsorption tests were done and, based on the results, the adsorption isotherms are plot as molar adsorption coefficient vs. equilibrium concentration, Fig. 1 and Fig.2.

The ion exchange process is a special type of chemical adsorption that is well described by the Langmuir equation, [9]. Still, Fig. 1 one doesn't revel the accurate shape of the Langmuir isotherm at the very low concentration when the process is under diffusion control.

The adsorption on AT-VP occurs as a reaction of forming the Cd - PV complex and is also a chemosorption. In this case, as in the previous, the adsorption conditions were well chosen and the saturation of the substrate was not reached.

Considering that in all cases the Langmuir equation describes well the process, the parameters χ_{max} and A were evaluated by representing the linear form of the isotherm:

$$\frac{c}{\chi} = \frac{1}{\chi_{max} A} + \frac{1}{\chi_{max}} c \quad (1)$$

Based on the A value, the adsorption heat was evaluated:

$$\Delta H^{ads} = -RT \ln A \quad (2)$$

Cadmium exists in water as cadmium hexa-hydrate, $[Cd(H_2O)_6]^{2+}$ which is an ion with high volume. The ion exchangers have a high number of adsorption points and the values of the maximum adsorption coefficients are consequently high. In the case of AT-VP, the much lower value could be a consequence of the distribution of the active centres on a reduced surface. One may drop this conclusion considering that PV has also a large volume but only one active end for complexation so that its adsorption could actually reduce the number of active centres on the surface.

Table 3

Adsorption characteristics of the cadmium ion on the investigated substrates

Substrate	C-100	CC-21	AT-VP
X_{max} [mg/g]	390.6	299.4	8.59
ΔH^{ads} [cal/moles]	-203.43	-363.13	-2445.12

The data presented in Table 3 indicate that the adsorption products are more stable in the case of the Cd-VP complexes and this may be considered a drawback if the regeneration of the substrate must also be consider.

The adsorption efficiency of the cadmium ion on the ion exchange substrates is very high over a wide equilibrium concentration range. However, at very low concentrations, the At-VP substrate proved to be more efficient. Changing the adsorption technological conditions (i.e. the ration substrate volume: solution volume and/or contact time) this substrate will increase its efficiency.

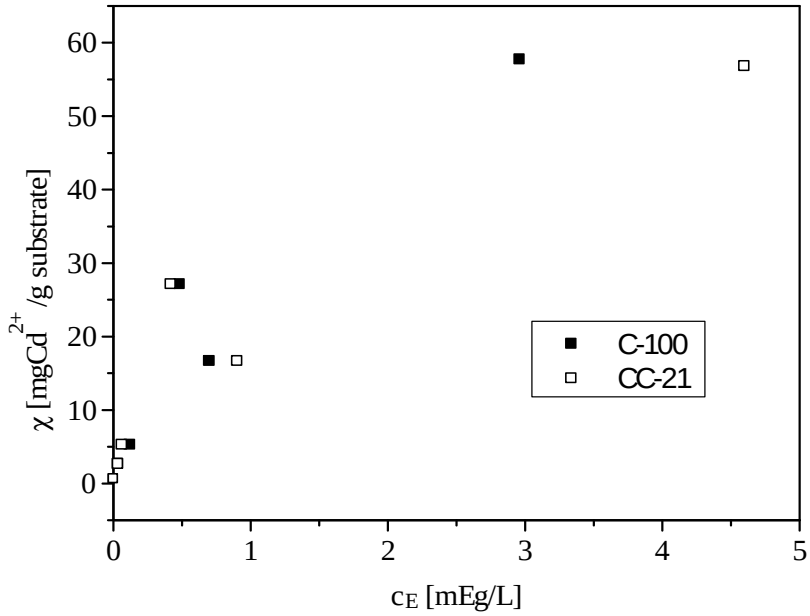

Fig. 1 Adsorption isotherms of the cadmium on ion exchangers

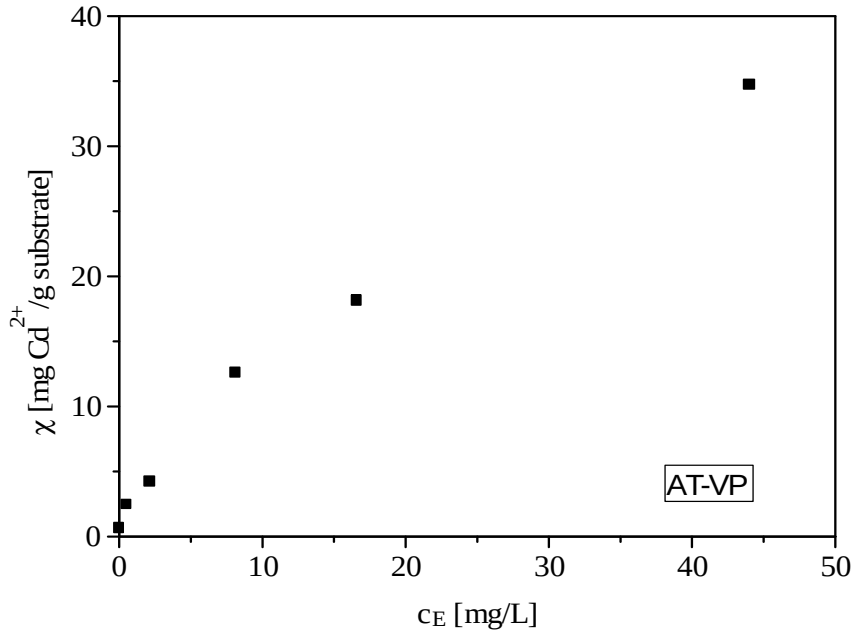

Fig. 2 Adsorption isotherm of the Cd^{2+} on the modified anionite

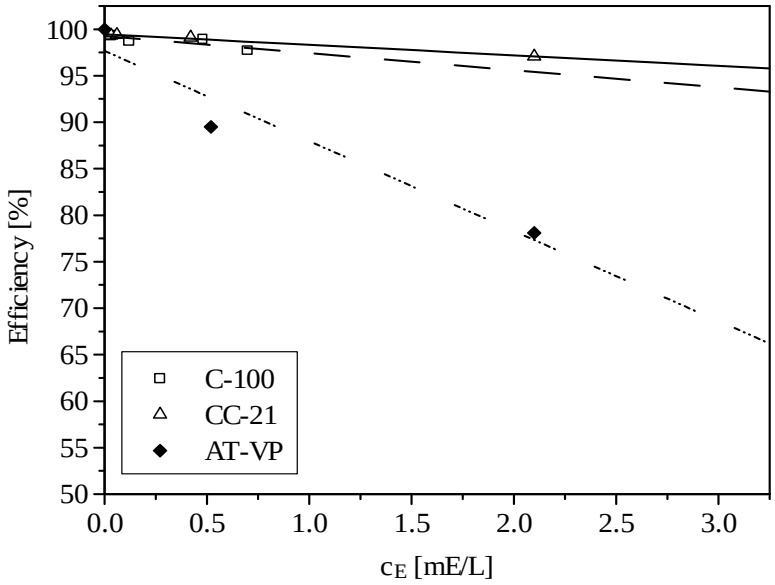

Fig. 3 Adsorption efficiency of cadmium ion

Previous studies were done using this adsorbent for advanced adsorption of other heavy metals. A comparative view is given in Table 4:

Table 4

Adsorption efficiency on AT-VP

C_I [Eg/L]	Efficiency [%]		
	Zn^{2+}	Cu^{2+}	Cd^{2+}
0.0001	39	72	-
0.001	36	18	100
0.01	7	12	78.1
0.1	3.5	5	58.5
Environment's pH	natural	natural	8-10

4. CONCLUSIONS

Ionic cadmium adsorption was tested on three substrates: two cation exchangers macro- respectively medium porous and a modified anion exchanger PV adsorbed onto its surface.

The adsorption isotherms, corresponding to the Langmuir equation described well the process, according to the theoretical premises of the chemosorption. The hydrated cadmium ion has a quite large volume and the adsorption on AT-VP was less efficient at medium concentrations but proved to be the most effective in very dilute solutions.

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