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1 **Removal of heavy metals from contaminated water using**  
2 **industrial wastes containing calcium and magnesium**

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## Abstract

Two industrial wastes (IW1 and IW2) were investigated as potential sorbents to retain cadmium and lead from contaminated water. The sorption experiments have been conducted through lab-engineered cartridge filtration system in order to get as close as possible to industrial processes. The effectiveness of IW1 and IW2 were compared to that of activated charcoal Norit® (AC), the best-known matrix for its excellent retention capacity. The sorption isotherms of metals on the three solid sorbents (IW1, IW2 and AC) were built, and then mathematically modelled. Free Gibbs energy ( $\Delta G^\circ$ ) of the sorption processes as well as the equilibrium parameter ( $R_L$ ) have been calculated for each pollutant-sorbent couple. The study revealed that: i) for cadmium sorption, IW2 was much more effective than IW1 and especially than AC (18-fold higher in term of maximal sorption capacity); ii) if IW2 was slightly less effective than AC to retain lead, it can be still considered as an interesting sorbent due to its low cost; iii) the sorption of cadmium was as spontaneous on AC as on IW1, and almost half as much on IW2; iv) regarding lead retention, the sorption on the three sorbents was spontaneous; (v) the retention of cadmium and lead was mainly explained by precipitation since otavite, cerussite and hydrocerussite were identified and characterized by X-ray diffraction of used sorbents. The study showed that the industrial wastes studied stood out as new efficient materials with sorption power equal to or greater than the reference material AC. The prospect of a new generation of industrial wastes with lasting efficiency as contaminated water depollution agents comes at a key moment in the search for new perspectives in the circular economy.

**Keywords:** sorption; metal; isotherm; water treatment; cartridge filtration technology

## 1 Introduction

26 Effects of metal(loid)s on human health and their persistence in environment are a global  
27 concern since the 80's. Often referred as heavy metals due to their atomic density, higher than  
28  $5 \text{ g cm}^{-3}$  (Alloway, 2012), medical diagnosis and reports have proved that some of these  
29 metal(loid)s have the potency to cause disabling diseases and human mortality when exposed.  
30 For instance, Cd, Pb, Sb and Hg have been designated as four of the ten most dangerous  
31 substances to public health (Flora et al., 2012; Bjørklund et al., 2017; Branca et al., 2018; Li et  
32 al., 2018). Although they are naturally produced in the environment through various geogenic  
33 processes, their rate of production increases due to the anthropogenic sources that span from  
34 atmospheric and domestic to commercial activities including agricultural, industrial,  
35 pharmaceutical and the release of domestic effluents (He et al., 2005). Consequently, human  
36 exposure to metal(loid)s increases at an alarming rate (Tchounwou et al., 2012) and  
37 stabilization/removal of these pollutants become a challenge to protect and preserve the  
38 environment and health of future generations.

39 Among the toxic metal(loid)s in wastewater effluents, Cd and Pb were cited as the main ones  
40 since they are respectively classified as CARC2/MUTA3/REPRO3 and  
41 CARC1/REPRO1/REPRO3) in the Regulatory European Classification of CMR chemicals.  
42 Considering the serious health consequences (Akpor et al., 2014), removal of these two metals  
43 from contaminated water has been extensively studied through various techniques and devices,  
44 including chemical precipitation, complexation, ion exchange, reverse osmosis and sorption.  
45 Chemical and physical sorption have been extensively studied considering organic and  
46 metal(loid)s pollutants and various sorbents like graphene, activated carbons, carbon nanotubes,  
47 magnetic sorbents, alumina, zeolites, kaolin, phosphate rocks, Mn-oxyhydroxyde, mesoporous  
48 silica, clays, chitosan, modified or not modified agricultural wastes, bio-sorbent, biomass-based  
49 materials and nanostructured materials (Sari et al., 2008; Karnib et al., 2014; Abdel-Raouf and  
50 Abdul-Raheim, 2017; Asuquo et al., 2017; Bisht et al., 2017; Feng et al., 2017; Burakov et al.,

51 2018; Tariq et al. 2018; Joseph et al., 2019; Ani et al., 2020; Boni et al., 2020) or mixture of  
52 mineral and organic materials (Fu et al., 2020). Among mineral materials, oxides nanomaterials  
53 have been extensively studied in the wastewater treatment with the aim to sorb organic  
54 pollutants and/or metal(loid)s (Xu et al., 2012; Davé and Chopda., 2014; Lu et al., 2016;  
55 Atkovska et al., 2018; Santhosh et al., 2019; Yaqoob et al., 2020). In contrast, and according to  
56 our knowledge, only few studies reported the removal of metal(loid)s from water using non-  
57 nanomaterials oxides (*e.g.* goethite, birnessite, magnetite; Fe-Al binary oxides; Hong et al.,  
58 2017; El Haouti et al., 2018; Ugwu and Igbokwe, 2019). Some of these oxides (Fe, Al and Mn)  
59 originated from industrial wastes while others resulted from water treatment residuals  
60 (Jacukowicz-Sobala et al., 2015; Ghorpade and Ahammed, 2018; Wolowiec et al., 2019).

61 Among industrial wastes, the production of fertilisers (*e.g.* calcium or magnesium carbonate)  
62 generates a large quantity of by-products rich in calcium and magnesium. Valorising these  
63 industrial wastes as metal(loid) sorbents would fulfil the EU policy that encourage the re-use  
64 of industrial by-products. To date, industrial wastes from the process used to obtain pure  
65 calcium and magnesium carbonates and oxides have never been studied as sorbent of  
66 metal(loid)s from contaminated water. Towards this direction, the current study focused on the  
67 removal of two carcinogenic, mutagen and reprotoxic pollutants (Cd and Pb) using two  
68 industrial wastes (low-cost products) and activated carbon as reference.

69

## 70 **2 Materials and Methods**

### 71 ***2.1 Metal pollutants***

72 The current study focused on artificial contaminated water by Cd and Pb. Cadmium sulfate  
73 ( $\text{CdSO}_4$ ) and lead acetate ( $((\text{CH}_3\text{CO}_2)_2\text{Pb})$ ) were diluted to obtain metal solutions (10, 20, 40, 60,  
74 80, 100, 150, 200, 250, 350, 500, 1 000, 2 000, 2 500, 5 000, 10 000, 15 000, 20 000, 25 000  
75  $\text{mg L}^{-1}$ ) in ultra-pure water. **Knowing that 25 mL of artificial contaminated water were eluted**

76 on the lab-made cartridge (section 2.3), the amount of Cd or Pb ranged from 0.25 up to 625 mg.  
77 The last mass is quite similar to the mass of cadmium removed from aqueous solution using  
78 poly(acrylic acid) stabilized amorphous calcium carbonate nanoparticles (Cai et al., 2010).

## 79 **2.2 Sorbents**

80 Activated Carbon (AC; Norit SA-2, Acros organics®) without any modification was chosen  
81 as reference since it is the most used sorbent, known for its very high adsorption capacity.  
82 Nevertheless, it is very expensive (Feng et al., 2017). The properties of this material are as  
83 follows: iodine number: 850; specific surface area: 950 m<sup>2</sup> g<sup>-1</sup>; apparent density: 460 kg m<sup>-3</sup>;  
84 particle size D<sub>10</sub>: 3 μm; particle size D<sub>50</sub>: 20 μm; particle size D<sub>90</sub>: 140 μm; ash content: 9%.

85 Two industrial wastes (IW1 and IW2), defined as by-products by the Scora company  
86 (Caffiers, France) were evaluated in the retention of the studied metal pollutants (Cd and Pb).  
87 They were dried at 105 °C before crushing and sieving with a mesh size of less than 315 μm.  
88 The metal concentrations in these industrial wastes were assessed after their *aqua-regia*  
89 digestion by flame atomic absorption spectrometry (FAAS; AA-6800 Shimadzu, Tokyo, Japan;  
90 Waterlot and Douay, 2009; Savio et al., 2010; Waterlot and Hechelski, 2019). The results were  
91 summarised in Table 1. The particle-size distribution of both industrial wastes was measured  
92 using a particle-size analyser (Mastersizer 3000; Malvern Panalytical; United Kingdom).  
93 X-ray diffraction (XRD) data measurements on the samples before and after pollutants elution  
94 dried at 110 °C for 2 h were performed by using a diffractometer BRUKER D8 with an  
95 anticathode in cobalt ( $\lambda K\alpha_1 = 1.74 \text{ \AA}$ ) equipped with a LynxEye detector. The X-ray patterns  
96 were acquired in the 2θ (10–80°) with a step size of 0.02° and 89.5 s per step (Kleib et al.,  
97 2018).

## 98 **2.3 Sorption experiments**

99 The columns used in the current study were from Teledyne Technologies Inc. (Redisep Rf  
100 column), measuring 8 cm in length and having a diameter of 1.5 cm. They were filled with

101 200 mg of compacted cotton on top of which, 1 g of industrial waste were added. The surface  
102 of each sorbent powder layer was then flattened in order to obtain a homogeneous surface. The  
103 artificial contaminated water (25 mL,  $n = 3$ ) was then eluted on the lab-made cartridge. The  
104 filtered contaminated solutions were then kept in amber glass pillboxes and stored at 4 °C prior  
105 to analysis. Note that all experiments were conducted under normal temperature and pressure  
106 conditions (20 °C; 1 atm).

#### 107 **2.4 Sorbate analysis**

108 At the end of the sorption experiments, the concentrations of Cd and Pb in solutions were  
109 measured by FAAS without any sample preparation, except dilution if necessary. Specifications  
110 on analyses were detailed in Waterlot et al. (2011). Limits of detection (LD) in water were  
111  $2.1 \mu\text{g L}^{-1}$  and  $41 \mu\text{g L}^{-1}$  for Cd and Pb, respectively (Waterlot and Hechelski, 2019).

#### 112 **2.5 Data analysis**

113 The sorption isotherms were investigated using two equilibrium models, which are namely  
114 the Freundlich and Langmuir models. The Freundlich isotherm model was used as its linear  
115 equation (eq. 1).

$$116 \quad \ln q_e = \ln K_f + 1/n \ln C_e, \quad (1)$$

117 where  $q_e$  is the amount of pollutant adsorbed per g of sorbent ( $\text{mg g}^{-1}$ ),  $C_e$  is the equilibrium  
118 concentration of the adsorbate ( $\text{mg L}^{-1}$ ),  $K_f$  and  $n$  are both the Freundlich constants, the first  
119 represents the relative adsorption capacity of the sorbent ( $\text{mg}^{1-(1/n)} \text{L}^{1/n} \text{g}^{-1}$ ) and the second gives  
120 information about adsorption intensity (dimensionless).

121 The Langmuir isotherm was used under its linear form as well (eq. 2).

$$122 \quad 1/q_e = 1/ C_e b q_m + 1/q_m, \quad (2)$$

123 where  $q_e$  is the amount of pollutant adsorbed per g of sorbent ( $\text{mg g}^{-1}$ ),  $C_e$  represents the  
124 equilibrium concentration of the adsorbate material ( $\text{mg L}^{-1}$ ),  $q_m$  is the maximum adsorption

125 capacity ( $\text{mg g}^{-1}$ ) and  $b$  is a constant associated to the free energy of adsorption ( $\text{L mg}^{-1}$ ). The  
126 latter is very interesting because it is related to the Gibbs free energy (eq. 3) (Djelloul 2014).

127 
$$\text{Ln}(1/b) = \Delta G^\circ/RT, \quad (3)$$

128 where  $\Delta G^\circ$  is the Gibbs free energy of the sorption reaction ( $\text{J mol}^{-1}$ ),  $b$  is a constant associated  
129 to the free energy of adsorption ( $\text{L mol}^{-1}$ ),  $T$  is the temperature (K) and  $R$  the universal gas  
130 constant ( $\text{J mol}^{-1} \text{K}^{-1}$ ). This Gibbs free energy is expressed by the equation (4).

131 
$$\Delta G^\circ = -RT \ln b, \quad (4)$$

132 The Hall parameter (or equilibrium parameter) (Hamdaoui and Naffrechoux, 2007) was  
133 calculated according to the following equation 5.

134 
$$R_L = 1/(1 + b \cdot C_0) \quad (5)$$

135 where  $C_0$  is the initial concentration of the adsorbate in solution ( $\text{mg L}^{-1}$ ) and  $b$  is a constant  
136 associated to the free energy of adsorption ( $\text{L mg}^{-1}$ ).

### 137 **2.6 Statistical analysis**

138 Influence of the three solid sorbents (IW1, IW2 and AC) on Cd and Pb concentrations  
139 measured in the filtered solutions were tested using a one-way analysis of variance (ANOVA)  
140 at all exposure concentrations. Normality and homoscedasticity of residuals were met for all  
141 tests. When significant differences occurred between treatments, multiple comparisons of mean  
142 values were made using post-hoc Tukey HSD tests. Differences were considered statistically  
143 significant at  $p < 0.05$ . Changes in Cd and Pb concentration in the filtered solutions depending  
144 on the initial exposure concentrations, the solid sorbents (IW1, IW2 and AC), and their  
145 interaction were analysed for both contaminants (Cd and Pb) using an ANCOVA followed by  
146 post-hoc Tukey analysis to test the different ANCOVA models using the R package  
147 “multcomp”. All statistical analyses were performed using R software (version 3.0.3,  
148 Foundation for Statistical computing, Vienna, Austria).

149

## 150 **3 Results and discussion**

### 151 *3.1 Sorption capacity of Activated Carbon (AC)*

152 Sorption isotherms of Cd and Pb on activated carbon were plotted in [Figures 1A](#) and [1D](#),  
153 respectively. Opposingly to Pb ([Fig. 1C](#)), a non-linear Freundlich isotherm was obtained for Cd  
154 by plotting  $q_e$  versus  $C_e$  values ([Fig. 1A](#)). The results showed that Pb was better adsorbed than  
155 Cd. The equilibrium data were analysed using the linearized form of Freundlich equation ([eq.](#)  
156 [1](#)) by plotting  $\ln q_e$  versus  $\ln C_e$  ([Fig. 1B & 1E](#)). The coefficients of determination were higher  
157 for Pb (0.999) than for Cd (0.985) showing a good linearity for both metals. The Freundlich  
158 constants  $K_{f-Cd}$  and  $K_{f-Pb}$  were  $0.210 \text{ mg}^{1-(1/n)} \text{ L}^{1/n} \text{ g}^{-1}$  and  $0.0990 \text{ mg}^{1-(1/n)} \text{ L}^{1/n} \text{ g}^{-1}$ , and constants  
159  $n_{Cd}$  and  $n_{Pb}$  were 1.25 and 1.00, respectively. These results mean that the relative sorption of  
160 Cd when the equilibrium equals  $1 \text{ mg L}^{-1}$  is higher than that of Pb. On the other hand, the  
161 sorption intensity of Cd is 25% higher than that of Pb. Although these trends correlated well  
162 with the conclusion in [Asuquo et al. \(2017\)](#), the Freundlich constants were somewhat at odds  
163 with those found by these authors ( $K_{f-Cd} = 6.99$ ;  $K_{f-Pb} = 6.53$ ;  $n_{Cd} = 4.00$ ;  $n_{Pb} = 4.85$ ) probably  
164 due to the BET surface area,  $4273 \text{ m}^2 \text{ g}^{-1}$  in [Asuquo et al. \(2017\)](#) and  $950 \text{ m}^2 \text{ g}^{-1}$  in the current  
165 study. In the same way, the Freundlich constants obtained by [Gaya et al. \(2015\)](#) were below  
166 from this study ( $K_{f-Cd} = 0.02$ ;  $K_{f-Pb} = 0.02$ ;  $n_{Cd} = 1.00$ ;  $n_{Pb} = 1.00$ ) using a regular activated  
167 carbon due to its very low BET surface area ( $< 5.41 \text{ m}^2 \text{ g}^{-1}$ ).

168 [Asuquo et al. \(2017\)](#) demonstrated that the Freundlich isotherm is less suitable for the  
169 description of Cd-sorption than the Langmuir isotherm. It is the most widely used model to  
170 describe the sorption of a solute from contaminated water since the basic theory considers that  
171 sorption takes place at specific homogeneous sites within the sorbent. The Langmuir isotherms  
172 of Cd and Pb were plotted in [Figures 1C](#) and [1F](#). As shown in these two graphs, very good  
173 linear curves were obtained, the coefficients of determination being 0.995 for Cd and  $> 0.999$   
174 for Pb. The values of maximum adsorption capacity using the Langmuir equation were 247 mg

175 Cd g<sup>-1</sup> and 3488 mg Pb g<sup>-1</sup>. These values seem somewhat at odds with those reported in literature  
176 (Minceva et al., 2008; Asuquo et al., 2017; Okeola et al., 2017; Joseph et al., 2019).  
177 Nevertheless, the study of Karnib et al. (2014) showed maximum adsorption around 178 mg  
178 Cd g<sup>-1</sup> on AC and up to 1000 mg Pb g<sup>-1</sup> using treated NaOH-AC (Gaya et al., 2015). Anyway,  
179 Pb ions had a greater accessibility to the AC surface than Cd. This experimental result correlated  
180 well with the theory on solid surfaces since metal(loid)s of higher electronegativity and shorter  
181 hydrated ionic radius should adsorb more readily (Minceva et al., 2008).

## 182 **3.2 Sorption capacity of Industrial Waste (IW)**

### 183 *3.2.1 Characterization*

184 The particle size distribution was D<sub>10</sub>: 29 µm; D<sub>50</sub>: 153 µm; D<sub>90</sub>: 344 µm, for IW1 and D<sub>10</sub>:  
185 7 µm; D<sub>50</sub>: 103 µm; D<sub>90</sub>: 753 µm for IW2. The metal concentrations were reported in Table 1.  
186 The great difference between the two sorbents is the percentage of calcium and magnesium,  
187 respectively 3.8-fold lower and higher in IW2 than in IW1. It is worth mentioning that the  
188 concentrations of K, Al, Fe, Mn, Pb, Zn and As are the highest in IW1. The XRD analysis  
189 revealed the presence of two crystalline species in IW1 and IW2 (Figures 2A, 2B, respectively).  
190 Calcite (CaCO<sub>3</sub>) and quartz (SiO<sub>2</sub>) were the two main crystalline species in IW1 whereas  
191 hydromagnesite (Mg<sub>5</sub>(CO<sub>3</sub>)<sub>4</sub>(OH)<sub>2</sub>, 4H<sub>2</sub>O) and calcite were identified in IW2.

### 192 *3.2.2 Removal capacity of Cd and Pb by IW1*

193 As shown in Figure 3 (3A, 3B, 3D and 3E), the Freundlich models (non-linearized and  
194 linearized) were not appropriate to explain the sorption processes of Cd and Pb. It is well  
195 accepted that the Freundlich model assumes heterogeneous adsorption surface and active sites  
196 with different energy. For both metals, this sorption process can be successfully applied for  
197 sorbed metal concentrations below 90 mg Cd g<sup>-1</sup> and 125 mg Pb g<sup>-1</sup>. In contrast, the Langmuir  
198 sorption isotherm has been successfully applied to Cd and Pb sorption processes (Fig. 3C &  
199 3F). Excellent coefficients of determination were obtained for both metals (R<sup>2</sup> > 0.999), which

200 means that Langmuir was the most suitable model to describe the sorption process of Cd and  
201 Pb on IW1. Similar trend has been already mentioned with metal oxides sorbents (Trivedi et  
202 al., 2001; Kumar et al., 2014; Guo et al., 2018). The values of maximum adsorption capacity  
203 using the Langmuir equation were 311 mg Cd g<sup>-1</sup> and 1575 mg Pb g<sup>-1</sup>. These results correlated  
204 well with those described in the literature since the sorption of both metals on nano-metal (Zn,  
205 Ti, Al, Mn, Fe) oxides ranged from 29 to 625 mg Cd g<sup>-1</sup> and reached up to 780-1128 mg Pb g<sup>-1</sup>,  
206 depending on the sorbent, the temperature, the duration contact and the pH (Kumar et al.,  
207 2014; Guo et al., 2018; Liu et al., 2018).

208 The solid sorbents IW1-Cd and IW1-Pb were analysed by XRD after the filtration of Cd and  
209 Pb contaminated water on IW1. The X-ray diffractogram (Figure 4) revealed the presence of  
210 otavite (CdCO<sub>3</sub>) and hydrocerussite (Pb<sub>3</sub>(CO<sub>3</sub>)<sub>2</sub>(OH)<sub>2</sub>). The retention of Cd and Pb from  
211 contaminated water by CaCO<sub>3</sub> or CaCO<sub>3</sub>-based nanoadsorbents was well documented, as well  
212 as their respective mechanisms (McBride, 1980; Rangel-Porras et al., 2010; Mlayah and Jellali,  
213 2015; Ponomarev et al., 2019; Wang et al., 2020). Depending on pH, precipitates like otavite,  
214 cerussite (PbCO<sub>3</sub>) or hydrocerussite were identified and mechanisms related to precipitation,  
215 complexation and chemisorption were highlighted. The difference between Cd<sup>2+</sup> and Pb<sup>2+</sup> is  
216 their ionic radius, explaining that at low concentration of Cd<sup>2+</sup>, substitution of Ca<sup>2+</sup> in accessible  
217 surface sites occurred (the ionic radius of Cd<sup>2+</sup> being similar to Ca<sup>2+</sup>). Cai et al. (2020)  
218 demonstrated that CdCO<sub>3</sub> was not simply the result of the reaction between Cd<sup>2+</sup> and CO<sub>3</sub><sup>2-</sup> but  
219 the result of two consecutive mechanisms, the first step being an adsorption onto the amorphous  
220 calcite surface and the second one, a precipitation from CaCO<sub>3</sub> to CdCO<sub>3</sub>. At high levels of Cd  
221 and Pb in water, the highest affinity of calcite for Pb was demonstrated (Rangel-Porras et al.,  
222 2010) and, depending on solids and the initial concentration of contaminated samples, removal  
223 capacities of Cd and Pb were up to 821 mg g<sup>-1</sup> and 1350 mg g<sup>-1</sup>, respectively (Mlayah and  
224 Jellali, 2015; Wang et al., 2020).

225 It is worth mentioning that the disadvantage of using IW1 is its high concentration of Al,  
226 Zn and As (Table 1). In view of the sorption capacity of this sorbent, the use of another solid  
227 sorbent with lowest metal concentrations would be preferable for a safety utilization.

### 228 3.2.3 Removal capacity of Cd and Pb by IW2

229 The Freundlich and Langmuir isotherms of Cd and Pb on the second industrial waste (IW2)  
230 were summarized in Figure 5. Non-linearized and linearized Freundlich isotherms of Cd (Fig.  
231 5A & 5B) and Pb (Fig. 5D & 5E) using IW2 were better than those obtained with IW1 since  
232 good determination coefficients were obtained for both metals ( $R^2 > 0.999$ ). The Freundlich  
233 constants  $K_{f-Cd}$  and  $K_{f-Pb}$  were  $0.026 \text{ mg}^{1-(1/n)} \text{ L}^{1/n} \text{ g}^{-1}$  and  $0.025 \text{ mg}^{1-(1/n)} \text{ L}^{1/n} \text{ g}^{-1}$ , and constants  
234  $n_{Cd}$  and  $n_{Pb}$  were 1.01 and 0.99, respectively. Therefore, the relative sorptions of Cd and Pb  
235 when the equilibrium equals  $1 \text{ mg L}^{-1}$  are the same. The equilibrium data analysed using the  
236 linearized form of Langmuir equation (eq. 2) was obtained by plotting  $1/q_e$  versus  $1/C_e$  (Fig. 5C  
237 & 5F). The determination coefficients were also higher than 0.999 for Cd and Pb, meaning that  
238 Freundlich and Langmuir isotherms were suitable for the description of experimental data. The  
239 values of the maximum adsorption capacity using the Langmuir equation were  $4569 \text{ mg Cd g}^{-1}$   
240  $^1$  and  $2638 \text{ mg Pb g}^{-1}$ . These values are significantly higher than those reported with IW1.  
241 Analysis of IW2 reveals the presence of Ca (5.8%; Table 1) and Mg (21%). In fact, both of  
242 these metals exist as  $\text{CaCO}_3$  (14.5%) and  $\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 4\text{H}_2\text{O}$  (74%) from the crude material  
243 (Figure 2B). The XRD analyses of IW2 after the filtration of Cd or Pb from contaminated water  
244 (named IW2-Cd and IW2-Pb, respectively) showed the presence of otavite in IW2-Cd and  
245 cerussite and hydrocerussite in IW2-Pb (Figure 6). Affinities of Cd and Pb for magnesium  
246 oxides are also well known and are similar to calcium oxides. Another mechanism was  
247 demonstrated using flowerlike MgO nanostructures to explain the high capacity ( $1980 \text{ mg Cd}$   
248  $\text{g}^{-1}$  and  $1500 \text{ mg Pb g}^{-1}$ ) of magnesium oxides (Cao et al., 2012). The authors explained these  
249 results by a solid-liquid interfacial cation exchange between magnesium and both metals

250 studied (Cd and Pb) as adsorption mechanism that depends on the ability of hydrated-metal to  
251 lose their outer hydration sphere to give hydroxyl-metal complexes. Pehlivan et al. (2009)  
252 reported the effectiveness of natural Turkish dolomite ( $\text{CaMg}(\text{CO}_3)_2$ ) for removing Pb from  
253 aqueous solution. The authors stated that metal adsorption on dolomite surfaces has been  
254 described in terms of two mechanisms that are cation exchange in the interlayer and specific  
255 adsorption resulting from surface complexation at low concentration, as it was observed with  
256 calcite sorbent. In contrast, precipitation mechanism occurred at high concentration following  
257 two steps; first, Pb ions adsorb onto calcite and then move into Ca sites, despite the large ionic  
258 radius of  $\text{Pb}^{2+}$  relative to  $\text{Ca}^{2+}$  (Sturchio et al., 1997).

### 259 ***3.3 Efficiency of the solid sorbents***

260 If we consider the overall concentration range, 10-25000  $\text{mg L}^{-1}$ , Cd and Pb retention in  
261 sorbents depended on both the sorbents type and the initial concentration in solution (Table 2,  
262 3,  $p < 10^{-4}$ ) but interactions between both factors were not significant ( $p > 0.05$ ). Thus, Cd and Pb  
263 retentions were significantly higher in the AC ( $p < 0.001$ ) compared to both oxides, but they  
264 were not significantly different between IW1 and IW2 ( $p > 0.05$ ). Only for an initial  
265 concentration higher than 20000  $\text{mg L}^{-1}$ , Cd retention in IW2 and AC were not statistically  
266 different (Supplementary material 1). For initial concentration in solution higher than 2000  $\text{mg}$   
267  $\text{Cd L}^{-1}$  or 5000  $\text{mg Pb L}^{-1}$ , Cd and Pb retentions were significantly higher in IW2 than in IW1.  
268 From a practical point of view, these results mean that AC was superior to IW1 and IW2 for Pb  
269 and Cd when their concentrations in solution were below 2000  $\text{mg L}^{-1}$ . However, the choice of  
270 the sorbent depends on the strategy used in the water treatment process. Indeed, IW2 is cheaper  
271 than AC and its sorption capacity the highest. The Langmuir parameter  $q_m$  of the three sorbents  
272 for Cd and Pb must be compared, as it is closely related to sorption efficiency. Depending on  
273 the sorbent,  $q_m$  may be ordered according to their efficiency to sorb Cd as:  $\text{IW2} > \text{IW1} > \text{AC}$   
274 ( $4569 \text{ mg Cd g}^{-1}$ ,  $311 \text{ mg Cd g}^{-1}$  and  $247 \text{ mg Cd g}^{-1}$ , respectively). For Pb sorption, this order

275 was AC > IW2 > IW1 (3488 mg Pb g<sup>-1</sup>, 2638 mg Pb g<sup>-1</sup> and 1575 mg Pb g<sup>-1</sup>). In view of these  
276 results, IW2 appeared as the most effective sorbent for the Cd retention, 15-fold higher than  
277 IW1 and 18-fold higher than AC used as reference. However, although IW2 presented a better  
278 Pb sorption capacity compared to IW1 (1.7-fold higher), it was less effective than AC (1.3-fold  
279 smaller).

280 The most recent literature review related to the removal of metals using adsorbents  
281 adsorption of metals reported a classification of these materials. Thus, it is well accepted that  
282 they can be classified according to carbon based materials (activated carbon, activated carbon  
283 cloth, activated carbon fibre), nanomaterials (nanoparticules, nanotubes, nanorods, nanowires),  
284 composite and nanocomposite adsorbents, miscellaneous adsorbents and low-cost adsorbents.  
285 Low-cost materials are divided into three subclasses depending on their origin: agriculture solid  
286 waste and industrial by-products (metal(hydr)oxides, waste slurry, fly ash, red mud, bio-solids),  
287 natural materials (clays, zeolites, silica, alumina, kaolinite, bentonite, montmorillonite, chitosan  
288 and (hydr)oxides) and bio-sorbents (biopolymers, peat and biomass). According to the dataset  
289 from several reviews (Renu et al., 2017; Joseph et al., 2019; Wilowiec et al., 2019; Gupta et al.,  
290 2021; Qasem et al., 2021; Zaimee et al., 2021), the most relevant adsorbents for Cd are modified  
291 chitosan ( $q_m = 248 \text{ mg g}^{-1}$ ), orange peel ( $q_m = 248 \text{ mg g}^{-1}$ ), razor clam shells ( $q_m = 501 \text{ mg g}^{-1}$ ),  
292 zeolite ( $q_m = 649 \text{ mg g}^{-1}$ ), graphene oxides ( $q_m$  up to  $793 \text{ mg g}^{-1}$ ), metal oxides ( $q_m$  up to  $1500$   
293  $\text{mg g}^{-1}$ ). For Pb, the authors reported excellent retention with zeolite ( $q_m = 210 \text{ mg g}^{-1}$ ), razor  
294 clam shells ( $q_m = 657 \text{ mg g}^{-1}$ ), graphene oxides ( $q_m$  up to  $1000 \text{ mg g}^{-1}$ ), oyster shells ( $q_m = 1591$   
295  $\text{mg g}^{-1}$ ), nanocomposites ( $q_m = 1167 \text{ mg g}^{-1}$ ) and metal oxides ( $q_m$  up to  $3900 \text{ mg g}^{-1}$ ). This  
296 means that the two industrial wastes (IW1 and IW2) studied are in the top ranking of adsorbents  
297 according to their Cd and Pb retention capacity and IW2 is the best-known Cd-adsorbent  
298 described in the literature.

### 299 ***3.4 Thermodynamic characteristics of the solid sorbents***

300 To go further from a thermodynamic point of view, the Gibbs free energy ( $\Delta G^\circ$ ) of the  
301 sorption processes of Cd and Pb on AC, IW1 and IW2 has been calculated from eq. 4 using the  
302 Langmuir parameter  $b$  (Djelloul 2014). For Cd sorption, the numerical values of  $\Delta G^\circ$  were  
303 negative and followed the order AC < IW1 < IW2 (-14.91 KJ mol<sup>-1</sup>, -14.35 KJ mol<sup>-1</sup> and -7.81  
304 KJ mol<sup>-1</sup>, respectively). In this regard, the sorption phenomenon of Cd onto the three sorbents  
305 were found to be exergonic. However, it is important to mention that the spontaneous sorption  
306 processes of Cd on AC and IW1 were similar and 1.9-fold higher than IW2. For Pb sorption,  
307 values of  $\Delta G^\circ$  are also negative and can be ordered as follows: IW1 < IW2 < AC (-11.890 KJ  
308 mol<sup>-1</sup>, -10.635 KJ mol<sup>-1</sup> and -9.954 KJ mol<sup>-1</sup>, respectively). In this case, we can considerer  
309 similar values of free energy meaning that Pb sorption on the three sorbents studied proceed  
310 spontaneously forward the formation of products in equivalent amounts.

311 The Hall parameter ( $R_L$ , also called equilibrium parameter) was assessed from the Langmuir  
312 parameter  $b$  according to the equation 5 (Hamdaoui and Naffrechoux, 2007). Depending on the  
313 sign of this parameter, the sorption is defined as irreversible ( $R_L = 0$ ), favourable ( $0 < R_L < 1$ ),  
314 linear ( $R_L = 1$ ) or unfavourable ( $R_L > 1$ ). Similarities in the  $R_L$  values were highlighted for Cd  
315 with AC and IW1 (Figure 7A). In both cases,  $R_L$  values drastically decreased from 0.80 to 0.11,  
316 and then below 0.1 from 2500 to 25 000 mg L<sup>-1</sup>. This result indicated that the sorption is  
317 favourable in the range of the Cd concentration studied. In addition, the higher the initial  
318 concentration, the more favourable the sorption is, even tending towards an irreversible  
319 phenomenon. To a lesser extent, the  $R_L$  values also decreased with IW2 when the initial Cd  
320 concentration of the solution increased. Indeed, it ranged from 0.98 to 0.15, demonstrating a  
321 favourable sorption. Note that the lowest  $R_L$  values obtained with AC and IW1 correlated well  
322 with the lowest values of the Gibbs energy, which corroborates with the fact that the Cd sorption  
323 on AC and IW1 was more spontaneous and less reversible than on IW2. For Pb, values and  
324 evolution of the  $R_L$  obtained with AC, IW1 and IW2 are shown in Figure 7B. For these three

325 solid sorbents, all parameters dropped similarly when Pb concentrations increased. However,  
326 values for this parameter were quite different, ranging from 0.98 to 0.12 for AC, from 0.95 to  
327 0.059 for IW1 and from 0.97 to 0.095 for IW2. In all cases, these values confirmed the  
328 favourable nature of the Pb sorption on the sorbents studied and correlated well with the order  
329 of the sequence  $AC > IW2 > IW1$  established regarding the free Gibbs energy.

330

#### 331 **4 Conclusions**

332 Two industrial by-products (IW1 and IW2) were evaluated as sorbent for the retention of Pb  
333 and Cd from artificially contaminated water. In order to be able to conclude on the effectiveness  
334 of IW1 and IW2 as sorbent for Cd and Pb, all experiments were carried out in parallel on  
335 activated charcoal Norit® (AC), the best-known matrix for its excellent retention capacity. The  
336 aqueous solutions of Cd and Pb (from 10 to 25 000 mg L<sup>-1</sup>) were eluted on lab-engineered  
337 cartridges filled with the selected solid sorbents in order to be close to industrial practices.

338 Sorption isotherms were constructed and investigated according to the mathematical models  
339 of Freundlich and Langmuir. In addition, free Gibbs energy of the sorption processes ( $\Delta G^\circ$ ) as  
340 well as the equilibrium parameter ( $R_L$ ) have been calculated for each pollutant-sorbent couple  
341 and were compared. All these data allowed to conclude that for Cd sorption, IW2 was much  
342 more effective than IW1 (15-fold higher) and AC (18-fold higher). The sorption of Pb was more  
343 important on AC than on IW2 (1.3-fold higher) which retains itself 1.9-fold more Pb than IW1.  
344 The X-ray diffraction indicated the presence of otavite, cerussite and hydrocerussite in the solid  
345 sorbents suggesting that sorption of Cd and Pb was based on precipitation mechanism. Finally,  
346 the calculations of  $\Delta G^\circ$  and  $R_L$  have revealed that the sorption of Cd is as spontaneous on AC  
347 as on IW1, and almost half as much on IW2. Regarding Pb retention, the sorption on the three  
348 sorbents is spontaneous and no significant deviation was observed. **Further experiments are**  
349 **necessary to check the sorption capacity of other divalent cations by these two industrial wastes.**

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355

356 **Declaration of competing interest**

357 The authors declare that they have no known competing financial interests or personal  
358 relationships that could have appeared to influence the work reported in this paper.

359

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**Table 1.** Main chemical composition of industrial wastes used as sorbents

	Ca (%)	Mg (%)	K (g kg <sup>-1</sup> )	Na (g kg <sup>-1</sup> )	Al (g kg <sup>-1</sup> )	Fe (g kg <sup>-1</sup> )	Mn (g kg <sup>-1</sup> )	Cd (mg kg <sup>-1</sup> )	Pb (mg kg <sup>-1</sup> )	Zn (mg kg <sup>-1</sup> )	Cu (mg kg <sup>-1</sup> )	As (mg kg <sup>-1</sup> )
IW1	22	5.5	1.8	0.3	6.87	6.4	0.8	0.2	3	42	1.5	7
IW2	5.8	21	0.65	0.7	0.65	0.65	0.02	0.5	0.8	5	1.1	0.5

**Table 2.** Results of the ANCOVA investigating the effects of the contaminant concentration in solutions, the filter types (CA, IW1 or IW2) and their interaction on the filtration of Cd and Pb.

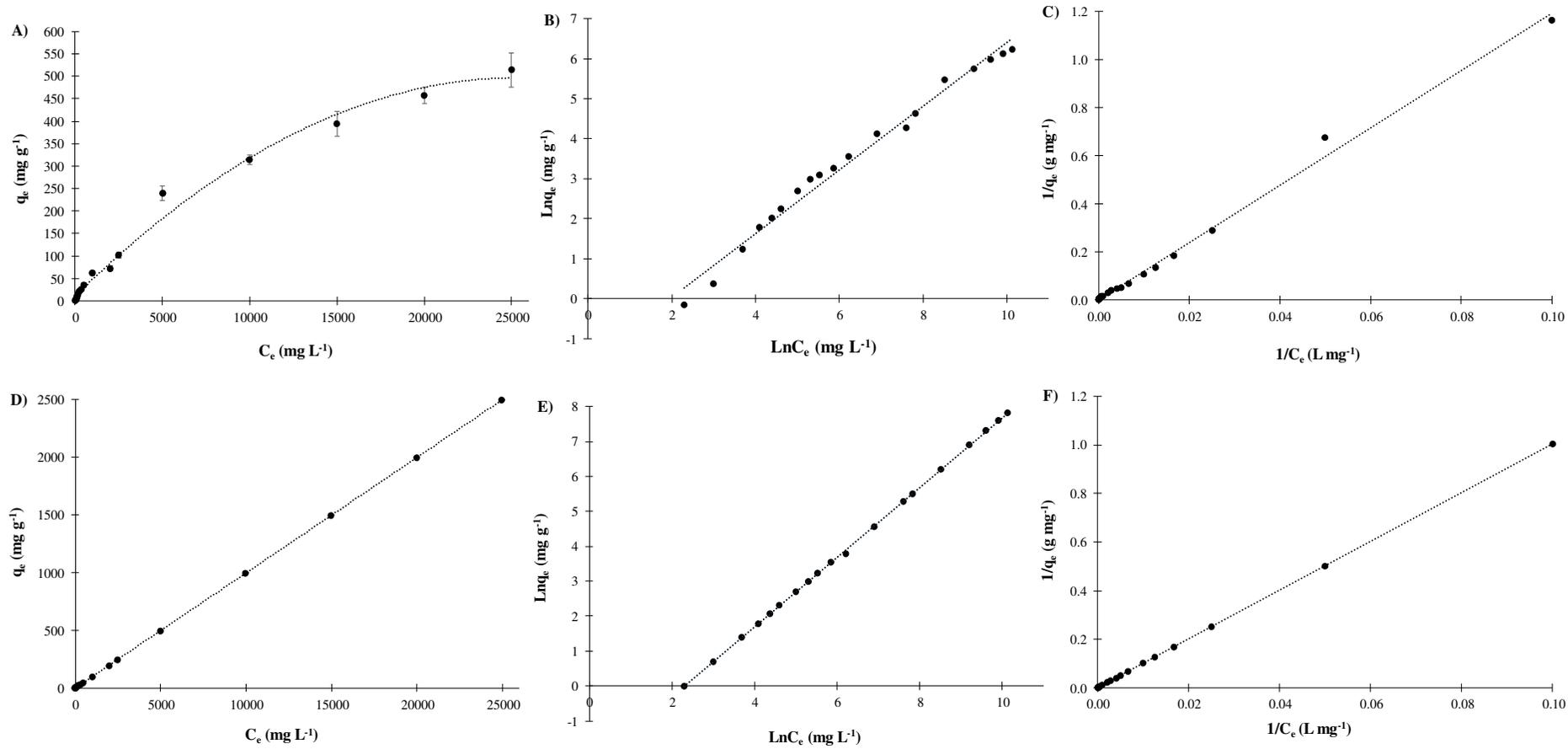
Parameters	Df	Mean sq	Fvalue	<i>p</i> -value
<b>Cd</b>				
Initial concentration	1	432.2	228	10 <sup>-16</sup> ***
Sorbent	2	18.8	9.5	10 <sup>-4</sup> ***
Initial concentration × Sorbent	2	2.9	1.5	0.2
Residuals	165	1.9		
<b>Pb</b>				
Initial concentration	1	571.5	276.1	10 <sup>-16</sup> ***
Sorbent	2	38.2	18.4	10 <sup>-7</sup> ***
Initial concentration × Sorbent	2	0.5	0.3	0.8
Residuals	165	2.1		

Significance levels: ‘\*\*\*’ 0.001 ‘\*\*’ 0.01 ‘\*’ 0.05. Df: Degree of freedom, F-value: Fisher value, Mean sq: Mean of squares

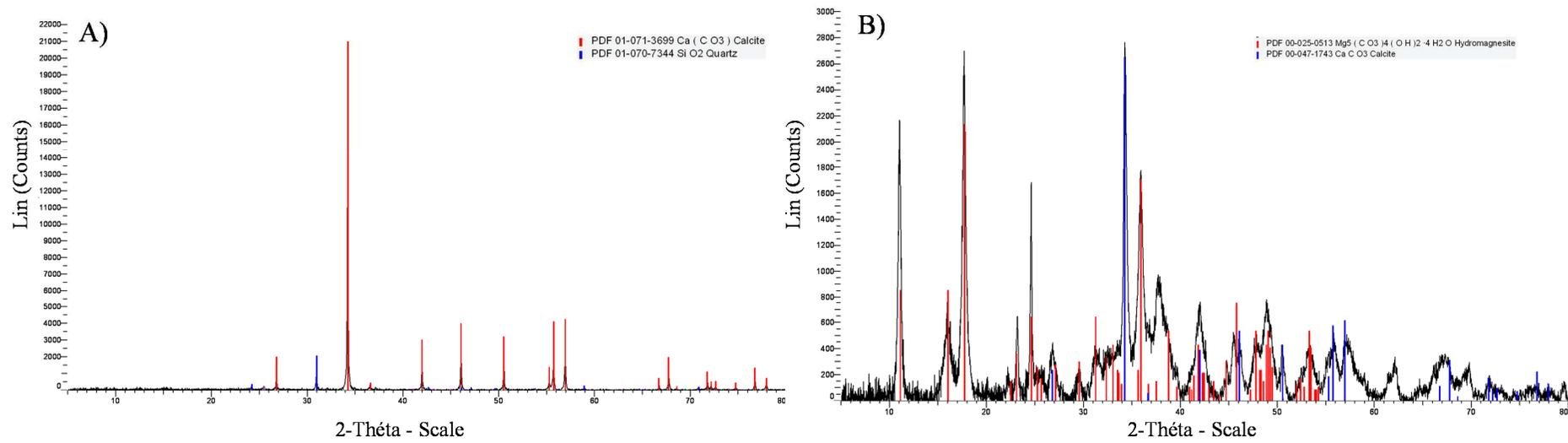
**Table 3.** Results of the post-hoc Tukey analysis investigating the differences between ANCOVA models.

<b>Parameters</b>	<b>Estimate</b>	<b>Std. Error</b>	<b>t-value</b>	<b>p-value</b>
<b>Cd</b>				
IW1 - CA	-1.3590	0.3125	-4.344	10 <sup>-4</sup> ***
IW2 - CA	-1.3705	0.3125	-4.384	10 <sup>-4</sup> ***
IW2 - IW1	-0.0125	0.3125	-0.040	0.999
<b>Pb</b>				
IW1 - CA	-1.1370	0.2992	-3.800	10 <sup>-4</sup> ***
IW2 - CA	-1.1193	0.2992	-3.741	10 <sup>-4</sup> ***
IW2 - IW1	0.0177	0.2992	0.059	0.998

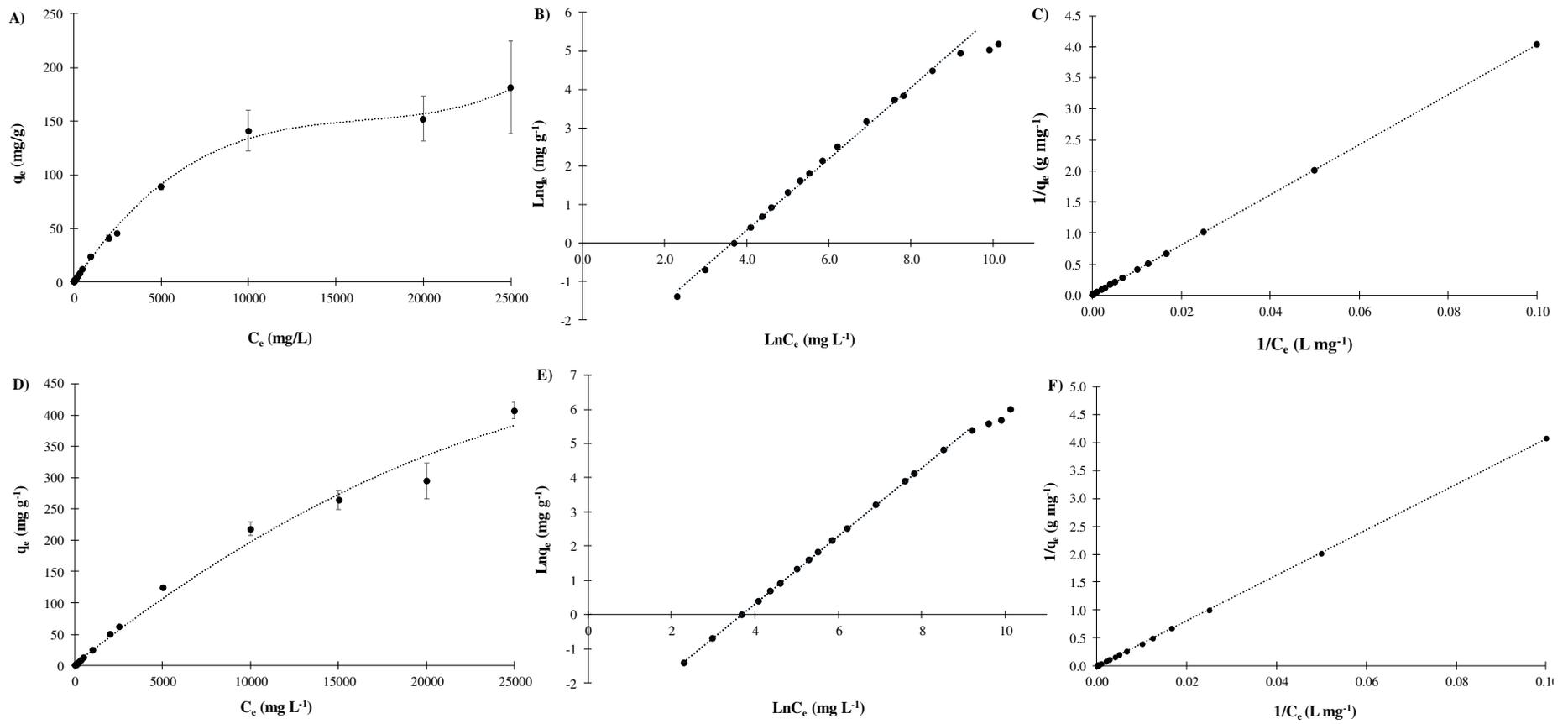
Significance levels: '\*\*\*' 0.001 '\*\*' 0.01 '\*' 0.05. t-value: Student value, Std. Error : Standard error



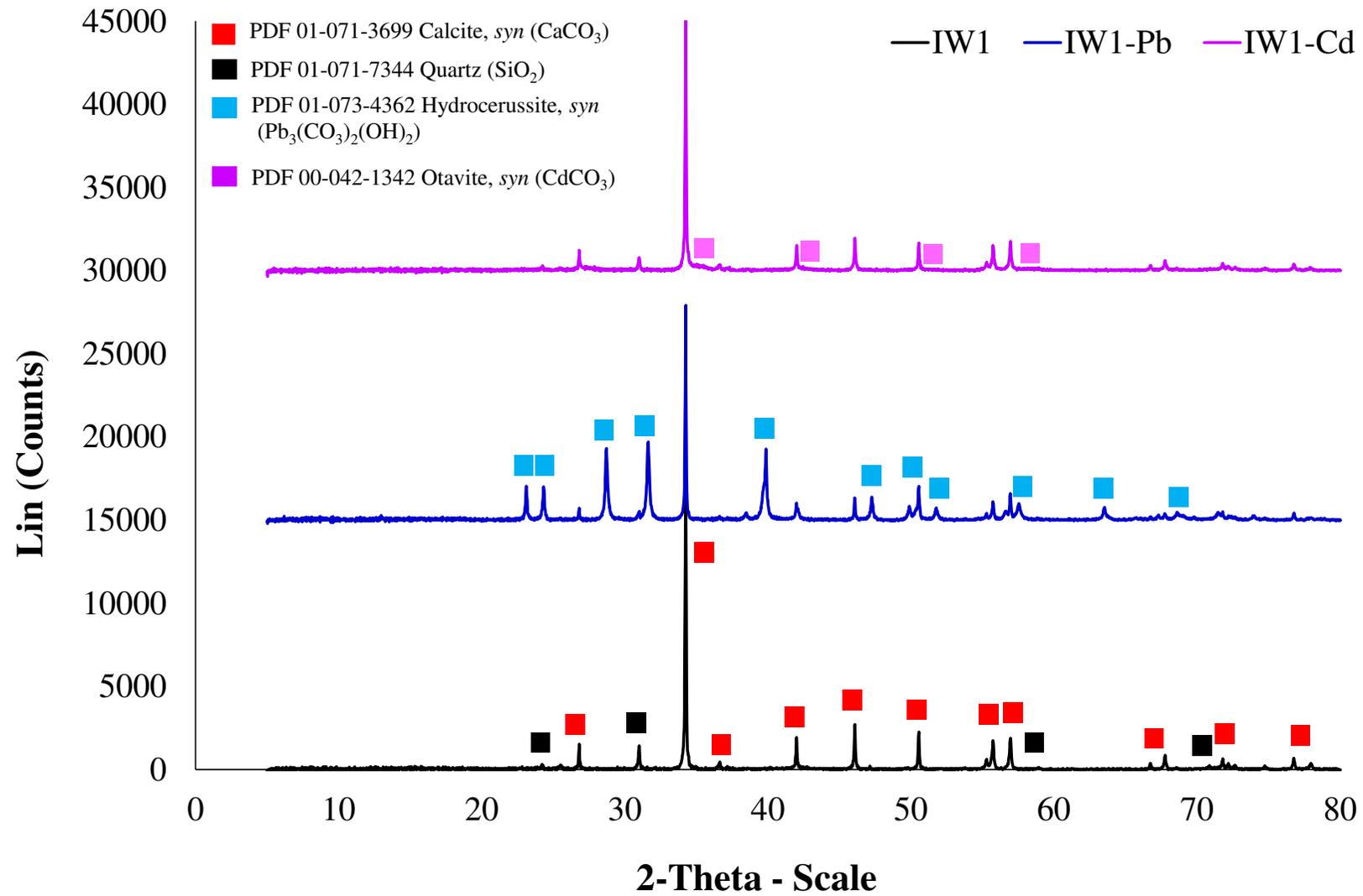
**Figure 1:** Freundlich and Langmuir isotherms of Cd (A, B, C) and Pb (D, E, F) on activated carbon (AC)



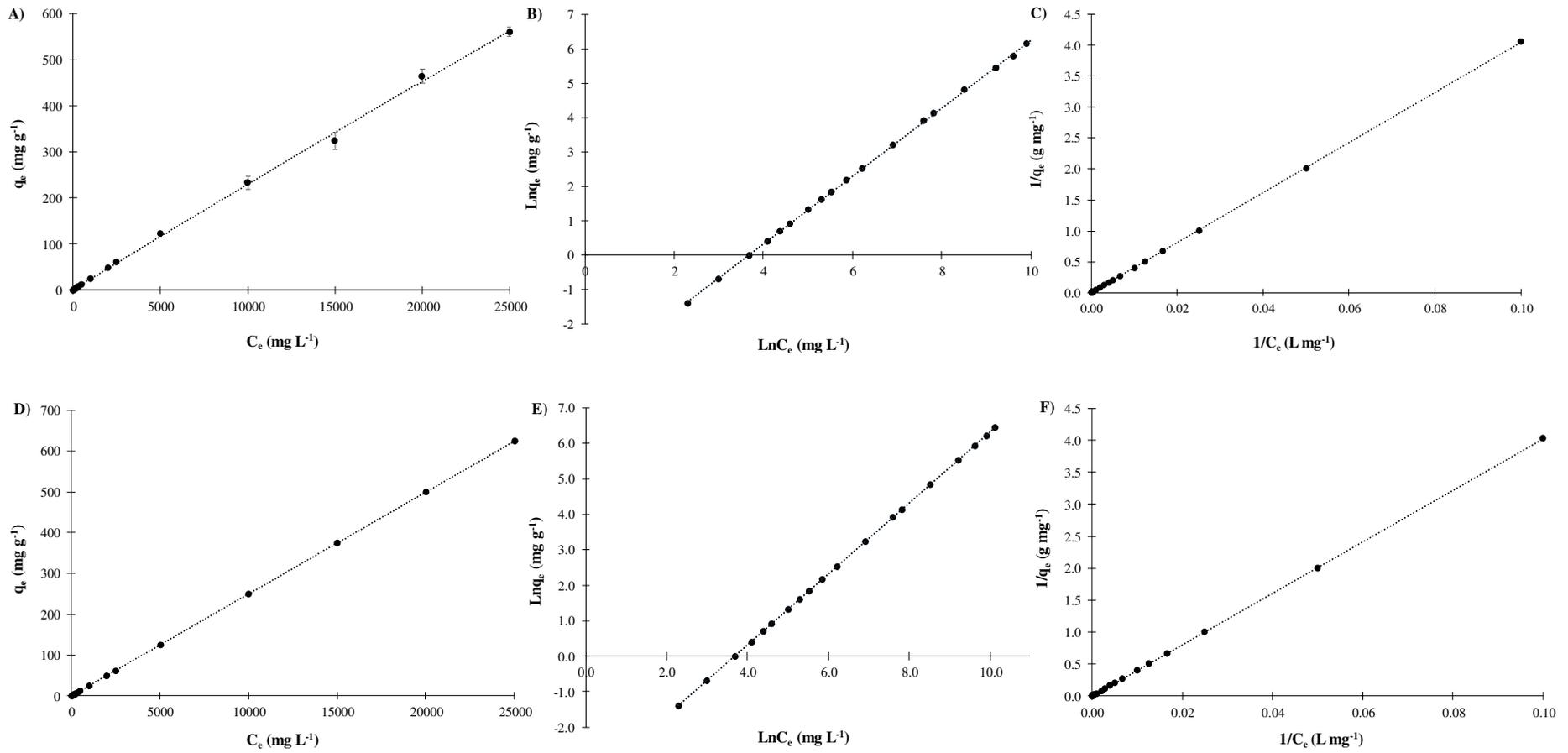
**Figure 2:** Characterization of IW1 (A) and IW2 (B) by XRD



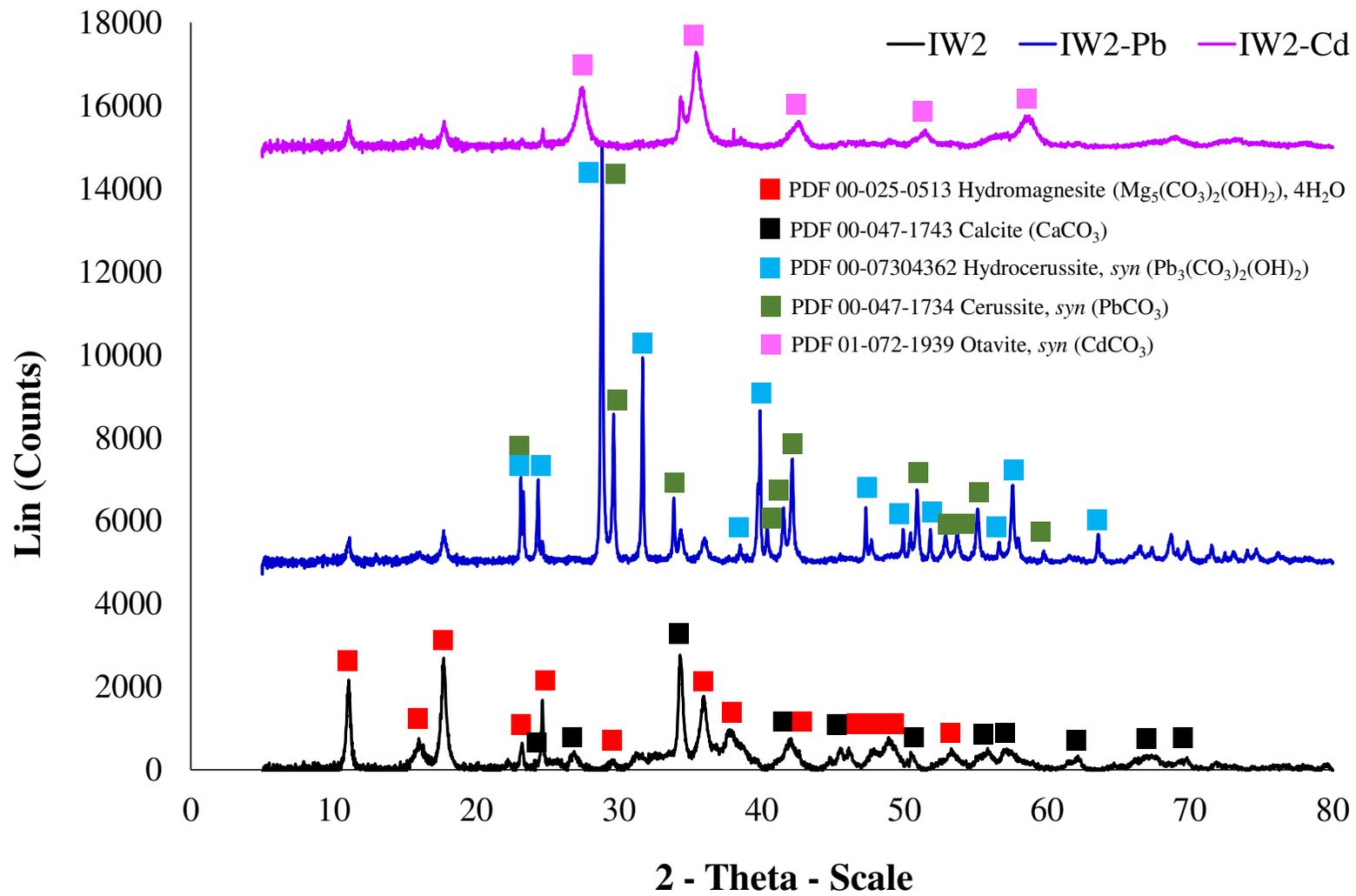
**Figure 3:** Freundlich and Langmuir isotherms of Cd (A, B, C) and Pb (D, E, F) on industrial waste IW1



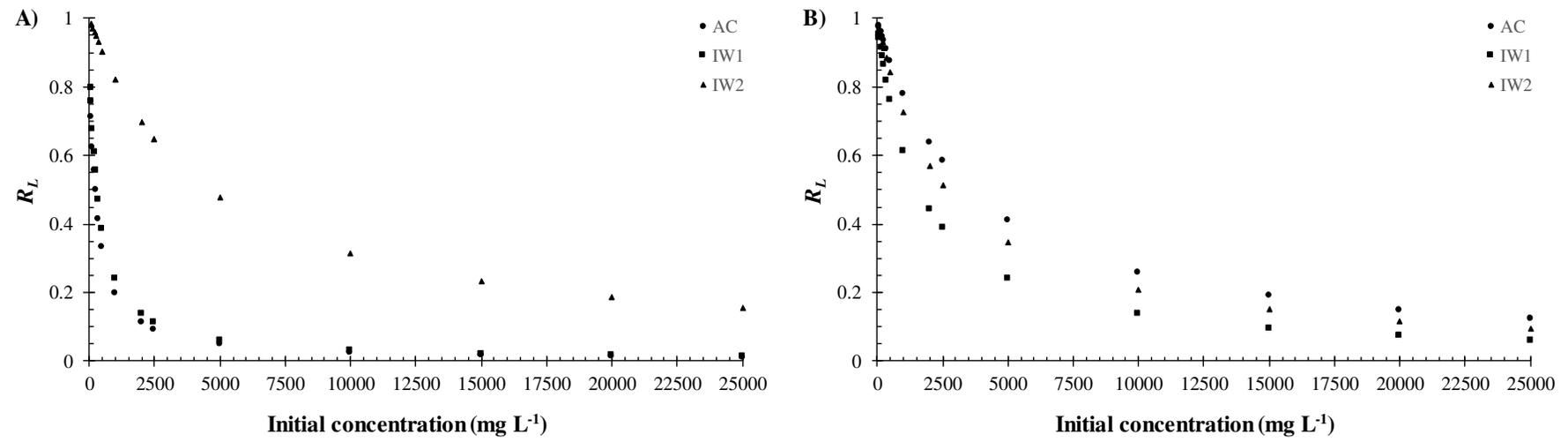
**Figure 4:** XRD diffraction pattern of IW1 before and after filtration (IW1-Cd, IW1-Pb)



**Figure 5:** Freundlich and Langmuir isotherms of Cd (A, B, C) and Pb (D, E, F) on industrial waste IW2



**Figure 6:** XRD diffraction pattern of IW2 before and after filtration (IW2-Cd, IW2-Pb)

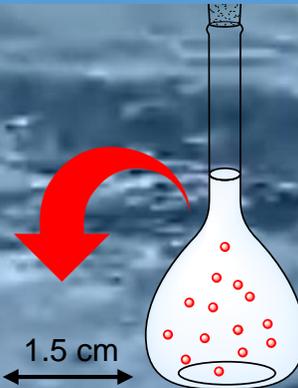


**Figure 7:** Variation of the Hall parameter: A) Cd and B) Pb

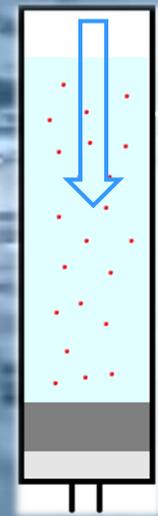
Contaminated water

2 studied pollutants

Cd=cadmium  
Pb=lead



1.5 cm



Contaminated water

Redisep Rf column

Sorbent

Cotton

2 investigated sorbents

IW1=Industrial waste 1

IW2=Industrial waste 2

1 reference sorbent

AC=activated charcoal



Decontaminated water

