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Heavy metals uptake from aqueous effluents by novel adsorbent derived from tannin extracts. Role of tannin source.

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Abstract: Novel tannin-based adsorbents were tested on heavy metals removal. Up to 10 heavy metals (Cd^{2+}, Cr^{3+}, Pb^{2+}, Hg^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, UO_2^{2+} and Mn^{2+}) were removed with different adsorbents that involved tannins from *Acacia mearnsii de Wild*, *Schinopsis balansae*, *Cupressus sempervivens* and *Pinus pinaster*. These tannin extract were gelified with formaldehyde in basic medium. The whole study was conducted under a statistical point of view, so ANOVA tests were carried out in order to evaluate the optimum concentration of formaldehyde, the most reactive tannin extract and the easiest metals for being removed. These considerations drove to the optimum *tanningel* derived from cypress, concentrated formaldehyde, with a high affinity to UO_2^{2+}, Hg^{2+} and Pb^{2+}. Lastly, equilibrium and kinetic studies were carried out on these systems.

Keywords: Heavy metals; water treatment, tannins, adsorption.

1. Introduction

Concerns about the presence of heavy metals in aqueous effluents are well known and they appear linked to a large variety of industries in modern life [1]. Some of them are the ones related to metal finishing, electroplating, plastics, pigments and mining, which threatens to the environment and human lives in a very severe way [2]. It is still a challenge for researchers to find new and cheaper mechanisms of heavy metals removal from wastewater, since they represent a harmful and noxious contamination due to their tendency to be accumulated in the food chain.

Heavy metal removal from aqueous solution can be achieved by several conventional methods: chemical precipitation [3], coagulation and flocculation [4], adsorption onto vegetal wastes [5] and special treatments such as nanofiltration [6] or reverse osmosis. All of these treatments may be effective with very high metal concentrations, but usually they are expensive and ineffective if we work with low levels (1-100 $mg \cdot L^{-1}$).

Adsorption technology has recently become a real alternative to traditional wastewater treatment due to its relatively simplicity and efficiency. Moreover, a large number of low-cost adsorbents from wastewater treatment can be found, which make this method strongly recommended since they are obviously cheap, widespread and highly efficient [7].

In the context of pollution remediation, natural raw materials are an interesting potential source of low-cost adsorbents [8-10]. One class of such materials is that of the *tannins*, a term which covers many families of chemical compounds. Their name comes from their traditional use in tanning animal skins for the production of leather [11], and today they are also widely used in tannin-modified adhesive formulations [12], as adsorbents for pollution control of industrial effluent [13], and as flocculants [14]. Their natural origin is as secondary metabolites of plants [15], occurring in the bark, fruit, leaves, etc. Whereas *Acacia* and *Schinopsis* bark constitute the principal source of tannins for the leather industry, the bark of other, non-tropical trees such as *Quercus ilex*, *Q. suber*, *Q. robur*, *Castanea sativa* and *Pinus pinaster* can also be tannin-rich.

From a chemical point of view, there are three kinds of tannins: hydrolysable, condensed and combined ones [16]. These products are rather chemically complex and they are usually taken from a natural matrix, without a very exhaustive purification. Because of that, it is rather difficult to know their structure exactly although probable approaches can be found in specific literature [17] (figure 1).

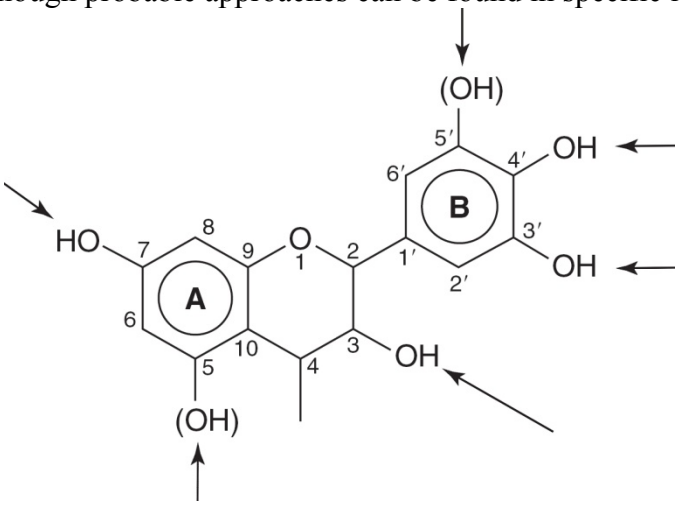

Figure 1: Probable flavonoid unit in a condensed tannin.

Tannin gelation is a chemical procedure that immobilizes tannins in an insoluble matrix [18] so that their properties of interest, e.g., metal chelation, are then available in an efficient adsorbent agent. In addition, the material resulting from their gelation (sometimes called *tannin rigid resin*) presents interesting properties in terms of resistance, non-flammability, and mechanical undeformability [19,20]. This process has been widely described in the scientific literature and in patents. One may find examples of basic gelation in the scientific literature [21-23], and in patents such as US patent 5,158,711[24]. Moreover, acid gelation is described by other workers [25, 26].

The applicability of these products is more than evident and gelation has been reported to be an effective way for removing heavy metals [21, 22, 27] and other wide variety of cationic substances and

dangerous products [26, 28]. However, the full study on how to optimize the tannin gelation in order to produce a more efficient *tannin rigid resin* for heavy metal removal is not performed yet. That is the scope of the present work.

To this end, we have selected four tannin sources (*Acacia mearnsii de Wild*, called *Weibull black*; *Cupressus sempervivens*, called *Cypress*; *Schinopsis balansae*, called *Quebracho* and *Pinus pinaster*, called *Pine*). Theses extracts were gelified with two doses of formaldehyde and they were tested with each metal. The ANOVA tests drove to the best formaldehyde dosage, the best tannin sources and the most removable metals. Finally, we have performed a theoretical modelization under the Langmuir hypothesis for the most relevant systems.

2. Results and Discussion

3.1. Kinetics of heavy metal removal

The efficiency of the adsorption process must be measured according to a parameter called "adsorption capacity" (q), defined by equation (1):

$$q = \frac{(C_0 - C_l)V}{W} \quad (1)$$

where
C_0 is the initial contaminant concentration, (mg L^{-1}),
C_l is the equilibrium contaminant concentration in bulk solution, (mg L^{-1}),
V is the volume of solution, (L),
and W is adsorbent mass (g).

Adsorption capacity tends to increase up to a maximum q level, which is reached after the equilibrium period. The determination of this period is performed according to kinetic studies and can be easily modeled by three kinetic hipothesis: Lagergren model (pseudo-first order) [35], Ho model (pseudo-second order) [36] and Elovich model [37].

The first experimental model (Lagergren) is given by equation (2):

$$q = q_e \quad q_e \cdot e^{-K_l \cdot t} \quad (2)$$

where
q_e is the amount of adsorbate retained per adsorbent mass is equilibrium, (mg·g^{-1});
K_l is the first-order Lagergren constant, (min^{-1}),
t is the experimental time, (min).

Ho's model is given by equation (3):

$$q = \frac{t}{\frac{1}{h} + \frac{t}{q_e}} \quad (3)$$

where h is Ho's constant, (mg·g^{-1}·min^{-1}).

Finally, Elovich's model is presented by equation (4):

$$q = \frac{1}{\beta_e} \ln(\alpha_e \cdot \beta_e) \; | \; \frac{1}{\beta_e} \ln t \quad (4)$$

where α_e is the initial adsorption rate, ($mg \cdot g^{-1} \cdot min^{-1}$),
and β_e is the desorption constant, ($g \cdot mg^{-1}$).

Table 2 shows the analytical results of these adjustments for four *tanningels* and three metals, since results were similar in the rest of the systems. As can be appreciated, the large majority of the involved systems presented high correlation factors r^2, in many cases above 0.95. The three models fit reasonably well to each pair of metal-*tanningel*. Attending to the standard deviation factor (data not shown) the best model for the removal of Hg^{2+} is the hypothesis of Elovich, whereas for the other two metals (UO_2^{2+} and Pb^{2+}) Ho's model is the best one.

Table 1. Analytical adjustments for kinetic models.

	Hg^{2+}	UO_2^{2+}	Pb^{2+}	Hg^{2+}	UO_2^{2+}	Pb^{2+}
			Lagergren model			
		PFc			**QFc**	
q_e (mg/g)	302	119	208	244	76	109
K_L (min^{-1}) $\cdot 10^3$	2.34	4.67	24.79	0.63	0.87	16.58
r^2	0.873	0.908	0.984	0.902	0.894	0.997
		WFc			**CFc**	
q_e	226	90	84	164	135	176
K_L(min^{-1}) $\cdot 10^3$	0.41	8.85	8.48	14.65	18.19	47.61
r^2	0.944	0.974	0.964	0.797	0.964	0.944
			Ho model			
		PFc			**QFc**	
q_e	330	135	228	269	83	112
h (mg/g·min)	0.97	0.77	8.17	0.26	0.10	4.06
r^2	0.946	0.966	0.996	0.949	0.939	0.988
		WFc			**CFc**	
q_e	262	94	88	181	148	190
h (mg/g·min)	0.13	1.42	1.25	3.48	3.65	14.89
r^2	0.967	0.993	0.997	0.887	0.982	0.992
			Elovich model			
		PFc			**QFc**	
α_e (mg/g·min)	4.07	2.12	43.36	1.05	0.41	192.66
β_e (g/mg)	0.020	0.041	0.030	0.023	0.075	0.084
r^2	0.991	0.991	0.873	0.964	0.95	0.762
		WFc			**CFc**	
α_e (mg/g·min)	0.62	292.72	177.10	64.68	20.23	535.80
β_e (g/mg)	0.024	0.132	0.135	0.047	0.470	0.050
r^2	0.944	0.807	0.829	0.912	0.869	0.861

3.2. General heavy metal removal test

After confirming the equilibrium period was enough with 1 week of stirring, several considerations may be done in order to guarantee the statistical significativity. The first one has to do with the reproducibility of the trials.

ANOVA test can be carried out considering just two variables in order to analytically explain the target variable *Percentage removal*: one may be the specific category of each *tanningel* and the other one can be the particular trial (numbered by 1 or 2). Figure 2 presents the graphical expression of this

ANOVA, where each point represents the estimated margin means of the removal percentage for the ten metals. As can be seen, the two lines are subsequently crossed, which is due to the absence of significativity of this variable. This is analytically confirmed by the p-value of this parameter (0.99). Consequently, reproducibility exigencies are adequately satisfied.

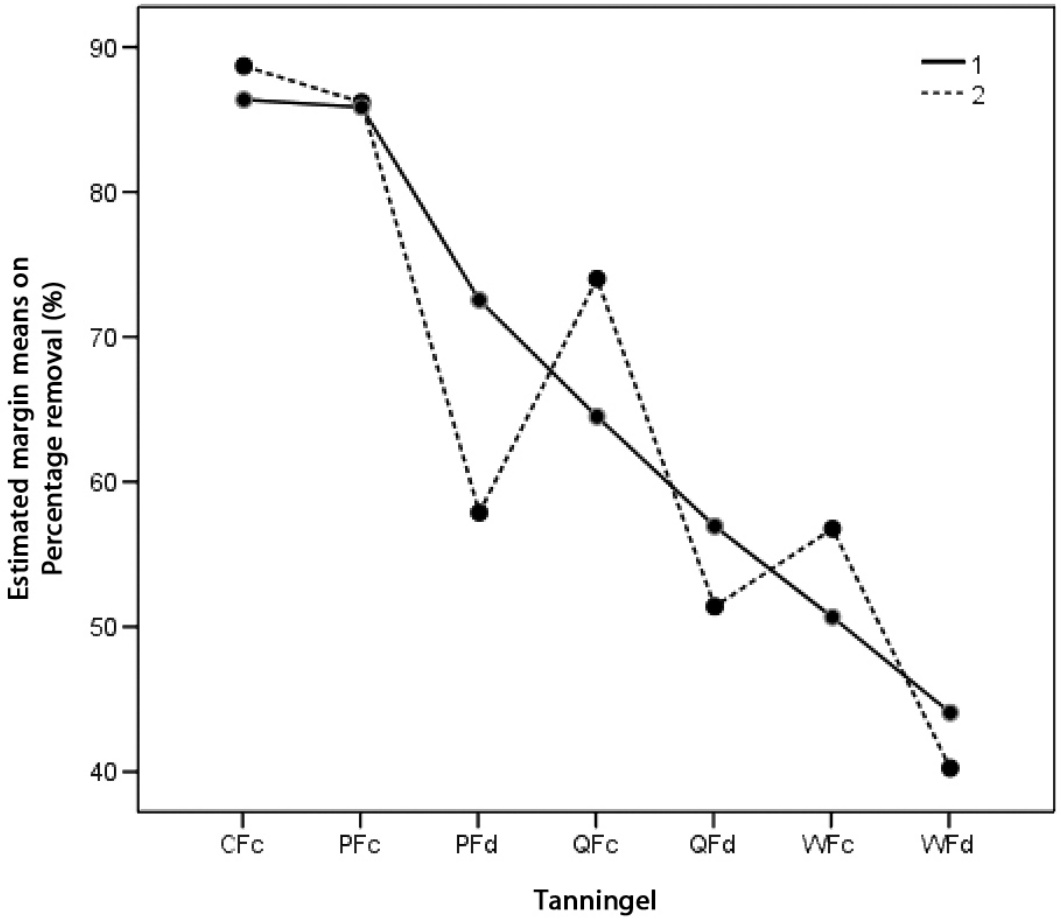

Figure 2: Indistinguishability of the adsorption trials.

3.2.1. Formadehyde content in gelation process

A similar consideration can be done regarding the formaldehyde content in the gelation process. As can be observed from table 1, two different doses were applied: one corresponds to 1 mmol g^{-1} and the other one corresponds to 3.68 mmol g^{-1}. These levels were selected according to previous works [30]. Again, ANOVA test gives us a definitive conclusion when it sets p-value of this parameter equal to 0 (table 3). That means there is a clear and significative influence of this variable and, according to Tukey's homogeneous groups, the level which drives us to the best adsorbent is 3.68 mmol g^{-1}, that is, the upper level.

Table 2. Significant variables in the ANOVA test for three parameters. Statistical summary.

Variable	F-value	p-value
Tannin	26.868	0
Heavy metal	25.011	0
Formaldehyde	30.092	0
Metal x Tannin Interaction	2.25	0.04
r^2 (%)	87.1	

3.2.2. Tannin extract

A preliminary approach to the influence of the tannin extract in the adsorption equilibrium *tanningel*-heavy metal is to perform a classical multiple comparison taking into account only the specific metal and each tannin extract type. This is showed in figure 3.

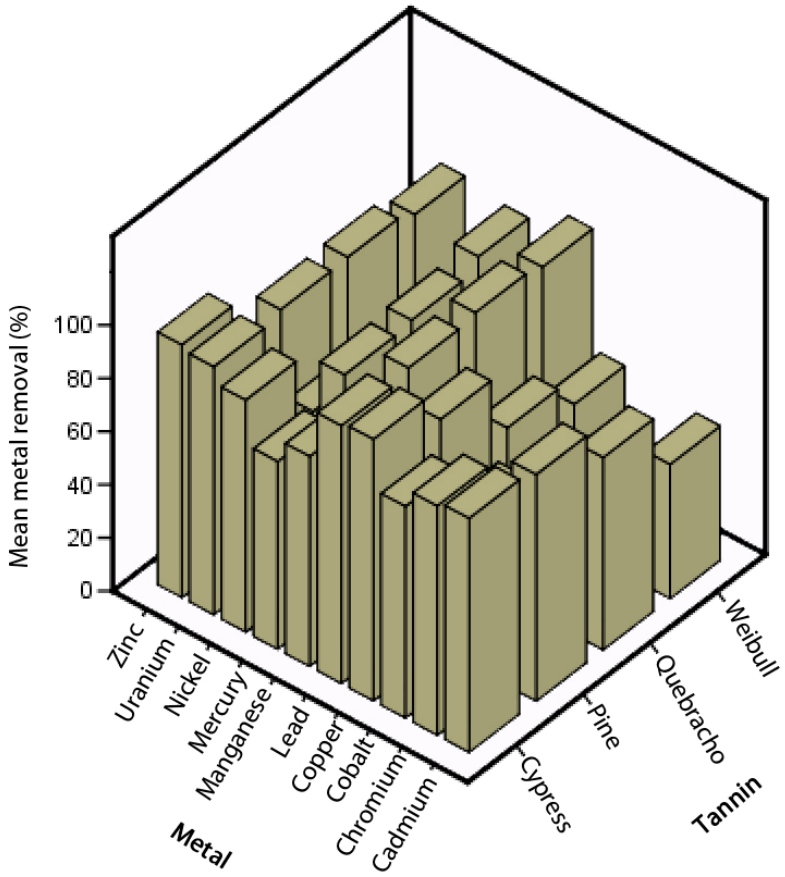

Figure 3: General comparison tannin extract and heavy metal removal.

In this figure, columns present the increasing metal removal regardless the rest of variables, such as formaldehyde concentration. It is an unclear representation because there are a huge number of percentage removal data in it. Therefore, a more specific analysis must be carried out.

ANOVA test is done involving the whole system, that is, our phenomenon (heavy metal adsorption from aqueous effluents by *tanningels*) may be explained according to the three variables: tannin extract, heavy metal and formaldehyde concentration. That will drive us to the traditional Tukey's homogeneous groups; those will help us to identify the best adsorbents and the most removable metals. Table 3 shows the main statistic data for this ANOVA test.

According to this statistical study, one can approach the influence of the specific tannin extract in the final response. Four separate and well differenced groups are presented according to Tukey's Honestly Significant Difference (HSD) test, one for each tannin extract. This shows us the most effective tannin is Cypress, then Pine and Quebracho. Finally, the less effective tannin extract is the one derived from black wattle, named Weibull (*Acacia mearnsii de wild*). The means removal percentage that stated these differences were 87.5, 75.6, 61.7 and 47.9 respectively. These differences have been observed previously in other works [30], but never referred to such variety of heavy metals.

3.2.3. Heavy metal ion

On the other hand, table 4 presents the HSD Tukey's homogeneous groups according to metal removal. This shows us how the chemical species of metal influence on the final interaction between metal and *tanningel*.

Table 3. Tukey's homogeneous groups according to metal type in heavy metal removal. Percentage values.

Metal	Subgroup 1	Subgroup 2	Subgroup 3
Cobalt	39.4		
Manganese	41.4		
Zinc	50.1		
Nickel	50.2		
Chromium	50.3		
Cadmium		72.1	
Copper		72.5	
Mercury		84.2	84.2
Uranium			94.6
Lead			99.5

As can be observed, three subgroups are arranged according to heavy metal type. The highest affinity to *tanningels* is presented by the last metal group, which involves Hg^{2+}, UO_2^{2+} and Pb^{2+}. It is remarkable that this last group present a mean heavy metal removal percentage above 90%. This may be due to the intrinsic relationships in adsorption processes between this ions and the *tanningel* themselves, which may enhance these linkings. This fact has been observed before [38], but with a significantly lower efficiency.

According to these preliminary results, we selected these three metals (Hg^{2+}, UO_2^{2+} and Pb^{2+}) and we performed an equilibrium study onto the four *tanningels*: PFC, WFC, QFC and CFC.

3.3. Isotherms and theoretical modelization

In order to evaluate not only the efficacy of the treatment but also the efficiency, the percentage removal must be complemented by other objective target. Traditionally, adsorption capacity (q) was defined for this scope according to the expression 1 in section 3.1.

The physical system heavy metal-adsorbent may be ruled by adsorption-like relationships. Taking into account the need of characterizing how these adsorbents work on metal removal, a model must be presented in order to fully characterizing the adsorption process. To this end, adsorption capacity q should a reference measure of the efficiency of the removal of the specific contaminant in relationship with the amount of adsorbent. This is a extensively used in such processes and must put in relationship q and the remnant adsorbate concentration.

The main adsorption model is the one Langmuir presented in the early years of the 20th century [39]. The fact that it is theoretically deduced makes it still feasible and appropriate. It assumes that the molecules striking the surface have a given probability of adsorbing. Molecules already adsorbed similarly have a given probability of desorbing. At equilibrium, equal numbers of molecules desorb and adsorb at any time. The probabilities are related to the strength of the interaction between the adsorbent surface and the adsorbate. That is the physical meaning of the equation (5):

$$q = q_{max} \frac{c_l}{b + c_l} \qquad (5)$$

where
q_{max} is the maximum q capacity (mg of metal·[mg of adsorbent]$^{-1}$),
and b is the Langmuir adsorption constant (mg of metal·L^{-1}).

This expression is usually applied under its linear form [40], which gives us the goodness of the model, but it is not recommended for a precise estimation of parameters. Reliable values of q_{max} and b are only obtained through non linear least squares data adjustment, since there is no need of homocedasticity, homogeneity of variance or normal distribution of errors [41].

Accordingly, these non linear adjustment were carried out for up to twelve adsorption systems that includes the three best adsorbents plus the one derived from *Acacia mearnsii* (Weibull black) and the three heavy metals which present more affinity by the adsorbents, they are UO_2^{2+}, Pb^{2+} and Hg^{2+}. The experimental data were obtained in similar stirring conditions, at 20ºC and after an equilibrium period of 1 week.

As an example, figure 4 presents the isotherm for PFC- UO_2^{2+}. This is a representative curve, very similar to the rest of them. At a first glance, it presents the typical shape of L-class in the specific classification [42]: a concave initial region followed by a saturation zone in the last part of the curve. This is usual in those systems where the adsorption becomes more difficult as the pollutant concentration increases.

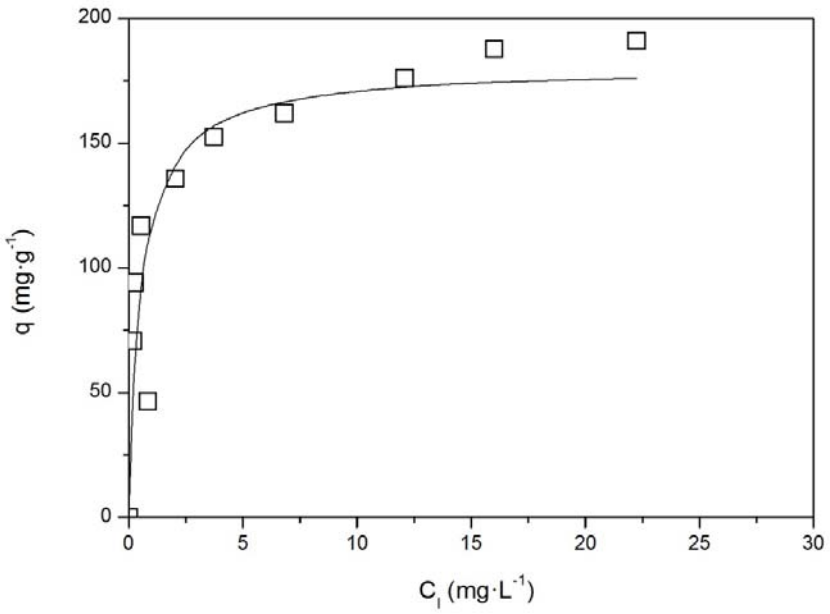

Figure 4: Isotherm for PFC- UO_2^{2+} adsorption system.

Table 4 presents the statistical summary for every adsorption system. As can be checked, the values of q_{max} confirms the hierarchy of adsorbents, being the least efficient the one derived from *Acacia mearnsii* (labeled as WFC), which presents a mean q_{max} level of 159 mg·g^{-1}, whereas PFC and CFC present 226 and 229 respectively.

Table 4. Non linear Langmuir adjustment data for each adsorption system. Units in text.

Metal \ *Tanningel*	CFC	PFC	QFC	WFC
Pb^{2+}	q_{max}=287.9 b=1.15 r^2=0.87	q_{max}=188.5 b=0.41 r^2=0.89	q_{max}=125.3 b=0.35 r^2=0.97	q_{max}=98.8 b=0.67 r^2=0.98
UO_2^{2+}	q_{max}=225.7 b=2.44 r^2=0.81	q_{max}=179.4 b=0.49 r^2=0.82	q_{max}=154.9 b=3.37 r^2=0.97	q_{max}=155.2 b=7.34 r^2=0.94
Hg^{2+}	q_{max}=175.4 b=7.78 r^2=0.95	q_{max}=311.5 b=6.10 r^2=0.81	q_{max}=622.3 b=61.1 r^2=0.96	q_{max}=223.2 b=14.1 r^2=0.98

Graphically, the adequacy of each adjustment can be appreciated under a linear plot. This is represented in figure 5, where predicted *q* (according to Langmuir's expression and the corresponding parameter data in table 5) is plot versus experimental q values. The nearer to the angle bisection the points are placed, the more accurate the adjustment is. As can be appreciated, the large majority of experiments are placed inside an error margin of ±10%, which is commonly accepted as a significative accuracy level.

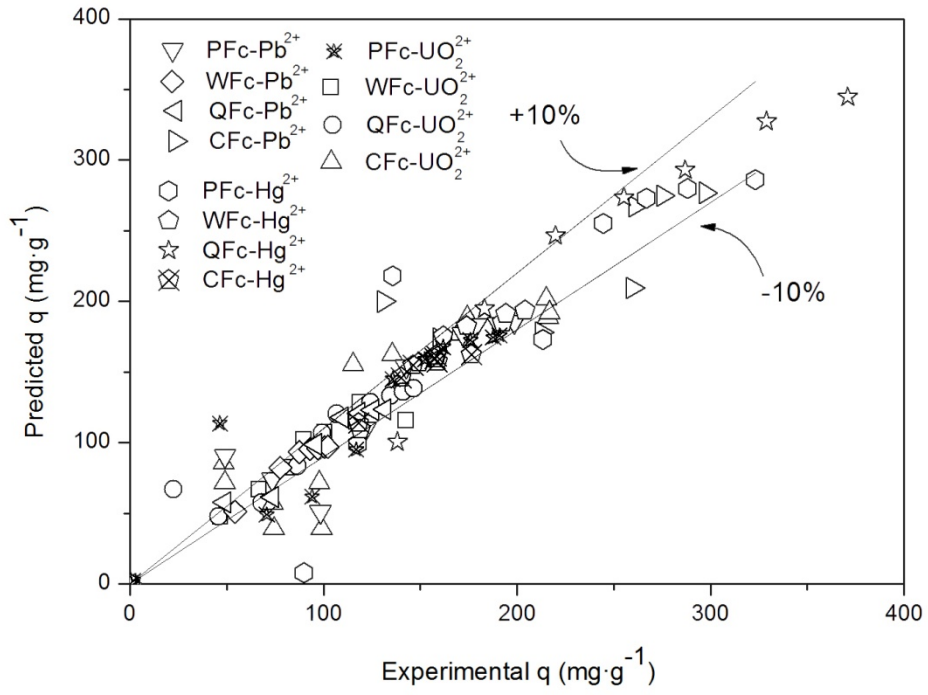

Figure 5: Predicted versus experimental *q* values.

If compared with other adsorbent materials, *tanningels* present a very competitive adsorption capacity, since the values obtained in the current work are inside the range of those presented by Babel and Kurniawan [43] including a wide variety of waste materials or Bhattacharyya and Gutpta [44] regarding the use of natural and modified clays.

3. Experimental Section

2.1. Tannin extracts and gelation process

Acacia mearnsii de Wild (Weibull black) and *Schinopsis balansae* (Quebracho) tannin extracts were kindly supplied by TANAC Inc (Brazil).

Tannins from cypress and pine were lab-extracted according to the normalized method described elsewhere [29, 30]. 100 g of pine bark or cypress husks were milled in a cutting mill (RETSCH, SM 2000 model) and they were put in 600 mL of tap water. Then, 5 g of NaOH (PANREAC) were added and the mixture was stirred in magnetic stirrer at 90ºC for 1 h. Solids were separated by filtration and liquid fraction was dried in oven (65ºC) overnight. The resultant was considered the tannin extract.

Tanningels were prepared according to the basis of Nakano et al. [21]. 5 g of tannin extract were dissolved in 32 mL of NaOH (PANREAC) 0.125 mol L^{-1} and 30 mL of distilled water at 80ºC. When mixture was homogeneous, certain amount of formaldehyde were added and reaction was kept at the same temperature for 8 hours until polymerization was considered completed. Then, the apparent gummy product was lead to complete evaporation of water remain and dried in oven (65ºC) overnight. After drying, tannin rigid gels were crushed and sieved to produced 38-53 µm diameter particles. They were washed successively with distilled water and HNO_3 0.01 mol L^{-1} (PANREAC) to remove unreacted sodium hydroxide. Finally, the adsorbent was dried again in oven. Differences are found between this preparation way and the description made by Yurtsever and Sengil [31], mainly concerning the amount of formaldehyde.

2.2. Model compounds and metal analysis

Metal salts were supplied by Merck. Each one presents different degrees of hydration, however the final concentration of metal in the bulk solution is calculated only on the basis of the heavy metal ion. The specific chemical compounds were: $Cd(NO_3)_2.4H_2O$, $CoCl_2.6H_2O$, $Cr(NO_3)_3.9H_2O$, $Cu(NO_3)_2.2.5H_2O$, $HgCl_2$, $MnSO_4.H_2O$, $Ni(NO_3)_2.6H_2O$, $Pb(NO_3)_2$, $UO_2SO_4.4.5H_2O$ and $Zn(NO_3)_2.6H_2O$.

Up to four different analytical methods were used for measuring the metal concentration. For Cd^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+} and Ni^{2+} the classical analytical process developed by Qi and Zhu [32] was used.1 mL of sample was put into a 25-mL flask and 5 mL of borate buffer (sodium borate and sodium carbonate in equal quantities, pH 10) were added. Subsequently, 2 mL of 4-(2-pyridyl-azo)-resorcinol (PAR) 5 10^{-4} M were added and the mixture was diluted to the mark with distilled water. Then, the solution was mixed and absorbance at 505 nm in a 1-cm optical glass cell was measured after 20 min.

Pb^{2+} content was determined by modifying this method according to Pollard et al. [32]. PAR was used in a five times higher concentration than in the previous case and absorbance was measured at 530 nm after 30 min.

UO_2^{2+} was analytically determined also according to Pollard [32]. 5 mL of sample were mixed with 10 mL of pH-8 buffered solution and 2 mL of PAR $2.5 \cdot 10^{-3}$ M. This mixture is heated for 10 min at 115ºC in consciously sealed vials. Once the temperature of the solution decrease, it is put in a 25 mL-flask and distilled water is added up to the mark. Immediately, absorbance is determined by visible spectroscopy at 530 nm in a 1-cm optical glass cell.

Cr^{3+} was determined according to Yotsuyanagi [33]. This is carried out as follows: 1 mL of simple is put into a vial and 1 mL of pH-5 buffered solution and 3.5 mL of PAR $2.5 \cdot 10^{-3}$ M and 10 mL of distilled water are added. The sealed vials were then heated for 2 h at 115ºC. Absorbance is determined in the same way as indicated for the case of UO_2^{2+}.

Finally, Hg^{2+} is determined according to Manchón-Vizuete et al. [34]. 5 mL of sample are introduced in a 25-mL flask and 10 mL of HCl 6 M are added. Distilled water is added up to the mark and absorbance is determined at 231 nm in a 1-cm quartz cell.

Spectrophotometric determinations were carried out with an HEλIOS UV/VIS spectrophotometer.

2.3. Equilibrium studies

In order to test the ability of each *tanningel* in the removal of heavy metals a standard protocol of adsorption was developed. Samples of aqueous solutions with the corresponding pollutants concentration (25 mg L^{-1}) were put into 100 mL-flask. A fixed amount of *tanningel* was added to each flask (50 mg) with different volumes of contaminated aqueous solutions. A period of 7 days was established for guarantee equilibrium.

2.4. Kinetic studies

For confirming the equilibrium period of these adsorbents, kinetic approaches must be carried out. To this end, 100 mL of solutions with initial concentrations of 50 mg·L^{-1} of UO_2^{2+} , Pb^{2+} and Hg^{2+} were treated with 50 mg of PFC, CFC, WFC and QFC. The presence of heavy metals in the bulk solution were measured at different intervals and the decay was modeled according to three kinetic models: Lagergren, Ho and Elovich. Similar trials were performed with other metals (results not showed).

Both equilibrium and kinetic studies were carried out under strict thermal control and magnetic stirring.

2.5. Mathematical and statistical processes

Design of experiments was carried out by using SPSS 14.0 for Windows (SPSS).

The basis of the statistical method is found in the interaction of variables. Briefly, it can be summarized as follows:

a) Up to eight different combinations regarding the two variables (tannin extract and formaldehyde concentration) were attempted. The feasible combinations were just seven of them, since the gelation of cypress extract with diluted formaldehyde was not possible (table 1).
b) Each feasible combination was synthesized twice and subsequently tested on each heavy metal solution. The resulting target variable was the percentage removal of metal.
c) The results were evaluated under subsequent ANOVA tests: one for the reproducibility of the synthesis (indistinguishable observation) and another one for evaluating the effective influence of formaldehyde concentration, tannin source and metal type. This drove us to identify the best adsorbents and the most removable metals. All of these variables were statistically significantly, hence the conclusions are consistent.

Table 1. Gelation experiments.

Tannin extract	Formaldehyde (mmol·g^{-1})	Does it gelify?	Symbol
Cypress	1	No	
Cypress	3.68	Yes	CFC
Quebracho	1	Yes	QFD
Quebracho	3.68	Yes	QFC
Pine	1	Yes	PFD
Pine	3.68	Yes	PFC
Weibull	1	Yes	WFD
Weibull	3.68	Yes	WFC

4. Conclusions

Tanningels have been confirmed as promising adsorbents for the removal of several heavy metal ions from aqueous effluents. Statistical approaches pointed out that high content of formadehyde is needed for the most efficient *tanningel* and cypress was the best tannin source, followed by pine, quebracho and acacia. On the other hand, the best *tanningels* performed a very significant metal uptake with lead,

uranium and mercury. Every adsorption system responded to Langmuir's model with a very high correlation factor and significantly high adsorption capacities.

Acknowledgments

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