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completely how pollutants interact in natural heterogeneous soil systems in real high-concentration cases. e top of this is to have a universal method to face all possible cases of this and similar kind and predict their dynamics and interactions. e work presented here is to set the rst steps to solve and meet this ambitious and leading goal.

Materials and Methods

Sampling methods

In this section the main aspects on sampling during the whole process of this research in solid, liquid and solid-liquid phases are described.

Soils

t Field scale

Seven random sandy soils were used to carry out di erent tests in this work. ese were taken from di erent areas in central Asturias of Spain at random spots as follows (GPS coordinates, latitudes and longitudes respectively): a. 43° 35' 12.1812", -5° 56' 35.0412"; b. 43° 21' 18.396", -5° 52' 18.5586"; c. 43° 21' 14.832", -5° 52' 18.5298"; d. 43° 33' 4.572", -5° 37' 19.8402"; e. 43° 32' 55.8666", -5° 37' 25.6836"; f. 43° 21' 6.2166", -5° 52' 30.561"; g. 43° 21' 10.476", -5° 52' 26.0142". For the collection of each sample herbs and soil top layers were removed with a hand fork. Each sample was taken from eld surface with a maximum depth of 20 cm with a hand trowel. e samples were collected in plastic bags and transported immediately to the laboratory

$$\ln q = \ln k + \frac{1}{n} \ln C$$

Equation 3 - 3

2º Get the equivalent linear equation from equation 3 - 3:

$$\ln q = \ln k + \frac{1}{n} \ln C \quad u\, y = a + b\, x$$

Equation 3 - 4.

where $\ln q = y, \ln C = x, \ln k = a$ and $\frac{1}{n} = b$.

3º Do the graph from equation 3 - 4 and get the constant values of k and n by intersection values of y versus x for this equation, of the inverse of logarithm and fraction.

t Constant adsorption

Constant adsorption equation was used to test and show the f7

Experimental tests

Experimental system was designed in di erent tests in order to determine the e ect of temperature, pH, stirring speed and salts on bio-availability, environmental quality for microbial growth or phenol adsorption. ese tests were carried out in slurry reactors with polluted sandy soils. Each test was conducted in triplicate and its results were represented in mean values.

Soil samples were placed in 250 mL Erlenmeyer asks (reactors), in di erent solid/liquid (w/w) ratios, depending on the test. Initial phenol concentrations were prepared from appropriate dilution of a phenol standard solution (2000 mg/L). e same procedure was followed when nutrient salt solutions were considered.

Reactors were placed in an orbital incubator, New Brunswick G.25 model, protected from sunlight. To avoid interferences due to microbial degradation processes, sodium azide 0.02% (w/w) was used as antimicrobial agent. e tests were as follows:

pH and salts: Di erent salt solutions were used to control systems pH, their compositions are shown in Table 1. Each solution is described by letter A, B, C, D, E or F. Even though all soils were used for this test, focus was on samples with a pH approximately lower or equal to seven (pH 7), in this case soils T4, T5 and T6 as it is shown in Table 2. Other experimental conditions were kept constant: temperature equal to 28°C, S/L equal to 0.2 and stirring speed equal to 150 rpm.

Slurry reactor

t Soil concentration

e e ect of soil concentration on bio-availability and adsorption of phenol was tested at S/L interval from 0.01 to 0.82 (weigh/weigh relation). During this test other experimental conditions were kept constant: pH equal to 7 ± 0.5, temperature equal to 28ºC and solution E (Table 1). e soil sample for this test was T1.

Stirring speed: e e ect of stirring speed on bio-availability and adsorption of phenol was tested at the interval 150 ± 50 rpm (the circular motion had as a radius of 3 cm). During this test other experimental conditions were kept constant: pH equal to 7 ± 0.5, S/L equal to 0.2, temperature equal to 28ºC and solution E (Table 1). Soil samples were T1, T2 and T3.

Isotherms: e same experimental conditions were used to nd the di erent isotherm equations for soils T1, T2, T3, T4, T5, T6 and T7. Solution F, described in Table 1, was used to carry out this test with initial phenol concentrations between 30 to 300 mg/L. Other experimental conditions were kept constant: temperature equal to 28ºC, stirring speed of 150 rpm and S/L relation equal to 0.2.

Temperature: System temperature was evaluated at two di erent intervals. e rst interval corresponded to slight variations, it was around 28 ± 2°C for soils T1, T2, T3, T4, T5, T6 and T7 (Table 2). Its speci c experimental conditions were S/L equal to 0.2 and solution E (Table 1); the second one was conducted with greater variations, it was around 27.5 ± 22.5°C for soil sample T1. Its speci c experimental conditions were S/L equal to 0.1, solution F (Table 1) and di erent phenol initial concentrations in an interval from 27 to 134 mg/L. Other experimental conditions were kept constant in both tests: pH equal to 7 ± 0.5 and stirring speed equal to 150 rpm.

Salts: e e ect of salts (taking into account their nature and concentrations) on the phenol bio-availability and soil adsorption capacity was conducted by study of adsorption equilibrium on soil sample T1. Salts, such as sodium chloride (NaCl), magnesium sulphate ($MgSO_4$), ferric chloride ($FeCl_3$), potassium hydrogen phosphate (K_2HPO_4), sodium carbonate ($NaHCO_3$), chloride ammonium

Compounds	Liquid solution characteristics					
	A	B	C	D	E*	P*
Phenol (mgt)	300	300	300	300	300	+
Sodium azide (c...i. wt'wt)	0_02	0_02	0.02	0.02	0.02	0.02
NaHCO: (g L)	- Tc 17.299 0S12g L)g L-1420281H389.391IC420 81H 9.4510.003(0.02)9L)0.0LC Cm5 TcG61 m 03(0.01 366 02420 81H 9.FeC13					

samples had low concentration of organic matter (OM) as it is shown in Table 2, it was less than 0.7% in most of them. Only two soils, T1 and T7, had organic matter above this value, around 3.78 to 2.98% respectively.

ese results showed that soils T2, T3, T4, T5 and T6 had very poor conditions for plant and microorganism growth according to the literature [36,37]. Also, in the same way, these samples with less than 0.7% of OM did not have very good encouraged granulation, tilth, porosity, bulk density, water in ltration and availability, plasticity, cohesion, adsorption capacity and nutrient souce [38,39].

It has been reported that similar soils, like soils T1 and T7, had relative bu ering capacity around its pH value for its OM concentration [36]. ese were around the value of strongly alkaline, 9.16, to moderately alkaline, 8.01, respectively for these samples.

Additionally, it was not clear that OM was the main factor to determine the CEC value of all soil samples. Only for soils with high OM concentration, soils T1 and T7, this variable had a linear increment, where a high CEC value meant a high OM value. In other cases, specially with soils T2, T4 and T6, with intermedia CEC values, OM concentration did not have a clear relation with it. is was, probably, due to its characteristics, nature or other soil properties. Moreover, the e ect of OM concentration over other soil variables in soil samples was also not evident at naked eye to its complex nature [38].

Electrical conductivity: Soil samples had di erent electrical conductities (EC) in this order: T4>T7>T3>T6>T2>T1>T5 as it is shown in Table 2. is was related to soil disolved components because they carried electrical current in liquid phase under experimental conditions.

e relation of EC and pH of soil samples was not clear because soils with high conductivity had neutral alkaline pH values, like soils T4 and T7. Also samples with low EC had high and low pH values, like soils T1 and T5. ese factors, maybe, were more related to soil nature and its composition [40].

Soils with high EC had high CEC values like soils T2, T3, T4, T6 and T7. It is important to highlight that it has been reported that soils with high EC have high bioavailability of their nutrients, cations and anions, as disolved salts [41-45]. Nevertheless, in this sense, experimental EC values below 200 µS/cm were a clear indication that there were not enough available nutrients in some soil samples and it could show low organism activity, especially for soils with low EC and low OM at the same time, like soils T2, T3, T4, T5 and T6.

Other important variable related with EC was the clay concentration. Soils with the highest EC had the highest clay%, like soils T3, T4 and T7. is is so because the clays were the support of cations that later were mesured in disolution with other anions by EC [46,47].

Volumetric density: e volumetric densities of soil samples were around 0.7 to 1.30 g/cm^3 as it is shown in Table 2. e interelation of this variable with pH and CEC was not evident for all soil samples [42]. is factor was more related with sand and silt proportions and their paking arragement [48]. Soil samples with the highest sand and silt porcentage had approximately the highest volumetric density, that was the case of soils T5, T2 and T1. However, this was not a linear correlation in all soil samples due to soil morphology, especially for soils T6, T7, T4 and T3.

It has been reported that high soil volumentric densities are related indirectly with poor nutrient and environmental conditions to support micro and macro-organismos in high concentrations [49]. is could be the case of soils T1, T2, T3 and T5 because they had the highest volumetric density values.

e analysis of soil samples with these highest volumetric density values and other soil properties can show how the environmental conditions were for these soils for living organisms, and it can be explained as follows: a high volumetric density and a low anion concentration (high CEC and low EC) in soil T1 meant low mineral nutrient availability; a high volumetric density and a low OM concentration in soils T2 and T3 meant low organic nutrient availability; a high volumetric density and low cation and OM concentrations in soil T5 meant low mineral and organic nutrient availability .

In the case of soils T1, small black coal particles, 100% organic matter, were observed in soil grains. Without this huge visible amount of organic matter the volumetric density of this soil should have been bigger [38,48].

Additionally, in case of macro-organism growth conditions, it was observed that none of soil samples exceeded the volumetric density for roots and plant growth of 1.40 g/cm^3 [50].

Particle size: All soil samples were texture clasi ed as sandy soils due to their size distribution of particles as it is shown in Table 2. In all coil stetticlclrganu7iof pes as it is sho(t)-4(et)012(t)5(i)-6(cl)-6n5clrganu a hige5(a hia(t)-5(ra)109(h)4(o)16(w)-3(n in T)i)-6(i)J -0c(o)16 ial as irte

In this section the main previous considerations to have stable and reproducible conditions during the experimental tests are mentioned. is is structured in two main subsections: (1) pH and salts and (2) soil concentration and stirring speed. As it can be deduced by its names in these subsections are described the e ect of pH, salts, soil-liquid relation and stirring speed on phenol soil adsorption equilibrium.

Given the situation of complex natural soil samples, as it has been shown in previous section, it was requiered to have a set of experimental conditions where a comparative and reproducible analysis could be done with independence of soil sample.

e object of this was to nd out which pH, salts (type and concentration), solid-liquid relation and stirring speed had to be used to have reproducible and comparative results during the experimental tests.

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e st step was to increase the bicarbonate salt concentration to 500 mg/L in systems as it is described in table 1, solution B. is increment in all cases allowed increasing the pH and stabilized its value in the required pH interval of 6 to 9 a er only 12 hours. Nevertheless, for the media of soil T6, the pH stabilization was not reached even a er 72 hours under this condition. Despite this result, the mean pH value in all studied systems a er this test was 7.9 ± 1.56. In Figure 2, letters A and B, it can be seen how the pH of media under natural conditions (represented by letter A) changed to the new pH values due to the addition of bicarbonate salt. (represented by letter B).

In order to have media pH of soil T6 around the required pH interval, it was required to increase the bicarbonate salt to 600 mg/L as it is shown in Table 1, solution C. As it can be seen in Figure 2, letter C, the increment bicarbonate salt to this concentration allowed reaching the required pH interval for all samples in less time, especially for soil T6. is pH value was around 8.36 ± 0.45. e pH equilibrium for T4 and T5 was reached a er just two hours, ten hours less than the previous test. In case of media of soil T6, this pH equilibrium was reached a er just 24 hours, 48 hours less than the previous test. An important factor to highlight in this point is that this salt concentration allowed sustaining the pH equilibrium without signi cant variation independent of soil nature. is last interesting conclusion was the reason for choosing 600 mg/L as an ideal bicarbonate concentration for subsequent tests.

When the e ect of other salts in the system was evaluated (solution D, Table 1), like $FeCl_3$, K_2HPO_4, $NaHCO_3$, NH_4Cl, K_2SO_4 and $CaCl_2$ [60-64], an imbalance in the pH values of the systems was observed again as it can be appreciated in Figure 2, letter D. is imbalance of pH was more signi cant for soil T6 media, with a di erence in absolute value of 3.01 units of pH. e new mean pH value in all systems a er this test was 7.02 ± 1.93. Even the di erence in pH values of other systems was small with respect to previous test, in absolute values of pH units of 0.73 for T4 media and 0.23 for T5 media, it was, therefore, required to nd a better method to control the pH. e reason for this was that the presence of new salts in the media changed its properties in an unpredictable way with respect to pH due to the heterogeneous nature of soil samples. Again, the setback was on how to compare di erent

achieving two important things: similar operating condition for pH and salt concentrations in all cases independently of their nature and the possibility to compare all the results. is with the idea to have robust conclusions in this work.

Soil concentration and stirring speed: Stirring factor determines the relation between soils, solvents, microorganisms, nutrients and pollutants in ex-situ soil bioremediation studies. e start point is to know how the operation conditions in uence and change the soil adsorption equilibrium to avoid any misinterpretation of initial conditions in the global process [5].

t Soil concentration

Di erent soil concentrations were tested to analyze the in uence of this factor on nal phenol soil adsorption equilibrium in sandy soil samples.

ere is a trend in soil ex-situ bioremediation to use indistinctly soil concentrations without any consideration of this factor [9,14,65] and in many cases it is still unclear how the optimization of this variable can improve the process goals. Even when this factor is considered in these processes the e ect of this variable on soil adsorption properties are poorly described in real cases for sandy soils [30,66,67].

ese tests were carried out by putting di erent solid/liquid (S/L, relation weight/weight) relations under the same experimental conditions to determine phenol adsorption kinetics and equilibrium point as it is shown in section 3.4.2.1. e results of these showed that it is possible to reach the adsorption equilibrium a er 6 hours independently of the S/L relation in the system (the results are not shown).

Even when the equilibrium was reached almost at the same time in all tests, small di erences were observed about phenol adsorption equilibrium for each S/L relation. Only for a small interval, from 0.01 to 0.11 S/L relations (0.01 S/L 0.11), was possible to have approximately ideal suspension conditions for particles, this being without signi cant interference between them for adsorption factors. Even for cases with S/L equal to 0.2 approximately (S/L 0.2) these di erences were reasonably negligible for this heterogenic case. ey were around 20 mg/L in mean terms. e same tendency has been reported by Fukui et al. [68] in tests with di erent S/L relations. is means that for any point under similar conditions, the equilibrium is constant independent of the S/L relation.

Also during these tests it was observed that soils formed conglomerate structures in the centre of asks almost immediately a er starting the tests (less than 1 hour). e high density of particles was the main reason, even when the stirring speed and turbulence of the media were high, where the Reynolds number was equal to 13860 (NRe=13860) [21]. is e ect was more signi cant when the soil-liquid relation was over 0.2 (S/L>0.2). Likewise, this soil con guration provided di erent experimental conditions during the adsorption process in the same reactor; there were particles in suspension, semi-

Equilibrium

In ex-situ bioremediation processes, it is necessary to know how the pollutants are distributed around phases to nd the best experimental conditions to achieve process goals. Without this consideration, it is not possible to predict the availability of pollutants in the liquid phase and know if the microorganisms can degrade them easily under a set of experimental conditions.

is section of equilibrium is structured in two subsections. ey are related with results of isotherm equations and soil properties related with phenol adsorption equilibrium.

e key factor, before microbial activity in a bioremediation process, is to predict the adsorption behaviour and understand its properties, in the equilibrium solvent-solute-adsorbent, to implement all required actions to quickly recover the polluted soil. ere are a lot of studies about how to predict adsorption behaviour with di erent isotherm equations and about which soil factors are more important in this process in ideal solid-liquid conditions. However, natural soil bioremediation cases with high pollutant concentrations are poorly evaluated.

e object of these tests was to nd a universal isotherm equation to predict the adsorption behaviour of high phenol concentrations in natural sandy soils and nd which soil properties can in uence this adsorption equilibrium under real bioremediation conditions before microbial activity.

sotherms:Equations used to describe the adsorption isotherms in solid-liquid systems are derived from the models developed for solid-gas systems [17]. Despite this, excellent results have been obtained to represent real cases of this kind in low concentration or in conditions where the nature of the adsorbent is homogeneous. e challenge here is to nd equivalent equations for heterogeneous conditions in natural environments like those that are easily to nd in soil bioremediation processes.

In this section, results of equation validations for phenol soil adsorption isotherms during experimental phase are shown.

Even adsorption isotherm equations that come from solid-gas systems, as it was mentioned above, there are many of them that are especially improved for ion exchange studies in solid-liquid systems [18-20]. More studies related to the adsorption equilibrium of contaminants in natural soil systems have been done for years. Most of them are specialized in adsorption equilibriums where the pollutants and soils are related in ideal conditions with low pollutant concentrations and high soil adsorption capacities, such as activated carbon, polymeric resins or pure minerals [20,75-80]. However, heterogeneous soil adsorption processes with high loadings of pollutants have been poorly evaluated due to its complexity [81-83].

e object of these tests was to nd an equation that it could be used to describe phenol soil adsorption isotherms independently of sandy soil nature in an ex-situ bioremediation process before microbial activity.

In order to carry out these tests, di erent soil samples were settled in di erent reactors under the same experimental conditions. is allowed us to do a real comparative analysis of the e ciency of tested equations. e speci c details of this are described in section 3.4.3. of methodology section. In order to t the equations to experimental data a graphical representation method was used as it is shown in section 3.3.1.

e correlation order for phenol adsorption isotherms was di erent for each soil sample and each tested equation. e order of accuracy between the experimental data and calculated data was bigger in the case of the Freundlich equation in relation to others. e t of the experimental data to tested equations was as follows, in the order of accuracy from the highest to the lowest: Freundlich (r^2=0.95)>constant separation factor (r^2=0.91)>linear adsorption model (r^2=0.21).

e small variation between Freundlich and separation constant isotherm, represented by correlation factor of 0.95 and 0.91 respectively, showed that both equations can be used to represent the

factors in uenced phenol adsorption equilibrium for some soils. For that reason additional analyses were needed to clarify this issue. is analysis is presented in the following section.

Soil properties:Standard protocols for ex-situ soil bioremediation processes are needed in order to achieve the process goals independently of soil nature and environmental conditions. As it was mentioned, the soil properties and their control can be key factor to enhance availability of pollutants in medium if it is analyzed correctly in soil adsorption process.

In this section, a comparative analysis of soil properties and how these in uenced the phenol soil adsorption process for studied soil samples is described.

In ex-situ soil bioremediation processes the pollutant distribution in the soil determines the guidelines to follow in the cleaning of these systems. Most studies which are related to this issue are focused on groundwater contamination, where contamination levels are generally low [10,80,82,83,86]. In these and other similar studies, the highest correlation coe cients (ř) of adsorption processes generally correspond to the tests conducted in systems with a high concentration of organic matter. Other factors prevailing in this connection is the percentage of clay and cation exchange capacity [25,75,87-90]. However, it is not completely clear how these factors in uence adsorption conditions with heterogeneous natural soils in high phenol concentrations.

e object of this analysis was to nd which soil properties could in uence the adsorption equilibrium under real bioremediation conditions before microbial activity.

e experimental data used to carry out this analysis were taken from the test described in the previous section (5.3.1) All details of experimental conditions and related information are described there.

e experimental results showltio thidwa 5.247 13d4(o)(en)19(t)11(u)-5(ld)]TJuee2fith hhe highest roperpion of organic atter5OM),cl elywy tpu.

)16(n t)-3(a)1(s)-8(e)of ooil pOM,7 13d4it is nhowlanin tTlet 2, rom tahhe -5(o)11(r)13(e)iec-3(a)-5(l a)-9(e)12(ri)19(t) ff oiovw73(.,Ed.9381 523.7578 Tm (2T1, T4, T6a)9(n)4(d cT7n)4(h)4(o)16(u)-5(ld)n a34-7(v)8(erhn a34dh)-6(h)4(e hig)-7(h)4(es)5(t) ehenol corhese fd.9381 523.7578 Tm (2)4(h)4(o)16(u)-5(ld)n a34-7(v)8(erh)-9(e)-5(den:o)-8(o)12(i)-5(l pT1>)-8(o)12(i)-5(l pT7>)-8(o)

ene mn3(o)16(ut)howlanin t8(e)-ns cwork it ias tn3(o)16(ut)etslet d o-1(u)-2(t i)-8(v)83(i)dtnd cediodtttea ieneyw8(e)-85(enfd.9381 523

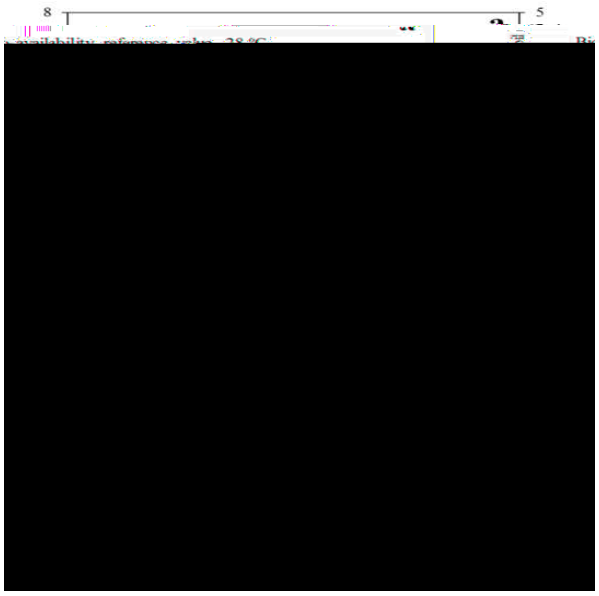

Figure 4: Schematic representation of temperature effect on phenol soil adsorption. Here is possible to observe the changes on phenol adsorption equilibrium, colums, and phenol bio-availability, lines, for temperature intervals of 28 ± 2ºC (A) and 27.5 ± 22.5°C (B). Data representation: A. Dots equal to 26ºC, continuous lines equal to 28ºC and slashes equal to 30ºC; B. Experimental data for soil sample T1 with reference temperature of 25ºC.

Temperature: e e ect of temperature on soil adsorption capacities of pure compounds with high content of organic matter has been widely described in literature. Presently, due to the great amount of polluted soils around the world, it is the time to know its e ects on real polluted soil environments.

In this section the results of the e ect of temperature on adsorption and bio-availability of phenol in sandy soil samples are presented.

In many phenol bioremediation processes it is common to see changes in temperature that enhance microbial activity. However, the e ect of this variable on soil adsorption properties is unconsidered during this process in many cases [98,99]. Little is known about the e ect of temperature on the adsorption equilibrium of phenol in natural sandy soils under high phenol concentration cases.

e object of these tests was to nd how temperature could in uence the adsorption and bio-availability of phenol during a process of ex-situ soil bioremediation in sandy soils before microbial activity.

Two di erent intervals of temperature were tested in this sense, one around 28 ± 2ºC and another one around 27.5 ± 22.5ºC. e other experimental conditions were kept constant and are described in section 4.4.4. e theoretical isotherms were represented by Freundlich equation.

e experimental data in the rst set of tests showed, represented in Figure 4A, that small changes in system temperature, around 28 ± 2°C, caused slight di erences in soil adsorption capacity and bio-availability of phenol for each soil sample. In the case of soil adsorption capacities (columns), these data showed that for four soil samples, T1, T2, T3 and T5, an increment in system temperature meant an increment in phenol adsorption with respect to the equilibrium. However, the opposite behaviour was observed for soils T6 and T7, where an increment system temperature meant a decrement of phenol adsorption with respect to the equilibrium. For soil sample T4, the change of system temperature in this interval did not a ect signi cantly its adsorption capacity, its variation has been less than 5%; in case of phenol relative bio-availability with respect to the phenol equilibrium concentration (lines), it was noted that small di erences between equilibrium conditions in that range of temperature were around ± 2.5% for each case in mean terms, as it can be seen in this gure. It meant that almost all equilibrium conditions were the same in that interval of temperature. e average standard deviation (SD) of concentration for each soil in this range of temperature was: T1SD= ±4.19; T2SD= ±2.45; T3SD= ±2.49; T4SD= ±0.94; T5SD= ±2.05; T6SD= ±1.64; T7SD= ±5.35. And for all soil samples together under these conditions it was ± 2.72 mg/L at equilibrium concentration. ese small di erences did not allow developing the real nature of this phenomenon. For this reason it was necessary to carry out more speci c tests for this work.

e second set of tests about the e ect of temperature on phenol adsorption capacity in the interval of 27.5 ± 22.5ºC showed, as it can be seen in Figure 4B, that an increment system temperature meant a decrement of phenol adsorption with respect to the equilibrium (columns). Its consequence was that there were more phenol molecules available in liquid phase for soil sample T1 (line). Between temperatures 5 and 1ºC it was noted that an increment in the system temperature meant an increment in soil phenol adsorption with respect to the equilibrium concentration. e reason of this behaviour, that it was the opposite of previous one, was probably due to the interrelation of phenol with some soil components whose concentration in liquid phase it had reduced [100,101]. Additionally, it was observed that reproducibility of results in this interval has had the highest standard deviation and this could be the reason of this behaviour even when triplicate analyses were done. For this reason an extra test on phenol adsorption was carried out.

When other experimental conditions to get the phenol adsorption isotherms for this soil in the same interval of temperatures were tested, more evident results were obtained, and they are represented in Figure 5. When the system temperature decreased, from 50 to 15°C, phenol soil adsorption equilibrium was displaced. is change in the system

Figure 5: Schematic diagram of temperature in uence on phenol adsorption capacity in soil sample T1 (From 5 to 50ºC). Geometrical and line symbols represent experimental and theoretical data respectively. The Freundlich equation was used to get theoretical data.

temperature increased the retention of phenolic molecules in the soil. e reason of this could be that at high temperature there was an increment of transport potential and at low temperature there was a decrement of this factor. However, it was not su ciently clear which were the main interrelation forces between particle active zone, phenol molecules and water with tested experimental conditions [102-104].

Also these data and their analysis, as it is shown in Figure 5, allowed nding out the complex behaviour of phenol soil adsorption at 5ºC. e reason for this could be, as it was mentioned before, the reaction of phenol with some salts in the soil structure. Nevertheless, its nature and composition was undetermined. Other more speci c tests have to be done in order to understand this phenomenon.

e results of these tests showed that system temperature could enhance the availability of phenol in the liquid phase and reduce the phenol concentration in soil if there is an increment in temperature. Further, these results showed that the characteristics of this equilibrium are determined by the interrelation of phenol-water-soil. Without this information, it is impossible to nd out this behaviour without empirical tests in each case. Other additional tests are required to nd out what happens with soil adsorption properties in systems with high charge of phenol and heterogeneous soils at low temperatures.

Salts: Nutrient salt applications are common practice in soil bioremediation processes because these can enhance the microbial activity and reduce the recovery time. However, in all cases it is not completely clear if these substances can increase the pollutant soil adsorption and reduce its bio-availability. It is still required to know if "the remedy is worse than the disease" in this sense.

In this section the results of salts e ect on phenol soil adsorption equilibrium in an ex-situ bioremediation process before microbial activity are presented.

In ideal conditions, ex-situ soil bioremediation is where microorganisms consume the pollutants and convert them into non-organic soluble or gaseous compounds inert to the environment and innocuous to human health. During this process, the microorganisms capable of consuming these contaminants quickly increase their number. Critical micro and macro nutrients, or bio-stimulants, are required in this process, like carbon, nitrogen, phosphorus, potassium, sodium. Without these nutrients, umail 4l1

a er reaching the phenol adsorption equilibrium, the isotherms were determined by Freundlich equation.

ese tests and results showed that phenol soil adsorption process in real environments is complex and di cult to predict. e salts, by kind and amount, increased, increased-decreased or decreased the phenol soil adsorption capacity. Also, these results have shown a competitive multilayer adsorption tendency. ese results, represented by its isotherms, are shown in Figure 6.

e results showed that an increment of K_2HPO_4 salt around 12 mg/L did not alter signi cantly the phenol adsorption equilibrium. However, concentrations of this salt, above this value (>12 mg/L), increased considerably the phenol retention in soil matrix and reduced

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