Single and Multi-component Adsorptive Removal of Bisphenol A and 2,4-Dichlorophenol from Aqueous Solutions with Transition Metal Modified Inorganic-Organic Pillared Clay Composites: Effect of pH and Presence of Humic Acid

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Abstract

Pillared clay based composites containing transition metals and a surfactant, namely *MAIOr-NaBt* (Bt = bentonite; Or = surfactant; $M = \text{Ni}^{2+}$, Cu^{2+} or Co^{2+}), were prepared to study selectivity and capacity toward single and multiple-component adsorption of bisphenol A (BPA) and 2,4-dichlorophenol (DCP) from water. Tests were also performed to account for the presence of natural organic matter in the form of humic acid (HA). Equilibrium adsorption capacities for single components increased as follows: $\text{NaBt} < \text{Al-NaBt} < \text{AlOr-NaBt} < \text{MAIOr-NaBt}$. The observed equilibrium loadings were ca. 5 and 3 mg g^{-1} for BPA and DCP, respectively, at neutral pH conditions and ambient temperature, representing an order of magnitude increase over the unmodified pillared clay capacities. Inclusion of the transition metal brought an increase of nearly two-fold in adsorption capacity over the materials modified only with surfactant. The *MAIOr-NaBt* adsorbents displayed remarkable selectivity for BPA. Multi-component fixed-bed tests, however, revealed competition between the adsorbates, with the exception of the *CuAlOr-NaBt* beds. Inclusion of HA, surprisingly, enhanced the phenols adsorption capacity. Preliminary regeneration tests suggested that the adsorbent capacity can be recovered via thermal treatment or by washing with alkaline solutions. The former strategy, however, requires surfactant replenishment. More complex schemes would be needed to deal with absorbed HA.

Keywords: *fixed beds; transition metals; phenolic compounds; humic acid; competitive adsorption*

1. Introduction

Phenolic compounds such as BPA and DCP are widely used as precursors in an extensive variety of industrial and agricultural manufacturing processes. For instance, BPA is a known raw material in the polycarbonate plastic and epoxy resin synthesis [1-7]. Meanwhile, DCP has been used as a precursor for the synthesis of herbicides and pesticides [8, 9]. There is a recurring presence of these compounds in water bodies due to frequent use, which has led to accumulation in the environment causing serious pollution problems [6, 7, 10-13]. It has been found that at low concentrations, these compounds are highly toxic, poorly biodegradable and present carcinogenic properties. BPA is known to affect hormone systems in many aquatic organisms and humans, rendering it an endocrine disruptor compound (EDC) [14-18] and forcing many countries around the globe to ban its use in, for example, plastic bottles used to feed infants. Because of their potential to cause further health related problems, the United States Environmental Protection Agency (EPA) has set a maximum allowable level of 1 mg L^{-1} for chlorophenol compounds in waste and drinking waters [19].

Several physicochemical processes have been proposed as alternatives to reduce or eliminate these contaminants [11, 13]. Amongst these, separation via adsorption has proven promising due to its efficiency in pollutant removal at low concentrations, simplicity of design, low operational cost, and absence of toxic by-products [20-22]. Numerous efforts have been devoted to the development of adsorbents with flexible and tunable surfaces targeted to particular adsorbates and the environment to which they are exposed [2, 5, 23-27]. Amongst such adsorbents, natural clays have gained significant interest due to charge density, cation exchange capacity, and its ability for intercalating polymeric organic compounds. In addition, natural clays are readily available and affordable [10, 28]. Several studies have shown that by introducing inorganic poly-

cations and cationic surfactant chains into the inter-lamellar spaces of the clay structure, its textural properties, thermal stability, hydrophobicity and adsorption capacity are significantly enhanced, making these inorganic-organic clay (IOC) composites suitable for the adsorption of hydrophobic pollutants, such as the phenolic compounds [28-31].

Despite the efforts in designing and tailoring the aforementioned adsorbents, their use for the removal of phenolic compounds in water treatment plants or at point sources have been limited due to the complex chemical nature of the contaminated water matrix. For instance, some aqueous environments present levels of organic matter (NOM) that affect the removal of the targeted contaminants, especially when it comes to waste and surface waters [32-34]. NOM comes from the decay of plants and residual animals, and it is a complex chemical arrangement, consisting mainly of HA, fulvic acid, and humin. HA constitutes a major fraction of NOM (c.a. 50-90%) and contains a heterogeneous mixture of molecules with various chemical functionalities such as carboxylic, phenolic, carbonyl and amine groups [35-37]. These functionalities have the ability to interact with many organic compounds and dissolved metals in water by electrostatic interaction and π - π stacking effect [38-41]. This evidently affects the solubility and mobility of targeted adsorbates in the medium and even transforms some of them to more toxic and carcinogenic by-products (e.g. in the presence of chlorine) [34, 42-44]. Likewise, it has been found that NOM also has the ability to interact with the surface of many adsorbents, affecting both selectivity and working adsorption capacities [35, 45-47].

The main goal of this work was to assess the equilibrium and dynamic adsorptive removal of BPA and DCP using transition metal-modified IOC adsorbents, both in single and multi-component fashion as well as in the presence of NOM. The selection choice for the IOC type was made based on results of previous studies focused on the removal of non-phenolic organic

contaminants of emerging concern [48-52]. The results presented here include the effect of solution pH and involved the use of IOCs that contained Co^{2+} , Ni^{2+} or Cu^{2+} sites as the driving force for selectivity. Fixed-bed breakthrough tests were employed to elucidate the effect of dynamic, non-equilibrium conditions on selectivity as well as competitiveness and transport of both phenolic compounds in the presence of HA as a NOM model. Although several reports have studied possible NOM adsorption mechanisms and have considered its influence on the adsorption of organic contaminants in various types of adsorbents (including IOC adsorbents) [34, 46, 53], most have been performed based on equilibrium tests, so little is known about the effect that NOM has on the adsorption of pollutants at continuous flow conditions. Furthermore, in an attempt to provide design and predictive tools, the modified dose-response (MDR) and Clark fixed-bed adsorption models were employed.

2. Experimental section

2.1 Reagents and material preparations

Aluminum pillared clay (Al-NaBt), surfactant modified pillared clay (AlOr-NaBt) and metal modified inorganic-organic pillared clay ($M\text{AlOr-NaBt}$, $M = \text{Co}^{2+}$, Ni^{2+} , Cu^{2+}) were prepared according to methods available elsewhere [50]. Reagents used for the modification of the bentonite materials were the following: distilled/deionized water, cetylpyridium bromide hydrate (98.0%), aluminum chloride (AlCl_3 , > 99.9%), sodium carbonate (Na_2CO_3 , > 99.0%), nickel (II) sulfate hexahydrate (99%, ACS Reagent), copper (II) nitrate hemipentahydrate (>99.99%, trace metal basis), and cobalt (II) nitrate hexahydrate (98⁺%, ACS Reagent).

Reagents used during the adsorption tests were: BPA (analytical standard), DCP (99%, ACS Reagent), hydrochloric acid (37%, ACS Reagent), sodium hydroxide (97%, reagent grade), and

HA. All of these were obtained from Sigma-Aldrich and used without further purification. Selected physicochemical properties of the adsorbates are listed in Table S1. The water employed during the adsorption tests was both distilled and deionized. IOC samples were characterized according to the procedures described in the Supplementary Material.

2.2 Equilibrium adsorption tests

A typical equilibrium adsorption experiment consisted of mixing 0.050 g of the adsorbent with 15 mL of the aqueous solution with initial concentrations of the corresponding phenolic compound or the HA (1, 5, 8, 12, 15 and 18 mg L⁻¹) inside 50 mL borosilicate centrifuge tubes. The solution pH was adjusted using 0.1 M HCl or NaOH solutions. Final values for pH were set to 2 and 12 for low and high pH, respectively. Whenever used throughout the text below, natural pH it will refer to the pH value of the phenolic compound in solution without any adjustments (ca. 6 – 7). The tubes were shaken at room temperature for 24 hours, which was adequate to reach equilibrium as determined during uptake tests as a function of time and the corresponding diffusion coefficient (Fig. S1 and Eq. S1). The solids and aqueous phases were separated via centrifugation at 8,500 rpm for 10 min.

Triplicates measurements were made, with the final equilibrium concentration of the phenolic compounds being estimated via high performance liquid chromatography (HPLC) on an Agilent 1100 Series HPLC module operating at the corresponding characteristic wavelength. This module is attached to a diode array detector (DAD) fitted with a deuterium lamp and a temperature control unit. Separation of the adsorbate from the aqueous solutions was performed with a Zorbax Eclipse XDB Column C8 using an acetonitrile/(water 1% formic acid) mixture at a flow rate of 1.0 mL min⁻¹ and at a 30:70 composition. The equilibrium-adsorbed amount of the phenolic compounds was calculated based on concentrations differences using Eq. S2.

2.3 Dynamic adsorption tests

The dynamic adsorption experiments were performed via a vertical setup where the flow driving force was limited to gravity. This was accomplished by using a vertical glass column with an inner diameter of 0.8 cm and total depth of 30 cm. The setup and dimensions are based on optimization tests performed by Hernandez-Maldonado and co-workers during adsorption of non-phenolic organic species from water also using IOCs and for both single and multi-components [54]. In general, the fixed-bed runs were performed at 25 °C and natural pH (between 6 and 7) with an inlet concentration of 10 mg L⁻¹ for each phenol and an average flow rate (Q) of 1.5 mL min⁻¹ at the bed outlet. The particles of the IOC adsorbent beds had a size range of 150 - 420 µm and a total mass of 4.7 g for an effective bed depth of 8.4 cm. Aqueous samples were gathered at the outlet of the column at regular time intervals and the concentration was determined using the HPLC system described above. Adsorption loading amounts were estimated using an expression that resulted from a steady-state adsorbate mass balance (Eq. S3).

A similar procedure was employed for the processing of feeds that included HA. For these cases, a portion of a HA stock solution was spiked into the phenolic compound feed solution to give a HA concentration of 2.5 mg L⁻¹.

3. Results and Discussion

3.1 Equilibrium adsorption isotherms

Equilibrium adsorption data for single phenolic components are gathered in Fig. 1. Visibly, the adsorption capacities were significantly influenced not only by the modifications made to the adsorbents (i.e., pillaring, surfactant and transition metals), but also by pH of the solution and the chemical nature of the adsorbates. No adsorption was observed for NaBt, except at low or high

pH. In general, the adsorption capacity increased as follows: NaBt < Al-NaBt < AlOr-NaBt < MAlOr-NaBt ($M = \text{Ni}^{2+}, \text{Cu}^{2+}, \text{Co}^{2+}$). This shows that the intercalation of surfactant and transition metals greatly improves the adsorption capacity toward phenolic compounds, plausibly due to formation of stable adsorbent-adsorbate complexes via combination of hydrophobic interactions and electron transfers between the adsorbate functional groups (aromatic rings and hydroxyl groups) and the adsorbent surfactant chains, hydroxyl groups, and metal centers. It should be noted that NiAlOr-NaBt exhibits the overall larger adsorption capacity (on per sorbent weight basis) followed by CuAlOr-NaBt and CoAlOr-NaBt. A possible explanation for this is the benefit of a larger metal cation loading (Table S2), which should result in more available effective adsorption sites. However, the effectiveness of the metal centers in capturing the phenolic adsorbate follows a different trend. If the adsorption capacities are normalized by metal cation loadings, then the trend in the performance of these adsorbents will be as follows: NiAlOr-NaBt < CuAlOr-NaBt < CoAlOr-NaBt.

A comparison of equilibrium adsorption data gathered at different pH solutions reveals that a natural pH condition results in better phenolic adsorption capacities. Alkaline pH conditions resulted in unfavorable loadings probably due to the protonation/de-protonation of the functional groups in both adsorbates (pK_a) and adsorbents (isoelectric point) (Table S1 and Fig. S2). Another possible explanation for having lower adsorption capacities at alkaline pH could be metal cation movement within the premises of sites that are inaccessible to the adsorbates, but necessary to balance the adsorbent structural charge. At natural pH conditions the surface charge of the adsorbates are neutral and, therefore, electrostatic interactions might not influence their adsorption onto the IOCs.

All IOCs have better affinity toward BPA over DCP probably due to the number of hydroxyl

groups and aromatic rings. The former provides greater ability to form hydrogen bonds while the latter provides a more hydrophobic character (high log K_{ow}) and more electron density, imparting ability to form stable complexes with metal cations (Table S1). Moreover, DCP molecules contain electron-withdrawing groups (i.e., chlorine atoms) that decrease the overall electron density of the aromatic ring, thus limiting the ability to transfer electrons to metal cations (electron deficient) and forming complexes [27, 55].

The data shown in Fig. 1 were fitted with Langmuir and Freundlich (Eqns. S4 and S5) isotherm models in an attempt to get further insights on the governing adsorption mechanisms. Model parameters as well as the corresponding fit Residual Root Mean Square Errors (RRMSE) (Eq. S6) are shown in Table S3. In general, the RRMSE values suggest that a Freundlich model best follows the experimental adsorption data trends. Indeed, the large interaction parameter (K_F) values correlate well with the apparent concave downward adsorption profiles exhibited by the metal-modified IOC and BPA pairs at natural pH solutions thus suggesting strong adsorbate-adsorbent interactions. Likewise, the heterogeneity factor (n_F) values were greater than unity and this correlates well with the heterogeneous nature of the surface of the IOC adsorbents.

It should be noted that the adsorption loadings of BPA and DCP observed during this work compare well with or excel those reported in the literature for other adsorbents including other clay-based variants, zeolites, activated carbon and even magnetic nanoparticles. For instance, the BPA adsorption onto unmodified and modified Fe_3O_4 nanoparticles results in loadings of 0.872 - 2.16 mg g^{-1} [22], 1.3 – 2.7 mg g^{-1} when employing zeolites synthesized from coal fly ash [56], and 3.5 mg g^{-1} when using granular activated carbon [1], all at similar conditions. These loadings are much lower than those observed in this work for metal-modified IOCs. Meanwhile, the BPA adsorption onto surfactant modified montmorillonite results in capacities of 13.3 – 20.0 mg g^{-1}

[30], 55.6 mg g⁻¹ in MIL-100(Fe) and 137.0 mg g⁻¹ in activated carbon [2], but these tests were performed at significant higher equilibrium aqueous phase concentrations (~ 300 mg L⁻¹) and at acidic pH levels. For the DCP adsorption from water, the literature include reports of loadings of 5.9 – 6.4 mg g⁻¹ onto Pd/Fe nanoparticles when supported on multi-walled carbon nanotubes at concentrations near 20 mg L⁻¹ and low pH [55], 8.0 mg g⁻¹ onto surfactant modified bentonite at concentrations of 100 mg L⁻¹, 17.94 mg g⁻¹ onto activated carbon [9] and 23 mg g⁻¹ onto surfactant-modified bentonite at equilibrium concentrations of approximately 25 mg L⁻¹ [8].

3.2 Fixed-bed of adsorption single components

Metal-modified IOC performance under dynamic conditions was assessed via fixed-bed adsorption experiments. Figs. 2A, 2C and 2E show the bed exit concentration profiles for BPA and DCP each fed as single components. Like in the equilibrium measurement tests, the IOC beds have better affinity toward BPA when compared to DCP at breakthrough point. In general, CoAlOr-NaBt beds had the better adsorption capacity at breakthrough for both phenolic adsorbates, followed by NiAlOr-NaBt and CuAlOr-NaBt (Table S4). This trend suggests once more that not all of the nickel cations are exposed to interactions with these phenols, as opposed to the cobalt cations. It should be noted that the slopes of the mass transfer zones displayed by the bed exit concentration profiles for BPA are less pronounced than those observed for DCP, probably due to stronger interactions between the surface of the IOCs with the former adsorbate. Another explanation for this behavior is the presence of higher resistance to mass transport due to differences in adsorbate molecular sizes; since BPA is significant larger than DCP (Table S1) [57, 58], which could limit its transport through the small pores of the IOCs, particularly the transition metal containing ones (see pore volumes in Table S2).

Reports in the literature for dynamic adsorption tests involving phenolic compounds are

scarce [3, 59, 60]. Santos and co-workers performed adsorption experiments for DCP and pentachlorophenol in a fixed-bed of coal fly ash [59]. These mineral residues exhibited a breakthrough capacity of ca. 0.98 mg g⁻¹ toward DCP at an initial concentration of 10 mg L⁻¹ with a flow rate of 4.3 mL min⁻¹, and a mass of 10 g. This value is comparable to most of the breakthrough capacities reported here (Table S4). However, given that coal fly ash displays a much larger higher surface area due to a porous structure consisting mainly of macropores and mesopores, it is not farfetched to assume that a metal-modified IOCs therefore undergoes more significant interactions with DCP and that capacity is therefore being limited by textural properties

3.3 Fixed-bed adsorption of multiple components

Figs. 2B, 2D and 2F show bed outlet concentration profiles for BPA and DCP that were fed simultaneously into *MAIOr*-NaBt fixed-beds. Evident from these results is significant competitive adsorption between the phenolic compounds. Adsorption capacities estimated at the bed breakthrough point and for multicomponent uptake are smaller than those estimated for single component, with the exception of the *CuAlOr*-NaBt bed case (Table S4). Considering that all the transition metal IOCs possess similar textural properties (Table S2), an increase in adsorption capacity in the *CuAlOr*-NaBt bed is probably due to interactions between the adsorbates (intra-molecular hydrogen bonding) paired with interactions with the copper centers. Given that Cu²⁺ has a 3d electron orbital that is almost full, such arrangement is plausibly suitable for complexation-like interactions with phenol compounds simultaneously since a larger number of electrons could increase the probability of back-donation and, therefore, lead to stronger interactions.

3.4 Adsorption in the presence of humic acid

Fig. 3 shows HA equilibrium adsorption isotherms gathered to elucidate the capacity of the IOC adsorbents toward bulky, complex moieties typically present in water. The data were gathered at natural pH solution and only for *MAIOr-NaBt* adsorbents since these showed the best phenolic adsorption capacities among the IOCs studied. Adsorption capacities for HA uptake were found to be an order of magnitude larger than those calculated for the phenols. Given that the HA average dimensions are considerably larger than those of the IOCs pore gallery width (Table S2), the results shown in Fig. 3 suggest that the external surface area of the *MAIOr-NaBt* adsorbents is responsible for driving the uptake of such a large adsorbate [49]. In addition, the adsorbate interaction with the IOCs could be influenced by the diversity of hydrophilic and hydrophobic moieties as well as functional groups present in the former, even including fractions of metal cations (Table S5). The wide range of functionalities could give way to a combination of interactions that include electrostatic and hydrophobic interactions, intra-molecular hydrogen bonding, and even formation of complexes [34, 38, 39, 61]. In terms of performance, the *NiAlOr-NaBt* adsorbent exhibited the largest HA adsorption loading, suggesting that a significant amount of adsorption sites (i.e., nickel(II) sites) is externally available. Another aspect that should be considered is that at the working pH, the HA surface is negatively charged and that of *NiAlOr-NaBt* is slightly positively charged, while for other metal-modified IOCs the surface is slightly negatively charged (Fig. S2).

Based on some reports from the literature for other IOCs and even zeolites, it must be emphasized that the equilibrium capacity values shown in Fig. 3 are significantly larger in comparison. For example, HA adsorption onto coal ash, raw bentonite, zeolite or palygorskite results in loadings in the range of 1.4 – 17 mg g⁻¹ [25, 36, 37]. However, the values reported here

are comparable to those reported for zeolitic imidazole frameworks, surfactant-modified zeolites and Fe surfactant-modified pillared montmorillonite: 45, 81 and 40 mg g⁻¹, respectively, at an equilibrium concentration of 2 mg L⁻¹ [24, 25, 38]. The latter comparison confirms that unique interactions with HA arise when incorporating surfactants and transition metals onto adsorbents.

Additional fixed-bed adsorption tests were performed in order to elucidate the level of competitive adsorption between HA (as a model compound for NOM) and the phenolic compounds (Fig. 4). A bed inlet concentration of 2.5 mg L⁻¹ HA was employed for these experiments. The selection was based on the NOM average occurrence in surface water (2 - 15 mg L⁻¹) and in an attempt to avoid saturation of the IOC adsorbents [32, 33]. Furthermore, according to several reports, the presence of high HA concentrations can hinder the adsorption uptake of targeted pollutants due to the effect of not only competitiveness, but also steric crowding (pore blockage) [32, 35, 37, 46, 47, 53, 62].

Fig. 4 shows the resulting MAIOr-NaBt fixed-bed outlet phenolic compounds concentration adsorption profiles. Table S4 shows the adsorption capacities estimated at the corresponding breakthrough points. It can be seen that, surprisingly, the presence of HA impacts the adsorption capacity of IOCs in a positive fashion. This could be attributed to the heterogeneous mixed character of the acid macromolecules, which have the ability to interact effectively with not only the surface of these IOCs (as previously discussed), but with the phenols. Some studies have shown that indeed there exists a synergistic effect between the uptake of HA, aromatic compounds and adsorbents, in which the acid acts as a “bridging molecule” between the latter two [38, 45, 63, 64]. For instance, Basly and coworkers have shown that there is an increase in the adsorption of cationic dyes in the presence of HA as co-adsorbate onto iron surfactant-modified pillared montmorillonites [38]. In that study, the adsorption uptake was enhanced from

13 to 250 mg g⁻¹ for weight ratios of 1/3 (dye/HA) at pH 7 and 2 mg g⁻¹ of dye equilibrium concentration. Although these results were focused on equilibrium adsorption tests, extrapolation to dynamic tests does not seem to be an exception.

Further evidence of the synergistic nature of the interactions between the HA, phenols, and IOCs comes in the form of the shapes of the breakthrough concentration profiles shown in Fig. 4. These appear shallower when compared to those gathered in the absence of the acid (Fig. 2), confirming the existence of greater interaction between these adsorbates and adsorbents. It may also suggest a higher resistance to mass transfer due to a reduction in adsorbate diffusion rates, through the beds, due to the presence of the HA macromolecules [34, 39].

As shown in Table S4, the cobalt containing IOC adsorbents exhibited the best DCP adsorption capacities at breakthrough point when compared against the results obtained for single-component adsorption. No apparent breakthrough was observed for the case of BPA within the experimental data gathering period (Fig. 4C), which suggests an even synergistic effect between the HA and the CoAlOr-NaBt adsorbent bed.

In general, MAIOr-NaBt adsorbents have shown that capturing targeted pollutants in complex scenarios might be possible. Employing layered fixed-beds, however, could attain better performance and scalability. For instance, in a previous study performed by Hernández-Maldonado and co-workers, copper and cobalt IOC fixed-beds had better adsorption capacities and affinities toward neutral and bulky contaminants such as carbamazepine [54]. Meanwhile, nickel IOCs had better capacities toward smaller compounds such as clofibric and salicylic acid, and partially calcined IOCs had better performance toward hydrophilic contaminants such as caffeine. A similar trend was observed in the present work, in which for neutral and bulky phenols, the cobalt and copper IOC fixed-beds showed better adsorption performance, even in

the HA presence. If all of the aforementioned adsorbent beds are therefore stacked in a layered fashion, then perhaps it will be possible to enhance the overall performance by allowing bed sections to target families of pollutants. Designing such scheme, however, is beyond the scope of the present contribution and we hope to report findings in the near future.

3.5 Modeling of breakthrough curves for single components

Two fixed-bed adsorption models typically used in prediction of fixed-bed outlet concentration profiles, the Clark (Eqns. S7-S9) and the modified dose-response (Eqns. S10 and S11) (MDR) models [3, 54, 58, 60, 65], were fitted against the experimental data shown in Fig. 2. This was an attempt not only to predict IOC adsorbent bed concentration profiles for phenols, but also the estimation of parameters associated with these models that are direct descriptors of adsorption capacities and rate coefficients. Deviations between models predicted and experimental data were quantified in the form of average relative error (ARE) (Eq. S12) and the modified Marquardt's percent standard deviation (MPSD) (Eq. S13).

Fits of these models onto the experimental fixed-bed data are shown in Fig. 5. Meanwhile, Tables S6 and S7 present the data generated from the model fits as well as direct comparisons between predicted and observed (equilibrium) saturation adsorption capacities. In general, bed saturation adsorption capacities were between 8 and 60% smaller than those indicated by equilibrium adsorption isotherms (Fig. 1). This strongly suggests that diffusion was probably a limiting factor in the continuous flow fixed-bed tests, which also correlates well with the lack of steepness in the curves shown in Fig. 2. Amongst the two models, the Clark model could be considered a more rigorous model since it gives weight to both mass transfer and equilibrium. However, based on ARE and MPSD values, this model was not a good fit to describe the IOC beds outlet BPA concentration profiles. This is also evident in the data shown in Fig. 5.

3.6 Adsorbent Regeneration

Thermal regeneration viability was assessed via TGA of NiAlOr-NaBt samples since, in general, these showcased the larger adsorption uptakes. Fig. 6 shows ramp TGA tests performed before and after adsorption from a 40 mg L⁻¹ solution of BPA or DCP. A difference in weight loss between the fresh and spent adsorbent was observed, particularly after the 400°C mark in the BPA case, and attributed to the removal of the corresponding adsorbate. Such difference accounts for adsorbed amounts of ca. 0.63 %, and 0.43% for BPA and DCP, respectively, and correlates well with the corresponding equilibrium adsorbed amounts: ca. 0.52% and 0.37% for BPA and DCP, respectively (Table S8). These data therefore suggest that the temperature required for effective desorption of the phenols should be near or above the 400 – 500°C range depending on the adsorbate. However, since the surfactant decomposes at temperatures in the 300 – 500°C range (Fig. S3), effective regeneration of the spent adsorbent will entail surfactant replenishing. In the HA case, a regeneration test (results not shown here) suggested that its full desorption or elimination is not achieved within an acceptable temperature range, likely due to its complex chemical composition. In fact, the HA employed in this study contained ca. 30 wt.% inorganic residual components (Table S5). This suggests that regeneration of metal based IOC adsorbents containing HA should be attempted by other means such as alcohol washing [24].

Another possibility is the use of a pH swing. For example, at alkaline conditions, some of the IOCs exhibited little or no adsorption of the phenols (see Figs. 1E and 1F). Fig. 7 shows single point BPA and DCP equilibrium adsorption capacities for fresh (Cycle 1) and regenerated (Cycle 2) NiAlOr-NaBt adsorbents. Regeneration was performed by washing the spent adsorbents with caustic soda solutions; the details of the procedure are shown in the Supplementary Material. In general, the adsorption capacity of NiAlOr-NaBt toward BPA remained nearly constant after two

cycles. However, for the case of DCP the data clearly suggest that washing the spent adsorbent with an alkaline solution is not effective; at least not at the conditions considered here. We also observed a weight loss of ca. 1 wt.% during Cycle 2 for both adsorbates. Analysis of TGA profiles (Figure S4) strongly suggests that the weight loss is related to loss of surfactant. Therefore, more experiments should be conducted to optimize the conditions (e.g., NaOH concentrations and regeneration time) before final conclusions can be reached regarding the recovery of adsorbent capacity using this regeneration alternative.

4. Conclusion

The adsorption of phenols using *MAIOr*-NaBt composites appears to be influenced by a combination of the chemical nature of the adsorbate, pH, and type of modification performed on the IOC. The presence of both a transition metal and cationic surfactant significantly increases equilibrium adsorption capacities. At natural pH, the adsorption of phenols is favored, whereas at alkaline conditions the opposite holds probably due to repulsion of electrostatic interactions. Although a remarkable selectivity toward BPA over DCP was observed, dynamic adsorption of phenols resulted in reduced uptake capacities, whereas the co-existence of HA at moderate concentrations increased the adsorption capacity of both adsorbates. In general, the data suggests that the adsorption driving force results from a combination of hydrogen bonds, hydrophobic interactions, and complexation with transition metals. The results also suggest that *MAIOr*-NaBt could be regenerated by a calcination thermal processes followed by surfactant replenishment or by washing the spent adsorbents with an alkaline solution.

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Supplementary data

Supplementary data associated with this article can be found in the online version.

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- Figure 2** Breakthrough of BPA and DCP in fixed-beds with metal-modified IOCs, for water feed at room temperature. (A, C, and E) adsorbates fed as single components or (B, D and F) adsorbates fed as a mixture. Data gathered for $C_i = 10 \text{ mg L}^{-1}$ and $Q = 1.5 \text{ mL min}^{-1}$. Abscissa units correspond to water volume processed per mass of adsorbent bed.
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Figure 6 Thermal gravimetric analyses for NiAlOr-NaBt material before (solid line) and after (dashed line) BPA (A) and DCP (B) adsorption from a 40 mg L⁻¹ solution. Profiles were gathered using air and a heating rate of 10 °C min⁻¹.

Figure 7 Fresh (Cycle 1) or regenerated (Cycle 2) NiAlOr-NaBt adsorption capacity for BPA or DCP. Regeneration performed via washing the spent adsorbent with an alkaline solution. Data contains error bars. All data were gathered for C_i= 40 mg L⁻¹ at 25 °C and a natural pH.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

+
humic acid