Progress in the design of nanoporous adsorbent materials containing transition metals for the removal of contaminants of emerging concern

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ABSTRACT
Significant attention has been paid to contaminants of emerging concern (CECs) for several years due to their persistence in water sources and toxicity. The necessity of upgrading current wastewater treatment technologies is vital to guarantee timely remediation of CECs, particularly given the scarcity of potable water for direct human consumption and even for agricultural irrigation. In this regard, the integration of transition metals onto porous adsorbent materials for use in water and wastewater treatment operations could play a significant role due to their ability to undergo specific interactions (i.e., complexation-type) with CECs at ambient temperature. Furthermore, coupling these interactions with hydrophobicity inducing species or phases in situ (i.e. hierarchically) further enhances affinity and capacity toward CECs. This review highlights the progress so far in the bench-scale design of transition metal-based nanoporous adsorbents, including hierarchical composites prepared via confined space synthesis, for the removal of CECs from water at ambient conditions.

1. Introduction
Contaminants of emerging concern (CECs) are embodied by chemicals found in pharmaceuticals and personal care products (PPCPs), compounds that are considered endocrine disruptors, antibiotics, pesticides, and herbicides, among others [1−4]. The classification of CECs has also evolved with industrial development, contaminant release matrix, wastewater treatment technologies and challenges, and regulations [5,6]. CECs are also persistent and accumulative in water, and several reports have evidenced the risks of CECs for human health and the environment, even when at very low concentrations [7−16]. Among the various possible pathways that explain how these contaminants end in waterbodies, one that remains considerably active is the release of industrial wastewater containing active ingredients such as those used in the manufacturing of PPCPs [17]. Others include the disposal of out-of-date PPCPs into landfills and the discharge of domestic wastewater containing PPCPs and metabolites excreted upon human uptake. Therefore, special attention must be placed on the use of reclaimed water, particularly during agricultural activities, due to both the uptake and accumulation of CEC by crops [10,13,18−20].

Most of the present-day water treatment plants rely on technologies that cannot effectively address CECs removal, even when combined within different train arrangements [21−23]. The effective removal is challenging due to the CECs’ very low concentrations (ng L−1 – μg L−1) as well as their wide range of physicochemical properties, and chemical stability. In many cases, addressing these aspects should require bottom-up design approaches and inclusion of non-traditional elements such as the use of active sites to induce specific interactions between a material (i.e. adsorbent, membranes) and the CECs. Most of the materials used in adsorption and membrane technologies to remove organic contaminants rely on steric phenomena and non-specific interactions (i.e. electrostatic forces), which do not suffice to remove contaminants present in traces and in multi-component fashion (i.e. CECs); this limits both capacity and selectivity, which in turns results in the need for more operational cycles and, therefore, small efficiencies.

One promising alternative to address these limitations is the bottom-up design of material surfaces. This encompasses a wide range of strategies, from the addition of specific surface chemical species that serve as unique uptake sites to the preparation of composites that display multi-functional character. For instance, the inclusion of transition metals as the material active sites or structural element in catalysts [24−32], functionalization of membranes [33−38], or adsorbents [39−42]. Some of the enhancements in chemical activity are principally due to the capacity of the metal d subshell to form specific bonds (e.g. weak chemisorption) with other molecules or atoms[43].

Adsorption appears to be a promising CEC remediation strategy due to its potential for surface-based interactions selectivity and capacity, relatively low energy consumption, ease of configuration, and...
no toxic byproducts. Porous adsorbent materials can be used to capture molecules onto the surface via steric hindrance and non-specific interactions such as electrostatic. Table 1 shows a compilation of CEC adsorbed amounts for porous materials that make use of such uptake mechanisms. Based on systematic quantum chemical computations, Wei et al. [39] have suggested four principal steps to be considered in the rational design of high-performance adsorbents: first is the evaluation or consideration of the molecular properties of the targeted contaminant or contaminants; second, evaluation of the possible adsorbent/adsorbate interaction mechanisms; third, consider the initial textural properties and structural stability of the adsorbent; and fourth, modify the adsorbent to enhance these possible interaction mechanisms. Furthermore, another important factor that should be considered in the adsorption process is the hydrophobicity, which is associated with the capacity of not agglomerating water molecules around the adsorbent surface and, therefore, allow for better adsorbent/adsorbate interactions.

The inclusion of transition metals onto the surface of an adsorbent could generate complexion interactions between the electrons or electron deficiency from d and s orbitals of the metal and bonds from the organic compounds, respectively [39]. Transition metals that would be adequate for the application at hand should be those in a state that exhibit empty 4s orbitals and complete 3d orbitals, to be able to offer the opportunity of reversible complexation via electron back donation. It should be noted that these complexion-based interactions are weak in the engineering sense (10–20 kcal mol\(^{-1}\)) and could still allow for feasible adsorbent regeneration pathways [44]. However, one of the most difficult challenges yet is how to sustain the complexion in the stationary phase while avoiding metal hydrolysis, maximizing site loading, and doing so in a cost-effective way. In addition, effective functionalization with transition metals requires substrates that are both chemically and physically adequate. To this end, the main goal of this review is to present how the incorporation of transition metals onto nanoporous adsorbents and confined space synthesis to produce hierarchical nanoporous adsorbents, respectively, effectively enhance the interaction with CEC pollutants and add hydrophobicity to produce a synergistic effect on the adsorption capacity and selectivity. It should be highlighted that the transition metal containing materials presented and discussed below have been tested at CEC aqueous concentrations at ranges that lie close to the values observed in the environment and, in most cases, the adsorbates include metabolites.

2. Incorporation of transition metals as adsorption sites

There are several techniques that can be utilized for the effective incorporation of transition metals onto an adsorbent structure, including wetness impregnation [45–47], spontaneous monolayer dispersion [45,48], grafting [49–53], and ion exchange [54–57]. Among these, grafting and ion exchange have produced better results with respect to water-stability and loading of metal. Both of these techniques ensure embedding of the transition metal onto the surface with sufficient strength as to avoid or minimize leaching during uptake of organic adsorbates, particularly in the case of grafting [49,52,53]. In addition, both techniques offer good control over the loading and stoichiometry of the loading of the transition metal and this helps with the optimization of transition metal content in the adsorbate [58,59]. For a material to be considered a suitable candidate for metal grafting, it must possess adequate textural (i.e. surface area and pore volume) and surface chemistry properties. The former is of utmost importance when taking into consideration that CEC adsorbates tend to be bulky molecules. For instance, mesoporous silicas not only possess large surface area and pore dimensions, but they also have tunable 1-D pore structure and flexible surface chemistry, the latter based on silanol groups [49,60,61]. Furthermore, the thick pore walls and large pore diameters (4.6–40 nm) could be advantageous to sustain structural hydrostability, high surface area, and pore width during lab-scale testing.

Rivera-Jimenez et al. [49] and Ortiz-Martinez et al. [52,53] achieved functionalization of a mesoporous silica using amino grafting techniques and later used the modified materials for the uptake of a set of CECs from water at ambient temperature and neutral pH. The mesoporous silica employed for these studies was SBA-15 (Santa Barbara Amorphous variant 15) which possesses a 1D pore channel (ca. 100 Å in diameter) with an amorphous yet OH rich surface, and also displays surface areas in the vicinity of 900 m\(^2\) g\(^{-1}\). Rivera-Jimenez incorporated Co\(^{2+}\), Ni\(^{2+}\), and Cu\(^{2+}\) using a grafting method where amino-organic moieties react with – OH groups from the SBA-15 surface to create electron-rich areas that allow for the anchoring of the desired metal (see Figure 1). Ortiz-Martinez et al. [52] complemented this work by enhancing the adsorbent hydrostability via complete blockage of wall micropores that otherwise will result in depolymerization sites [60]. Furthermore, it was determined that a thermal treatment prior to the incorporation of the metal breaks the amino/silica interactions and redirect these toward the amino/metal. In addition, they found that lower levels of hydration in the metal salts produced uniform and larger pore size (~80–90 Å), surface area (~375 m\(^2\) g\(^{-1}\)) and volume as well as larger metal
Table 1. Compilation of average adsorbed amounts observed for various CECs and adsorbent materials.

| CEC Description | Adsorbent Description | C (μg L⁻¹) | pH | Average Adsorbed Amount (μg g⁻¹) | Average Adsorbed Amount (μg cm⁻³) | Reference |
|-----------------|-----------------------|------------|----|-----------------------------------|-----------------------------------|-----------|
| Caffeine usage: psycho-stimulant | polycrystalline resin 5500 | 0.2–7 | 7 | 25.8 | 27.0 | [3] |
| Caffeine usage: psycho-stimulant | mesoporous silica SBA-15 | 1–100 | 7 | 5.1 | 0.3 | [3] |
| Caffeine usage: psycho-stimulant | mesoporous silica MCM-48 | 1,100 | 8 | 18 | 18 | [2] |
| Caffeine usage: psycho-stimulant | carboxyl-functionalized mesoporous silica MCM-48-G | 500 | 945 | 1,349 | 1,349 | [2] |
| Caffeine usage: psycho-stimulant | reduced graphene oxide encapsulated mesoporous silica MCM-48-G | 0.1–100 | 1,995 | 1,919 | 1,919 | [2] |
| Caffeine usage: psycho-stimulant | copper-amine-functionalized mesoporous silica SBA-15 | 1–110 | 7 | 0.1 | 0.0 | [4] |
| Caffeine usage: psycho-stimulant | chitosan – waste coffee ground-poly(vinyl alcohol) composite | C, = 2,000 | 6 | 8,210.0 | 8,210.0 | [5] |
| Caffeine usage: psycho-stimulant | clinoptilolite | 0.1–5; C, = 100 | 1,650.0 | 4,620.0 | 4,620.0 | [6] |
| Caffeine usage: psycho-stimulant | palygorskite | 0.3–11; C, = 100 | 270.0 | 486.0 | 486.0 | [6] |
| Caffeine usage: psycho-stimulant | graphene-activated carbon-chitosan composite | 100–2700 | 14,630.0 | 2,000 | 2,000 | [7] |
| Caffeine usage: psycho-stimulant | multi-wall carbon nanotubes | 240–3,260 | 7 | 1,770 | 319 | [8] |
| Caffeine usage: psycho-stimulant | MIL-100 Fe metal organic framework | 36–531 | 7 | 855.6 | 598.9 | [9] |
| Caffeine usage: psycho-stimulant | MIL-100 Fe/activated carbon composite | 1.3–68 | 7 | 2,810.7 | 1,686.4 | [10] |
| Caffeine usage: psycho-stimulant | activated carbon (Darco-KB-G) | 0.27–256 | 7 | 38,646.3 | 11,980.4 | [11] |
| Caffeine usage: psycho-stimulant | faujasite zeolite – activated carbon composite (Na[+H⁺]-CFAU) | 6–4,768 | 7 | 34,365.1 | 32,746.5 | [12] |
| Carbamazepine usage: antiepileptic | Cu²⁺-CFAU | 1–6,173 | 7 | 32,843.0 | 31,296.1 | [13] |
| Carbamazepine usage: antiepileptic | mesoporous silica SBA-15 | 100 | 7 | 30.9 | 2.1 | [14] |
| Carbamazepine usage: antiepileptic | hexagonal mesoporous silica (HMS) | 25–125 | 7 | 22.9 | 7.8 | [15] |
| Carbamazepine usage: antiepileptic | mercapto-functionalized HMS (M-HMS) | 15–100 | 7 | 30.9 | 10.5 | [16] |
| Carbamazepine usage: antiepileptic | amine-functionalized HMS (A-HMS) | 35–190 | 7 | 3.4 | 1.2 | [17] |
| Carbamazepine usage: antiepileptic | powdered activated carbon | 15–55 | 7 | 52.3 | 15.7 | [18] |
| Carbamazepine usage: antiepileptic | polyvinyl resin 5500 | 0.2–7 | 7 | 45.6 | 47.8 | [19] |
| Carbamazepine usage: antiepileptic | mesoporous silica SBA-15 | 1–80 | 7 | 9.5 | 0.6 | [20] |
| Carbamazepine usage: antiepileptic | copper-amine-functionalized mesoporous silica SBA-15 | 1–100 | 7 | 0.6 | 0.0 | [21] |
| Carbamazepine usage: antiepileptic | tezontle (PS1) | C, = 250 | 6 | 2.4 | 2.5 | [22] |
| Carbamazepine usage: antiepileptic | tezontle (PS2) | C, = 250 | 6 | 1.25 | 1.3 | [23] |
| Carbamazepine usage: antiepileptic | clinoptilolite | 20–80 | 0.097 | 0.3 | [24] |
| Carbamazepine usage: antiepileptic | palygorskite | 20–100 | 0.032 | 0.1 | [25] |
| Carbamazepine usage: antiepileptic | coconut shell-based PICACTIF TE (CTIF) | 0.0024 | ~7.7 | 0.9 | 0.8 | [26] |
| Carbamazepine usage: antiepileptic | cork (biosorbent) | 100–700 | 6 | 1840.0 | 1840.0 | [27] |
| Carbamazepine usage: antiepileptic | commercial activated carbon | 500–4,000 | 115.0 | 34.5 | 34.5 | [28] |
| Carbamazepine usage: antiepileptic | non-activated carbon | 500–4,000 | 13.0 | 3.9 | 3.9 | [29] |
| Carbamazepine usage: antiepileptic | granular activated carbon coal-based Diagen | 0.0024 | ~7.7 | 0.9 | 0.8 | [30] |
| Carbamazepine usage: antiepileptic | Fitosorb adsorbents 400 | 100–2500 | 11,200.0 | | | |
| Carbamazepine usage: antiepileptic | graphene-activated carbon-chitosan composite | 100–2500 | 11,200.0 | | | |
| Carbamazepine usage: antiepileptic | bio-solid derived biochar | 120–890 | 7 | 1059.4 | | [31] |
| Carbamazepine usage: antiepileptic | graphene | 2,500 | 6.5 | 22,800 | 684.0 | [32] |
| Carbamazepine usage: antiepileptic | reduced graphene oxide (rGO1) | 2,500 | 6.5 | 11,500 | 7,500 | [33] |
| Carbamazepine usage: antiepileptic | reduced flakes-graphene oxide (rGO2) | 2,500 | 6.5 | 103,000 | 6,570.0 | [34] |
| Carbamazepine usage: antiepileptic | CoFe₂O₄/reduce graphene oxide | 200–2,000 | 13,920.0 | 63,767.5 | 63,767.5 | [35] |
| Carbamazepine usage: antiepileptic | multi-wall carbon nanotubes | 2,500 | 6.5 | 55,000.0 | 2,457.0 | [36] |
| Carbamazepine usage: antiepileptic | single-wall carbon nanotubes | 2,500 | 6.5 | 185,000.0 | 990.0 | [37] |
| Carbamazepine usage: antiepileptic | carbon dot-modified magnetic carbon nanotubes | 500–1,100 | 7 | 17,200 | 18,077 | [38] |
| Carbamazepine usage: antiepileptic | metal organic framework UO-66 | 4,000 | 1,750 | 2,765 | | [39] |
| Carbamazepine usage: antiepileptic | metal organic framework MIL-100 Fe | 29–500 | 7 | 789.0 | 552.3 | [40] |
| Carbamazepine usage: antiepileptic | MIL-100 Fe/activated carbon composite | 0.2–12 | 7 | 2,585.2 | 1,551.1 | [41] |
| Carbamazepine usage: antiepileptic | activated carbon (Darco-KB-G) | 3–290 | 7 | 5,256.3 | 16,294.6 | [42] |
| Carbamazepine usage: antiepileptic | faujasite zeolite – activated carbon composite (Na[+H⁺]-CFAU) | 0.05–2,539 | 7 | 18,687.0 | 17,798.3 | [43] |
| Carbamazepine usage: antiepileptic | Cu²⁺-CFAU | 0.2–3,868 | 7 | 20,176.9 | 19,226.5 | [44] |

(Continued)
Table 1. (Continued).

| CEC | Adsorbent | C (μg L⁻¹) | pH | Average Adsorbed Amount (μg g⁻¹) | Average Adsorbed Amount (μg cm⁻²) | Reference |
|-----|-----------|------------|----|----------------------------------|-----------------------------------|-----------|
| Clofibric acid usage: lipid regulator | hexagonal mesoporous silica (HMS) | 30 – 140 | 7 | 17.3 | 5.9 | [61] |
| | mercapto-functionalized HMS (M-HMS) | 30 – 150 | 7 | 15.4 | 5.2 | [61] |
| | amine-functionalized HMS (A-HMS) | 10 – 50 | 7 | 44.6 | 15.2 | [61] |
| | multi-amine-functionalized superparamagnetic HMS (3 N-HMS-SP) | 15–80 | 7 | 171.0 | 34.7 | [61] |
| | multi-amine-functionalized mesoporous silica SBA-15 (3 N-SBA-15) | 18–110 | 7 | 140.0 | 9.4 | [61] |
| | mesoporous silica SBA-15 | 1 – 95 | 7 | 1.8 | 0.1 | [53] |
| | copper-amine-functionalized mesoporous silica SBA-15 | 1 – 65 | 7 | 17.3 | 1.2 | [56] |
| | powdered activated carbon | 20 – 100 | 7 | 29.5 | 8.9 | [66] |
| | graphene oxide | 500–3,000 | 5 | 4,950 | 8,910 | [66] |
| | metal organic framework MIL-100 Fe | 97–714 | 7 | 359.9 | 251.9 | [66] |
| | MIL-100 Fe/activated carbon composite | 104–788 | 7 | 190.0 | 114.0 | [66] |
| | activated carbon (Dasco-KB-G) | 0.03–5.041 | 7 | 8,395.4 | 2,602.6 | [66] |
| | faujasite zeolite – activated carbon composite (Na⁺,H⁺-CFAU) | 80–5,790 | 7 | 7,920.5 | 7,547.5 | [66] |
| | Cu²⁺-CFAU | 0.03–1,389 | 7 | 13,165.0 | 12,544.9 | [56] |
| Naproxen usage: analgesic | copper-amine-functionalized mesoporous silica SBA-15 | 1 – 80 | 7 | 10.5 | 0.7 | [56] |
| | metal organic framework MIL-100 Fe | 25–310 | 7 | 388.4 | 554.9 | [59] |
| | MIL-100 Fe/activated carbon composite | 1–35 | 7 | 851.3 | 1,418.9 | [56] |
| | activated carbon (Dasco-KB-G) | 0.04–0.44 | 7 | 743.0 | 230.3 | [56] |
| | faujasite zeolite – activated carbon composite (Na⁺,H⁺-CFAU) | 0.1–89 | 7 | 2,694.3 | 2,567.4 | [56] |
| | Cu²⁺-CFAU | 0.06–147 | 7 | 2,631.8 | 2,507.9 | [56] |
| Naproxen | hexagonal mesoporous silica (HMS) | 25 – 140 | 7 | 30.0 | 10.2 | [61] |
| | metal organic framework MIL-100 Fe | 30 – 150 | 7 | 60.0 | 20.4 | [61] |
| | amine-functionalized HMS (A-HMS) | 30 – 180 | 7 | 10.0 | 3.4 | [61] |
| | powdered activated carbon | 10 – 30 | 7 | 85.0 | 25.5 | [61] |
| | mesoporous silica SBA-15 | 1 – 215 | 7 | 5.3 | 0.4 | [53] |
| | copper-amine-functionalized mesoporous silica SBA-15 | 1 – 170 | 7 | 26.3 | 1.8 | [56] |
| Naproxen | granular activated carbon coal-based Calgon Filtrasorb 490 | 0.002–0.4 | ~7.7 | 0.7 | 0.6 | [78] |
| | coconut shell-based PICACTIF TE (CTIF) | 0.002–0.4 | ~7.7 | 0.5 | 0.4 | [79] |
| | cork (biosorbent) | 20–350 | 6 | 2,120.0 | 0.4 | [79] |
| | metal organic framework MIL-101 Cr | 1,400 | 5.4 | 30,055.0 | 18,634.1 | [67] |
| | metal organic framework MIL-101 Cr-COH | 1,000 | 5.4 | 40,425.0 | 25,063.5 | [67] |
| | metal organic framework MIL-101 Cr-NH₂ | 1,030 | 5.4 | 30,055.0 | 18,634.1 | [67] |
| | graphene oxide/metal organic framework MIL-101 Cr composite | 1,000 | 7 | 29,025.0 | 17,481.8 | [80] |
| | metal organic framework MIL-100 Fe | 29–162 | 7 | 1,317.4 | 922.2 | [59] |
| | MIL-100 Fe/activated carbon composite | 2–223 | 7 | 2,903.8 | 1,742.3 | [59] |
| | activated carbon (Dasco-KB-G) | 0.03–24 | 7 | 7,139.6 | 2,213.3 | [56] |
| | faujasite zeolite – activated carbon composite (Na⁺,H⁺-CFAU) | 0.47–886 | 7 | 2,525.1 | 2,406.2 | [56] |
| Naproxen | o-Demethyl naproxen naproxen metabolite | copper-amine-functionalized mesoporous silica SBA-15 | 0.5–40 | 7 | 31.8 | 2.1 | [53] |
| | metal organic framework MIL-100 Fe | 5.9–510 | 7 | 708.3 | 495.8 | [60] |
| | MIL-100 Fe/activated carbon composite | 2–223 | 7 | 2,507.0 | 1,504.2 | [60] |
| | activated carbon (Dasco-KB-G) | 4–1,859 | 7 | 2,203.8 | 682.2 | [56] |
| | faujasite zeolite – activated carbon composite (Na⁺,H⁺-CFAU) | 0.18–1,870 | 7 | 1,987.5 | 1,893.9 | [56] |
| | Cu²⁺-CFAU | 0.5–763 | 7 | 8,526.4 | 8,124.8 | [56] |
| Paraxanthine caffeine metabolite | copper-amine-functionalized mesoporous silica SBA-15 | 1 – 85 | 7 | 6.8 | 0.5 | [56] |
| | metal organic framework MIL-100 Fe | 20–729 | 7 | 446.7 | 312.7 | [59] |
| | MIL-100 Fe/activated carbon composite | 1–208 | 7 | 2,632.8 | 1,579.7 | [59] |
| | activated carbon (Dasco-KB-G) | 0.062–2 | 7 | 1,075.6 | 333.4 | [56] |
| | faujasite zeolite – activated carbon composite (Na⁺,H⁺-CFAU) | 0.33–302 | 7 | 2,662.6 | 2,537.1 | [56] |
| | Cu²⁺-CFAU | 0.14–73 | 7 | 2,868.4 | 2,733.3 | [56] |
| Salicylic acid acetaminophen metabolite | mesoporous silica SBA-15 | 2 – 100 | 7 | 1.1 | 0.1 | [53] |
| | copper-amine-functionalized mesoporous silica SBA-15 | 1 – 80 | 7 | 17.8 | 1.2 | [53] |
| | metal organic framework UiO-66 | 3,000 | 6 | 23,460.0 | 37,067 | [49] |
| | metal organic framework MOF-808 | 7,000 | 6 | 19,250.0 | 15,400 | [49] |
| | metal organic framework MOF-802 | 5,000 | 6 | 2,622.0 | 2,098 | [49] |
| | metal organic framework MIL-100 Fe | 48–510 | 7 | 39.7 | 27.8 | [49] |
| | MIL-100 Fe/activated carbon composite | 42–415 | 7 | 180.8 | 108.5 | [49] |
| | activated carbon (Dasco-KB-G) | 10–2,940 | 7 | 993.6 | 590.0 | [56] |
| | faujasite zeolite – activated carbon composite (Na⁺,H⁺-CFAU) | 4–3,383 | 7 | 1,620.4 | 1,544.1 | [56] |
| | Cu²⁺-CFAU | 0.03–1,873 | 7 | 2,053.1 | 1,956.4 | [56] |
loadings; this is crucial when attempting to address working capacity[52]. The improvements in all the aforementioned factors resulted in enhancement of the equilibrium adsorption capacity for naproxen at neutral pH (see Figure 2).

Ortiz-Martinez et al. also tested the aforementioned modified mesoporous silica materials for the uptake of other CECs (i.e. carbamazepine, caffeine, clofibrac acid, salicylic acid, and naproxen) with distinct physicochemical properties such as hydrophilicity, hydrophobicity, ionic strength, and chemical structures[52]. The results suggested that adsorbent/CECs interactions were heavily influenced by the functional groups contained in each CEC molecular structure and the given transition metal. The copper (Cu(II)) variant showed better affinity toward salicylic acid which is a small, acidic, and hydrophobic molecule. Ortiz-Martinez et al. later expanded the tests to include to multi-component equilibrium and fixed bed dynamic adsorption at concentration levels closer to those detected in waterbodies (i.e. μg L⁻¹) [1,53]. As evidenced by the results, the adsorptive removal of the SBA-15 grafted with Cu(II) showcase a better affinity toward anionic and acidic CECs. The multi-dimensionality capability of Cu(II) allows interactions with the aforementioned CECs through several adsorption mechanisms (i.e. electrostatic, hydrogen bonds, and metal coordination complexes). Also, as shown in Figure 2, the overall adsorption capacity of the Cu(II) grafted SBA-15 at a multi-component CEC equilibrium concentration of ca. 50 μg L⁻¹ is an order of magnitude larger compared to as–prepared SBA-15; the capacity is three times larger for single-component CEC adsorption. Ortiz-Martinez et al. also evaluated the adsorption of parent/metabolite CEC pairs (i.e. naproxen/ O-desmethylnaproxen, caffeine/paraxanthine, and carbamazepine/carbamazepine-10,11-epoxide) and the results showed that the SBA-15 modified adsorbent has better affinity toward the metabolites. It should be noted that adsorptive studies including metabolite molecules are highly valuable since they allow assessing the adsorbent potential in terms of how the adsorption driving force is affected by changes of particular functional groups in the adsorbates.

3. Tailoring of hydrophobicity

Several efforts have been made to decrease the negative impact of the interactions between water and the adsorbent during water treatment applications. However, this usually comes at the expense of sacrificing selectivity and capacity depending on the targeted contaminant. A promising alternative to address this is the incorporation of a secondary solid phase into or onto the adsorbent structure that will act as a hydrophobic barrier while the resulting composite still contains a transition metal to drive specific interactions between the adsorption sites and the contaminant (i.e. CEC).
Cabrera-Lafaurie et al. [54,62] reported that incorporation of cationic surfactants onto pillarized bentonite (NaBt) and faujasite (FAU) materials, respectively, followed by incorporation of a transition metal (i.e. Co, Ni, or Cu) via ion exchange, results in enhanced interactions and capacities with certain CECs. The pillarization of the clay with polyoxocations (i.e. Al based) is necessary to create two-dimensional galleries with great surface area (~300 m² g⁻¹; pore width ~20 Å) and pore volume. This was followed by functionalization with 1-hexadecylpyridinium bromide (HDPY⁺Br⁻) as is shown in Figure 3. In the case of the FAU zeolite, the apohost material already contains significant porosity and the only modifier was the addition of cetylpyridinium bromide (CPY⁺Br⁻) surfactant. The textural properties of these adsorbent variants are summarized in Figure 4 (left).

Both of the adsorbent materials were also tested for the uptake of salicylic acid and carbamazepine (see Figure 4 (right)). In the case of FAU, the adsorbent variant containing the surfactant and Cu(II) (i.e. Cu-CPY-FAU) exhibited the best salicylic acid capacity and selectivity. The former was a 25% increase compared to the adsorbent material containing just the surfactant (i.e. Na-CPY-FAU) and orders of magnitude larger than the uptake amounts seen in any of the zeolites modified solely with a transition metal. This is significant evidence of the advantage of incorporating both affinity and hydrophobicity capabilities into the design. Adsorption of carbamazepine in the faujasites was limited by steric hindrance due to the bulky dimensions of the CEC (i.e. effective pore sizes were ~8 Å for M⁺-CPY-FAU and ~18 Å for M⁺-DPY-NaBt). In the modified bentonite case, both salicylic acid and carbamazepine resulted in comparable uptake capacities and these were large enough to match those observed for the acid onto Cu-CPY-FAU. Carbamazepine adsorption capacity was almost twice that of the material not containing a transition metal (i.e. Al-DPY-NaBt), while for salicylic acid, the observed uptake improvements were 64, 39, and 33% for the Ni-, Co-, and Cu- variants, respectively. It should be noted that carbamazepine, unlike salicylic acid, remains without ionic charge at neutral pH, and the adsorption mechanism is therefore not dominated by electrostatic forces but instead by metal complexation.

The adsorption capacities observed in the aforementioned FAU and clay variants are comparable to or excel those reported to the adsorption of CECs onto other zeolites and clays. For instance, adsorption of

Figure 3. Schematic representation of the pillarization and incorporation of transition metals and surfactant onto bentonite clay adsorbent materials. Reprinted from Cabrera-Lafaurie et al. [62]. Copyright 2012 Elsevier.

Figure 4. (left) Surface area and pore volume of modified bentonite and faujasite adsorbents. (right) Adsorption capacity of modified bentonite and faujasite for salicylic acid and carbamazepine. C₀ = 14 mg L⁻¹, and neutral pH at equilibrium conditions. Data source: Cabrera-Lafaurie et al. [54,62].
salicylic acid onto Clinoptilolite (zeolite) and clays has resulted in equilibrium capacities in the vicinity of 2–5 mg g$^{-1}$ at an aqueous phase concentration of around 30 mg L$^{-1}$. Although the larger adsorption capacities were obtained using organoclay materials, the Clinoptilolite zeolite exhibited different affinities toward salicylic acid depending on the nature of the extra-framework cations\cite{63}. The reported equilibrium isotherm data indicate that the affinity increased as follows: Zn < Cu < Ni < Mn. These results as well as the ones presented above are strong evidence of the different levels of interaction that transition metals may provide during the uptake of a particular CEC.

Despite the enhancements brought by transition metal-surfactant modifications of porous adsorbents (i.e. simultaneous hydrophobicity and functionality), unfortunately, there is also a significant impact on the ultimate adsorption capacity of the materials given the concomitant reduction in surface area and pore volume. This probably limits the feasibility of these adsorbent variants when moving away from lab or bench-scale testing.

4. Hierarchical composites via confined-space synthesis

An alternative to lessen the impact of achieving simultaneous hydrophobicity and affinity on the adsorbent textural properties is the design of hierarchical composites via confined-space synthesis. Contrary to composites that arise from direct physical mixture of phases, the ones that exhibit an explicit hierarchical arrangement showcase superior integrity and stability. Furthermore, the effective surface optimization of hierarchical composites can be achieved a priori since phase growth extent is bound by the textural characteristics of at least one of the materials involved. This is not to imply that composites that result from physical mixtures or where there is no explicit phase hierarchy cannot perform well as CEC adsorbents. For example, composites based on biochar/carbon nanotubes combinations were tested for the uptake of sulfapyridine at mg L$^{-1}$ level concentrations and the performance was greatly influenced by the type of biochar employed\cite{64}. Other biochar-based composites include combinations of zero-valent iron nanoparticles with paper mill sludge and eucalyptus globulus wood-based biochars that were tested for the removal of pentachlorophenol \cite{65} and chloramphenicol\cite{66}, respectively. Meanwhile, composites prepared by physically mixing activated carbon with MgO and ZnO nanoparticles (i.e. transition metal based) have been tested for the adsorption of atrazine also in the mg L$^{-1}$ range of concentration\cite{67}.

González-Ramos et al. \cite{55}, and Fernández-Reyes et al. \cite{56}, have shown that composites prepared hierarchically via in situ growth of FAU into the macro- and meso-pores of activated carbon (AC) (i.e. confined-space synthesis as shown in Figure 5) result in adsorbents with superior affinity and capacity toward the uptake of various CECs. These composites are mostly microporous as the macro- and meso-pores are occupied by the zeolitic phase; surface area values are in the vicinity of 600 m$^2$ g$^{-1}$ (570 m$^2$ cm$^{-3}$). Transition metals (i.e. M = Ni$^{2+}$ or Cu$^{2+}$) were also added to these composites via ion exchange with excess amounts of metal source salts \cite{55,56}. It is important to note at this point of the discussion that, given the significant difference between the bulk density values of the carbon and the zeolite phase (0.31 g cm$^{-3}$ for AC and around 1.0 g cm$^{-3}$ for FAU), a comparison of CEC uptake capacities between the hierarchical composites and

![Figure 5. Schematic representation of the assembly of hierarchical composite adsorbents (CFAU and CMOF). Adapted with permission from Muñoz-Senmache et al. \cite{69}. Copyright 2020 American Chemical Society.](image-url)
the source phases entails a basis that is independent of chemical content. To that end, the reported adsorption data were normalized by the volume of adsorbent particle instead of weight.

Unlike the results presented in the previous section of this review for surfactant-based functionalization, the reduction in the BET surface area values of the hierarchical composite as a result of the confined synthesis is in the vicinity of 30%, while the pore volume was not significantly affected. Meanwhile, the observed salicylic acid adsorption capacity in the composites and the individual source components of the composites increased as follows FAU < AC < CFAU < Ni<sup>2+</sup>-CFAU for a considerable range of equilibrium concentration (i.e., ~20 μg L<sup>-1</sup> – 10 mg L<sup>-1</sup>). Based on these results, Fernández-Reyes et al. expanded adsorption tests for Cu<sup>2+</sup>-CFAU to several other CECs, including primary molecules and metabolites (caffeine, carbamazepine, and metabolites clofibric acid, 10,11-epoxy-carbamazepine naproxen, o-desmethylnaproxen, and paraxanthine), and both in single- and multi-component fashions. When compared against sole AC, the larger overall working capacity for most of the studied CECs in single-component was attained with Cu<sup>2+</sup>-CFAU. Furthermore, the composite also exhibited enhanced capture performance toward ionic CECs (such as clofibrac acid and salicylic acid) and about similar capacity for neutral CECs. In the case of multi-component CEC adsorption, the hierarchical composite has greater selectivity toward all the targeted CECs compared to the sole AC, evidencing the synergistic role of Cu(II) and hydrophobicity in the uptake mechanism.

Figure 6 displays a comparison of salicylic acid and carbamazepine adsorption capacities for hierarchical adsorbents containing Cu(II) sites and as a function of zeta potential at equilibrium pH (nearly neutral). Better CEC/adsorbent interactions are observed when hydrophobicity is addressed via a surfactant or a carbon shell. However, the fact that materials with similar electrostatic surface charge display different CEC uptake amounts is evidence of an additional driven force taking place, most likely π-complexation [39,52].

The outstanding performance observed for Cu<sup>2+</sup>-CFAU variants makes these promising adsorbents to move forward to a larger scale testing. However, these materials still have room for improvement in terms of overall capacity, since only 65% of the possible sites available for Cu(II) are occupied through the FAU lattice. When coupling this to the fact that the observed maximum CEC capacities are below saturation, it is evident that the uptake capacities of these materials can be further enhanced and therefore result in fewer adsorption and even regeneration cycles since exhaustion levels will be significantly increased. An alternative to enhance the level of transition metal stoichiometry is looking into the assembly of the periodic phase and employing other inclusion mechanisms, such as the metal coordination seen in metal organic frameworks (MOFs). In fact, some as-prepared MOFs have already been tested for the removal of CECs from water [40,42].

MOFs are composed of metal nodes (i.e. transition metals) and organic linkers building 3-D structures with well-defined pore structure, and large surface area and pore volumes. The ability to tailor MOF components to achieve specific capabilities is ushering a new era of material design. It has been demonstrated that transition metals contained in the MOF structures could play as active adsorption sites [40,42,68] and the large content of these sites enhances the probability for interactions with guest molecules (i.e. CECs). Despite the several apparent advantages, many MOFs are not completely stable in water and/or prone to hydrophilicity, just like their zeolitic counterparts.

Muñoz-Senmache et al. [69] have shown that it is possible to address the limitations of MOFs using the same in situ growth principle that was used for the preparation of CFAU hierarchical composites. Muñoz-Senmache et al. successfully grew a MIL-100Fe MOF phase within the meso- and macro-pores of activated carbon (CMOF; Figure 5). Again, the hydrophobicity of AC shell serves as a bulk water repelling layer that limits competition for active adsorption sites, and even improves the structural stability of the MOF. Like their zeolitic composite counterparts, the MOF-based composites are also mostly microporous as the macro- and meso-pores are occupied by the MOF phase; the surface area however is larger, in the vicinity of 1400 m<sup>2</sup> g<sup>-1</sup> or 850 m<sup>2</sup> cm<sup>-3</sup>. This hierarchical composite adsorbent (CMOF) was also tested for the adsorption of CECs (including primary molecules and metabolites) in both single- and multi-component
fashion. The observed single-component fashion adsorption capacities observed for CMOF were an order of magnitude larger compared to MIL-100Fe alone, while the overall capacity was reduced by about 9% when testing for the multi-component CEC adsorption (i.e. due to competitive adsorption). Figure 7 shows uptake capacities for several CECs in CMOF and other adsorbents, including those described above. In general, the CMOF offer competitive adsorption capacities, but further tests are required to elucidate differences between the type of transition metal forming the MOF structure and its resulting interaction with CECs. CMOF is based on a MOF that contains Fe as the metal node (i.e. MIL-100Fe), so perhaps the inclusion of other transition metals such as Cu might significantly increase the composite uptake capacity, either as part of the framework or as functionality in an analogous fashion to the cases discussed in this review. It is important to note that the physicochemical properties (i.e. pKa, LogKow) of the CECs covered in Figure 7 are quite different, which could suggest that the principal adsorption mechanism in the hierarchical composites is related to metal complexation.

Figure 7 also highlights differences regarding the uptake and the respective ways to modify and incorporate functionalities in the adsorbent design, as discussed through this review. These studies demonstrate the crucial role of the transition metal centers to interact strongly and selectively with CECs and the importance of reducing competition with water by increasing the hydrophobic characteristic, which improves the adsorption capacity and, in turn, enhances the possibility of effective interaction with attractive sites on each surface.

5. Regeneration

Reusability is an important aspect in the viability assessment of adsorbents for water treatment processes. Adsorbent materials that offer feasible regeneration pathways ensure multi-cycling capabilities and, therefore, this helps with sustainability. Many organic CECs exhibit relatively low melting points, making the use of thermal adsorbent reactivation a possibility. In the case of transition metal/CECs, there is no need for additional energy consumption during regeneration since the interactions fall in the weak chemisorption side. However, the overall stability of the adsorbent material needs to be inspected when considering thermal regeneration, including tolerance to the environment (oxidative versus inert, etc.) along with a proper assessment considering not only single-component systems but also complex water matrices.

In the case of amine grafted SBA-15 and surfactant containing FAU and NaBt, an additional step consisting in the replenishing of the organic moieties could be required after the thermal treatment. For instance, all the CECs mentioned above have melting points that lie within the 150–200°C range, except for caffeine (238 °C); the latter is extremely close to the starting decomposition point temperature of the amines and surfactant moieties. A schematic of the procedure to follow for thermal recycling of M^II-CPY^II-FAU is shown in Figure 8. For these cases, an alternative that can be considered to remove CEC from the adsorbed phase without replenishing of the adsorbent surface organic moieties is a pH swing, which could be especially favorable for ionic molecules (i.e. salicylic acid, clofibric acid, naproxen). Cabrera-Lafaurie et al. and Ortiz-Martinez et al. have shown that acid or alkaline pH levels can reduce the interactions between CECs and the adsorbents [52,54,62].

On the other hand, hierarchical composites can be thermally regenerated without any replenishing steps as long as the temperatures involved lie below the decomposition point of the carbon shell. Also, the thermal treatment atmosphere should be inert. Fernández-Reyes et al. tested the thermal regeneration of Cu^{II}-CFAU in a vacuum atmosphere, while Muñoz-Senmache, et al. developed a thermal treatment of CMOF under nitrogen gas. Both adsorbents were tested for multi-cycle adsorption of naproxen.
and carbamazepine, respectively, and the results showed that the adsorption capacities remained constant even after three cycles. Furthermore, X-ray diffraction data showed that the corresponding crystalline phase was still present after each cycle. This suggests that it is plausible to desorb the CECs via thermal treatment without much detriment to their long-range properties.

6. Conclusions and recommendations

Although it has been shown that exposed transition metal-based adsorption sites significantly enhance the capture of CECs from water, it is also quite evident that the inclusion of the hydrophobic shield is essential in the material design to achieve superior and synergistic uptake mechanisms. For instance, the preparation of hierarchical composites via in situ growth or confined synthesis of zeolite or zeolite-like materials within macro-/meso-porous matrices such activated carbon (i.e. shell/core like) and that contain a transition metal result in CEC loadings that are at least an order of magnitude larger than most of the adsorbents tested so far in the literature. These materials excel even during multi-component adsorption tests. However, several efforts remain to elucidate the universality of these adsorbent variants before deeming them apt for inclusion in water treatment plant operations. The following recommendations are aimed at addressing that:

- Maximizing the loading of transition metal sites per mass or volume of composite; this would translate to maximization of the observed CEC adsorption loadings.
- Testing zeolite or zeolite-like phases with smaller framework density. That is, materials with larger pore networks and, therefore, void volume, to further increase the ultimate loading capacities (i.e. result in less adsorption/regeneration cycles).
- Expanding the adsorption tests to include a wider array of CECs. This manuscript presents data for CECs of high occurrence and significant abundance, but these are not all inclusive. Data on the uptake of pesticides, other endocrine disrupting chemicals, and even perfluorinated compounds are also needed. Furthermore, there is a great need to evaluate adsorption performance at concentrations that lie within the current observable levels (i.e. equal or less than μg L⁻¹) instead of or above mg L⁻¹. This becomes even more important when considering limitations in diffusive transport due to smaller concentration gradients. Hence, the adsorption data must also include dynamic or fixed bed tests.
- Expanding multi-component adsorption tests to include non-CEC, competitive species including other organic pollutants, heavy metals, and even natural organic matter.
- More studies on regeneration alternatives are needed, including but not limited to washing spent adsorbents with low boiling point organic solvents (i.e. acetone) or supercritical fluids[70].

Figure 8. Schematic representation of thermal recycling of M⁺-CPY⁺-FAU. Reprinted from Cabrera-Lafaurie et al. [54]. Copyright 2014 Elsevier.
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