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Superior single- and multi-component siloxane removal from water using a faulted silica DON zeolite adsorbent†

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Removal of monomeric siloxanes from water *via* adsorption poses a significant challenge, particularly during water reclamation in closed-volume systems. In this study, both faulted and faultless variants UTD-1 pure silica zeolites with a DON-type framework were considered for the removal of monomethylsilanetriol (MMST), dimethylsilanediol (DMSD), and trimethylsilanol (TMS), in single- and multi-component fashion. The results showed that UTD-1_{faulted} exhibited the largest adsorption capacity for TMS, with a maximum adsorption uptake of 73.1 mg g⁻¹ in the 1 to 140 mg L⁻¹ aqueous concentration range. This is 7× larger than UTD-1_{faultless} and at least one magnitude larger than other materials such as activated carbon. The interaction of TMS with UTD-1_{faulted} is mainly with OH groups from siloxy-related faults present in the material, and multicomponent adsorption tests showed that TMS helps to drive the uptake of other siloxanes *via* co-adsorption. UTD-1 is a promising material platform for developing adsorption-based strategies for removing persistent monomeric siloxanes from aqueous environments.

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Environmental significance

Linear siloxanes are ubiquitous and may enter water sources, with some being capable of affecting the human central nervous system upon ingestion. In closed-volume systems, where water reclamation is perhaps mandatory, their concentration is much more prominent due to the intrinsic infrastructure. Existing commercial adsorbents lack capacity and selectivity toward linear siloxanes, particularly when in mixtures. Given that adsorption is amongst the separation platforms with smaller energy requirement footprints, developing adsorbent materials with siloxane selectivity and capacity would be ideal. Pure porous silica zeolites with framework surface faults, in the form of siloxy groups, are not only selective toward individual or single-component siloxanes for removal from water but also multi-component matrices.

Introduction

Siloxanes are a category of silicone derivatives containing Si–O bonding¹ arranged in linear or cyclic structures, extensively employed across multiple industries and consumer products.^{2–4} In 2020, the total worldwide production of silicon-based compounds was around eight million metric tons,⁵ and production will continue to grow in the coming years.^{6,7} Consequently, the concentration of siloxane compounds that could be released into the environment will also increase, and siloxanes are already detected in water, soil, air, and sediments.^{8–16} This also poses a potential risk to the environment and human health since some siloxanes are known to be

toxic, particularly those with low molecular weight. Linear siloxanes that have been detected in water and that are products of the hydrolysis of larger siloxanes include monomethylsilanetriol (MMST),¹⁷ dimethylsilanediol (DMSD), and trimethylsilanol (TMS).^{18,19} DMSD is toxic to humans if ingested for long periods, even at low concentrations (*i.e.*, mg L⁻¹),²⁰ while TMS has been associated with causing central nervous system problems.²¹ Such toxicity arises from the ability of the siloxane to permeate biological membranes and skin layers.²² Although MMST is used in dietary supplements, it is found in the environment in combination with DMSD and TMS since all are usually produced simultaneously during the hydrolysis of larger siloxanes. For instance, MMST, TMS, and DMSD have been detected in reclaimed water from closed-volume environments, such as the International Space Station (ISS); low molecular weight siloxane concentrations up to 10 mg L⁻¹ have been reported downstream in the ISS.^{19,23,24}

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Developing appropriate adsorbents could be an efficient and cost-effective solution for siloxane removal.²⁵ The United States National Aeronautics and Space Administration (NASA) has already focused on the usage of commercial adsorbents such as ion exchange resins^{23,26} and activated carbon;^{27–30} for instance, NASA has reported siloxane uptake capacities for TMS and DMSD of approximately 0.15 and 0.30 mg per cm³ of adsorbent, respectively.¹⁹ More recently, Hernández-Maldonado and co-workers³¹ prepared a hierarchical zeolite–carbon composite *via* confined space synthesis and reported adsorption capacities for TMS and DMSD of around 2.0 and 0.8 mg cm^{−3}, respectively, highlighting the importance of adding specific adsorbent–adsorbate interactions to the overall surface potential as well as hydrophobicity to increase selectivity toward the siloxane and uptake capacities.

Pure silica zeolite materials (PSZs), which contain only silicon and oxygen atoms, are highly hydrophobic^{32,33} and this holds significant importance for water treatment applications.^{34–37} Moreover, PSZs display exceptional high thermal stability, opening the possibility of being regenerated by thermal swing after being spent during adsorption.^{38,39} PSZs have been extensively tested as adsorbents for gas/vapor^{40–43} and liquid^{38,44–46} phase separations. For the latter, PSZs have even been considered for removing several micropollutants from water in computational studies by Chen *et al.*,⁴⁷ who showed the importance of pore diameters, surface areas, and crystal frameworks for the uptake of different problematic compounds. Although it is difficult to tailor extraframework moieties that act as specific adsorption sites in PSZs, exploiting silanol groups resulting from structural defects is an alternative. The presence or absence of these could significantly impact the PSZ material surface potential and its performance in adsorption and catalysis applications.^{48–50} Further, combining such defects with a larger pore channel could make PSZ an excellent alternative to achieve sound diffusion of adsorbates and high capacity, essential for continuous or dynamic adsorption scenarios. UTD-1 (University of Texas at Dallas, number 1) is a PSZ with a DON-type framework with pores bounded by 14 tetrahedral atoms, the first PSZ with extra-large pores with a diameter of approximately 10 × 7.5 Å.^{51,52} UTD-1 can exhibit structural defects or faults that cause silanol groups in its structure, which are formed to compensate for the positive charge of the structure-directing agent (SDA) used during the synthesis process. In turn, the silanol groups could act as active sites for the adsorption of target molecules, and the size of the UTD-1 pores enables a high selectivity in capturing molecules overtaking diffusion problems encountered in other zeolite types. UTD-1 has about 3.5% faults per unit cell, amongst the largest reported for a PSZ, and all are exposed to the pore surface.⁵² For instance, many of the surface faults of pure silica MFI are in positions that are sterically forbidden for interactions with guest molecules (*i.e.*, not near the main pore).⁵³

The main goal of this work is to evaluate the effect of structural faults in UTD-1 zeolite on the removal of monomeric siloxanes (MMST, DMSD, and TMS) from water in single- and multi-component fashion. To achieve this, faulted and faultless UTD-1 frameworks (*i.e.*, UTD-1_{faulted} and UTD-1_{faultless}) were

synthesized *via* hydrothermal methods following or modifying recipes published by Freyhardt *et al.*⁵¹ and Wessels *et al.*,⁴⁹ respectively. The resulting adsorbent materials were fully characterized *via* X-ray diffraction (XRD), nitrogen porosimetry, thermogravimetric analysis (TGA), water contact angle measurements, zeta potential analysis, and Fourier transform infrared (FT-IR) spectroscopy. FT-IR was also used in an attempt to elucidate adsorption mechanisms. Finally, multi-cycle adsorption studies with thermal-assisted and OH-replenishment treatments were performed to evaluate the possibility of regeneration of faulted UTD-1 adsorbents.

Experimental

Two UTD-1 variants were synthesized following methods reported elsewhere.⁵⁴ UTD-1_{faulted} was synthesized in hydroxide media, following the procedure outlined by Freyhardt *et al.*,⁵¹ while UTD-1_{faultless} was prepared according to the method reported by Wessels *et al.*⁴⁹ in fluoride media. The synthesis of both UTD-1 variants involved the use of bis(pentamethylcyclopentadienyl)cobalt(III) hydroxide ([Cp*]₂Co)OH) as SDA, which was effectively produced with a modification of a previously reported method.⁵⁴ Both faulted and faultless variants of UTD-1 were fully characterized to assess their crystallinity, textural properties, thermal stability, and hydrophobicity, among others. The adsorption capacities for MMST, DMSD, and TMS were evaluated under both single and multicomponent conditions. Detailed information on reagents, synthesis procedures, characterization, and adsorption protocols, including adsorption regeneration tests, can be found in the ESI text.†

Results and discussion

Synthesis and characterization of UTD-1 adsorbents

PSZs consist of silicon and oxygen atoms and are hydrophobic without acid sites. Thus, the competitive adsorption of metal cations in water treatment applications can be significantly reduced.⁵⁸ Two DON-type PSZ adsorbent materials were prepared here using [(Cp*)₂Co]OH as the SDA.⁵¹ One of these DON PSZ was prepared with framework faults or siloxy groups in its structure (UTD-1_{faulted}) to counterbalance the structural charges from the organometallic complex of the SDA.⁵² Subsequently, these siloxy groups give rise to silanol groups during the decomposition of the SDA; the elimination of the SDA is essential to fully expose the material porosity. The other DON-type material (UTD-1_{faultless}) was made in a fluorine medium to eliminate faults since, in this case, fluoride ions can counterbalance the positive charge of the SDA.^{49,51,52,59,60} The crystallinity and the DON topology of the adsorbents were corroborated *via* XRD. The XRD profiles shown in Fig. 1 are consistent with the previously reported XRD profiles of a fully detemplated DON-type zeolite.^{49,52,61} It should be noted that the presence of expected structural faults in UTD-1_{faulted} will not be readily apparent from crystallographic measurements as these are highly dispersed along the long range of the one-dimensional 14-ring channel, locally impacting the structure but not the long-range order or the dimension of the pores.^{49,59}



least a portion of the voids produced by the faults are indeed accessible to N_2 adsorbate molecules.

Finally, both UTD-1 variants were also analyzed to estimate the effective surface charges *via* zeta potential analysis. The profiles shown in Fig. 3 indicate that both variants have a negatively charged surface throughout most of the pH range, with an isoelectric point of around 4. These data will be employed throughout the discussion of the adsorption of siloxanes.

Single component adsorption

Fig. 4 displays the single component isotherms gathered for the adsorption of MMST, DMSD, or TMS onto UTD-1 at pH ~ 7 and ambient temperature. The data were fitted with the modified Dubinin–Astakhov isotherm model (MDA), and the saturation loadings were estimated under the assumption of full occupancy of the pore by densely packed adsorbates, wherein siloxanes molecules behave as spheres and fill perfectly within the adsorbent pore. The corresponding model parameters (see Table S1†) were determined using non-linear regression, and their suitability was assessed by computing the residual root mean square errors (RRMSE).

The maximum MMST adsorption loadings for UTD-1_{faulted} and UTD-1_{faultless} were 5.7 and 0.8 mg g⁻¹. Given that MMST is highly hydrophilic ($\log K_{OW} = -0.41$, Table 1) and has a strong tendency to self-condense,^{31,55} its preference for adsorbate–adsorbate interactions and its affinity for water would explain the lower interaction with both UTD-1 adsorbent variants, compared to TMS. However, the faulted material exhibits an MMST adsorption capacity approximately seven times greater relative to UTD-1_{faultless}. The adsorbate–adsorbent interaction is likely attributed to the hydroxyl groups of the MMST molecule and the silanol groups resulting from the imperfections in UTD-1_{faulted}. In the case of the DMSD, the adsorption loading was more significant compared to MMST, with UTD-1_{faulted} and UTD-1_{faultless} achieving loading values of 12 and 15 mg g⁻¹, respectively. The zeta potential results (Fig. 3) indicate that both UTD-1 variants possess significant negative surface charge profiles. Considering that DMSD contains positive regions due to its two methyl groups, it is plausible to suggest that the interaction between DMSD and the highly negative adsorbent surfaces primarily occurs through electrostatic interactions.



Fig. 3 Zeta potential measurements for UTD-1 materials.



Fig. 4 Single component equilibrium adsorption isotherms for (top) MMST and DMSD, and (bottom) TMS onto UTD-1. Conditions: ambient temperature and pH ~ 7 . Data includes error bars.

The slightly superior adsorption capacity of UTD-1_{faultless} for DMSD can be attributed to the material's hydrophobic nature. Although both UTD-1 variants exhibit hydrophobic characteristics, as indicated by the water contact angle measurements, the thermogravimetric analysis reveals that UTD-1_{faulted} does adsorb more water than the faultless variant (see Fig. 2). This increased water adsorption influences the DMSD adsorption capacity of the faulted variant, resulting in a somewhat reduced capacity for DMSD adsorption. Moreover, if the physical and chemical properties of DMSD and MMST are compared, it is observed that they are quite similar (Table 1), with the former being slightly more stable because of the three hydroxyl groups; this renders MMST more susceptible to self-condensation,⁵⁵ thereby leading to the possibility of less interaction with the adsorbent surface. The interactions are evidenced in values of the MDA model C parameter (see Table S1†), which is inversely related to the adsorption energy (ESI eqn (S2)†). Due to the weaker interaction between both adsorbent variants and MMST, the C parameter values are larger compared to DMSD, almost by an order of magnitude.

For TMS, the observed maximum adsorption loadings were 73.1 and 10.8 mg g⁻¹ for UTD-1_{faulted} and UTD-1_{faultless}, respectively (Fig. 4). Although both materials have the same framework topology (*i.e.*, DON) and almost identical textural characteristics, it is remarkable that the shape of the TMS adsorption isotherm in the case of UTD-1_{faulted} is quite rectangular, suggesting the presence of significant, specific interactions between the corresponding adsorption sites and the TMS, even at equilibrium concentrations below 10 mg L⁻¹. The



Table 1 Physicochemical properties of MMST, DMSD, and TMS

	Monomethylsilanetriol (MMST)	Dimethylsilanediol (DMSD)	Trimethylsilanol (TMS)
pK_a ⁵⁵	10.75	11.90	11.00
$\text{Log } K_{ow}$ ⁵⁵⁻⁵⁷	-0.87	-0.41	1.14
Molecular weight (g mol^{-1})	94.14	92.17	90.20
Kinetic diameter (\AA) ⁴⁷	4.30	4.34	4.55
Water solubility (g L^{-1}) ⁵⁵	>2000.00	2450.00	42.6
Boiling point ($^{\circ}\text{C}$) ⁵⁵	201.00	100.35	99.00

presence of OH groups in silica-rich surfaces is known to enhance the uptake of siloxanes significantly but from head-space biogas.⁶⁶ Therefore, given that UTD-1_{faulted} possess OH groups that counterbalance structural charges as a result of detemplation, it is plausible that these species are also serving as specific adsorption sites during the uptake of siloxanes from water; specifically in the TMS uptake.

As mentioned during the materials characterization discussion, the population of siloxy-related silanol groups in UTD-1_{faulted} is about 2.1 OH sites per unit cell. The maximum observed adsorption uptake of TMS is *ca.* 73.1 mg of TMS per g of UTD-1_{faulted} or about 3 TMS molecules per UTD-1_{faulted} unit cell (Fig. 4), and this strongly suggests preferential adsorption of TMS at the silanol group sites. However, it should be noted that UTD-1_{faultless} also possesses a surface capable of undergoing interaction with TMS. Akin to the scenario observed during DMSD adsorption, such interaction may arise from nonspecific adsorbate-adsorbent interactions as opposed to what is probably happening in the faulted variant. This can be corroborated by the comparable adsorption capacities that both UTD-1 variants exhibited toward DMSD and MMST (Fig. 4 (top)).

In general, the superior adsorption performance of UTD-1 materials is prominently due to the level of hydrophobicity of its silica-rich framework (*i.e.*, PSZ). And in the case of UTD-1_{faulted}, the performance is also due to the existence of sites for specific interactions. The adsorption capacity of UTD-1_{faulted} for TMS and DMSD contaminants is at least two orders of magnitude higher than that of commercially available adsorbent materials or even the zeolite-carbon composites previously tested for the removal of these contaminants at equilibrium concentrations around 10 mg L^{-1} (see Table S2†).^{19,31}

Mechanism for TMS single component adsorption

Since TMS was the adsorbate with the highest affinity toward UTD-1, an FTIR analysis was developed to elucidate the possible adsorption mechanisms. Fig. S5† gathers FTIR spectra for both UTD-1 variants after detemplation, where two broad IR bands related to the framework Si-O-Si and Si-O are located between $750\text{--}850 \text{ cm}^{-1}$ and $1000\text{--}1300 \text{ cm}^{-1}$. A band at 950 cm^{-1} in the UTD-1_{faulted} spectrum can also be observed, which is not present for UTD-1_{faultless} and is associated with framework defects or Si-OH from siloxy groups.^{67,68} Fig. 5 shows FTIR spectra for the variants after adsorption of TMS (*i.e.*, TMS@UTD-1_{faulted} and TMS@UTD-1_{faultless}). For UTD-1_{faulted}, it can be observed that there is a new band at 850 cm^{-1} . This could be related to Si-CH₃,

bonds stretching in the TMS molecules or to the Si-O-Si bending mode of weak bonds created by the interaction between TMS and the adsorbent surface, or plausibly due to the deformations of the Si-OH groups of TMS. An important fact from the TMS@UTD-1_{faulted} spectrum is the absence of the band related to faults (*i.e.*, band at 950 cm^{-1} in fresh UTD-1_{faulted}). This probably reinforces the hypothesis that the presence of OH groups on the surface of the adsorbent serves as site for the adsorption of the TMS.

The IR spectrum for TMS@UTD-1_{faultless} exhibits changes within the region between 850 and 1000 cm^{-1} relative to the spectrum of fresh material. This could be attributed to the adsorbed TMS phase, which introduces OH groups. Such a change is entirely distinct from that observed in the faulted material, and this provides further support for the previously proposed mechanism of TMS adsorption in UTD-1_{faulted}.

Multi-components adsorption

Evaluation of multi-component siloxane adsorption (*i.e.*, simultaneous adsorption of a mixture of siloxanes) onto either UTD-1 variant was carried out *via* single-point batch equilibration tests at two different initial concentrations. The aqueous phase solutions were prepared with an initial concentration of *ca.* 1 and 10 mg of organic carbon per liter of solution (*i.e.*, 1 and 10 mg C per L) of each contaminant at ambient temperature and $\text{pH} \sim 7$. From Fig. 6, although the UTD-1 variants show poor performance at 1 mg C per L regarding the binary DMSD-

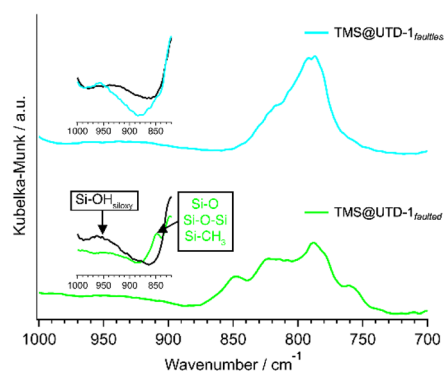


Fig. 5 FTIR spectra UTD-1 variants after TMS adsorption. Inset shows magnified portions of distinctive peaks found in the FTIR spectra. The solid black line data corresponding to the fresh adsorbent (Fig. S5†) spectrum have been included for better comparison.



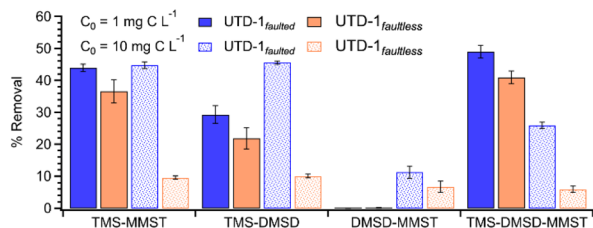


Fig. 6 Single point binary and ternary (far right) mixtures equilibrium uptakes for different siloxanes onto both UTD-1 variants. Conditions: the initial concentration of each contaminant was 1 and 10 mg C per L (*i.e.*, ppm C), ambient temperature, and pH \sim 7.

MMST adsorption, the adsorbents excelled for other binary combinations or ternary systems. However, from the adsorption results at 10 mg C per L, it is evident that UTD-1_{faulted} is superior when handling ternary mixtures. These findings are also consistent with those in the single-component adsorption tests (see Fig. 4), where the adsorbents exhibit similar behavior at low concentrations, such as 1 mg C per L. Still, the adsorption capacity shown by UTD-1_{faulted} at higher concentrations is superior.

A notable aspect that should be highlighted is that TMS appears to be the main driving force for the adsorption of the other two compounds. In the case of binary mixtures (Fig. 6, left), it is difficult to elucidate how much of the adsorbed amount corresponds to TMS *versus* the other contaminant (*i.e.*, the initial concentration of each adsorbate is 1 or 10 mg C per L). However, TMS positively affects the adsorption of other siloxanes and is the main contributor to the substantial uptakes; evidencing co-adsorption may be due to strong adsorbate–adsorbate interactions between TMS and other siloxanes.

Adsorbent regeneration

Tests with batch equilibrium adsorption of TMS onto UTD-1_{faulted} were chosen for adsorbent regeneration tests since this adsorbate–adsorbent system showed the highest interactions. As mentioned before, PSZs like UTD-1 have demonstrated exceptional thermal stability, making them suitable for thermal-based regeneration processes,⁵² and offering an advantage for the removal of adsorbent pollutants on spent UTD-1; which requires activation temperatures of around 700 °C (see Fig. S6† for thermogravimetric data). However, since the hydroxyl groups on the adsorbent surface promote the adsorption of contaminants such as TMS, which are also removed at temperatures higher than 500 °C, surface OH replenishment can be accomplished *via* rehydroxylation.⁶⁹

Restoring hydroxyls on the adsorbent surface through exposure to water refluxing was a successful process in recovering the capability of UTD-1_{faulted} to adsorb TMS. Fig. 7 shows the adsorbent amount of TMS after multiple cycles (*i.e.*, regeneration or rejuvenation of the adsorbent *via* thermal treatment and rehydroxylation). The efficiency of the adsorbent material remains constant even up to at least a third adsorption cycle, and the integrity of the material is not affected, as shown in the

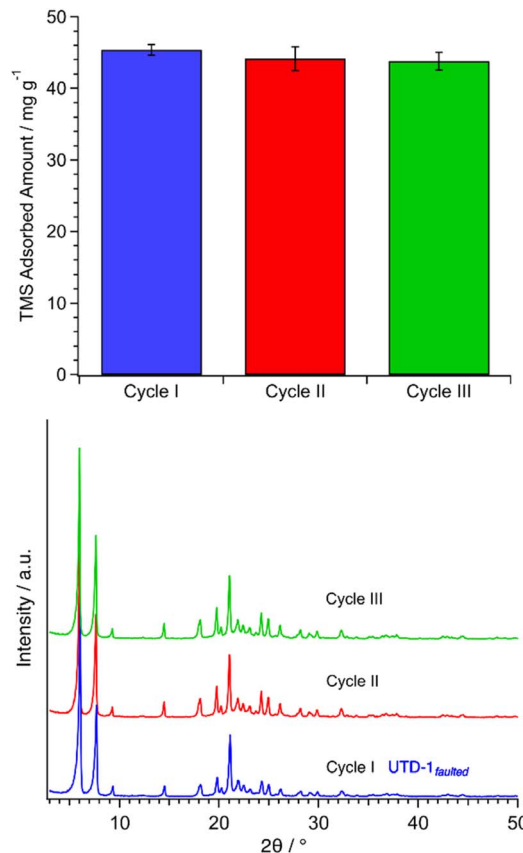


Fig. 7 (Top) Adsorbed amount of TMS onto fresh and regenerated UTD-1_{faulted}. (Bottom) XRD pattern of UTD-1_{faulted} prior to each adsorption cycle. The initial TMS concentration during the adsorption tests was 125 mg L⁻¹. Adsorbent regeneration was performed through thermal treatment and rehydroxylation.

XRD profiles. A two-cycle test was performed for attempting the regeneration of UTD-1_{faulted} upon being spent with the adsorption of a ternary mixture of siloxanes (TMS–DMSD–MMST) (see Fig. S7†). The results match those observed for the single-component (TMS) tests in terms of capacity and long-range adsorbent integrity.

Conclusions

The faults in the PSZ UTD-1 play an essential role in the uptake of the siloxanes from water, particularly TMS, since the target molecules could interact with the silanol groups from the surface. The interaction mechanism for DMSD appears to be *via* weak electrostatic forces. In the case of TMS, the uptake in UTD-1_{faulted} was the highest and exhibited a nearly rectangular isotherm shape across the evaluated equilibrium concentration range (up to 150 mg L⁻¹). The silanol content due to siloxy faults in the UTD-1_{faulted} surface is the dominant driving force in the uptake of siloxanes such as TMS, which was confirmed by FTIR. A faultless adsorbent variant (UTD-1_{faultless}) shows lower interaction with TMS as it does not contain silanol groups from siloxy faults. Furthermore, multi-component adsorption tests revealed that TMS drives the co-adsorption of the other siloxane



compounds when in a mixture. Finally, the recyclability of UTD-1_{faulted} was corroborated based on multi-cycle TMS adsorption tests; the adsorbent was successfully regenerated between cycles using thermal and rehydroxylation treatments.

Author contributions

Dariana Vega-Santander: conceptualization, methodology, investigation, formal analysis, writing – original draft. Rodinson Arrieta-Perez: investigation, formal analysis. Daniela Rivera-Mirabal: investigation, formal analysis. Gabriela Del Valle-Pérez: investigation, formal analysis. Miguel Sepúlveda-Pagán: investigation, formal analysis. Juan C. Muñoz-Senmache: investigation, formal analysis, writing – original draft. Yomaira J. Pagán-Torres: methodology, investigation, formal analysis, writing – original draft. Arturo J. Hernandez-Maldonado: conceptualization, methodology, investigation, formal analysis, writing – review & editing, visualization, project administration, funding acquisition.

Conflicts of interest

There are no conflicts to declare.

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