Indian Journal of Biochemistry & Biophysics
Vol. 58, December 2021, pp. 520-531

Facile synthesis and implications of novel hydrophobic materials: Newer insights of pharmaceuticals removal

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Received 15 December 2020; *revised 18 March 2021*

The residual escape of pharmaceuticals from wastewater treatment plants (WWTP) is a serious environmental concern due to the adverse effects towards living organisms. Therefore, it is important to devise the newer technologies for safe and efficient elimination of emerging micro-pollutants from effluents of existing water treatment plants. Bentonite is grafted with 3-mercaptopropyletrimethoxy silane by facile one-pot method to obtain dense composite material (MPTS/BENT).The materials are characterized by the FT-IR, XRD, BET and SEM/EDX analytical tools. Various parametric experiments conducted for the removal of tetracycline hydrochloride (TCH) and triclosan (TCS) using MPTS/BENT under batch experimentations. Further, column adsorption experiments have been performed.The incorporation of organosilane with bentonite is confirmed by FT-IR and EDX analyses. BET surface area analysis showed that the surface area of MPTS/BENT is significantly small compared with pristine clay. pH dependent sorption of TCH and TCS is almost unaffected within the pH 3.0 to 7.0. Rapid uptake of TCH and TCS by MPTS/BENT followed PSO kinetics. High percentage removal was achieved at wide concentration range of pollutants. The uptake of TCH and TCS is unaffected on increasing the background electrolyte concentrations for 1000 times. Column experiment confirmed the high efficiency of MPTS/BENT towards these pollutants. Moreover, the removal of TCH/or TCS from real water sample at varied pH values showed that the synthesized composite is selective and efficient towards these micro-pollutants. This study showed that the synthesized material, *i.e.*, MPTS/BENT could be efficiently employed for the additional purification of WWTP effluents.

Keywords: Fixed bed reactors, Hydrophobic materials, Mechanism of removal, Newer insights, Pharmaceuticals, Real matrix treatment

Pharmaceuticals and personal care products (PPCPs) received greater attention in recent times because of its uncertainty imposed to human beings for prolonged exposure at lower concentrations[1]. The drug compounds administered to human or live-stocks is only partially metabolized in the biological systems and in bulk *Ca.* 60-70% is excreted through the urine or feces and enhancing the pollutants load on the water bodies[2]. Moreover, the existing wastewater treatment (WWT) plants are not efficient or designed to eliminate these calcitrant pollutants efficiently hence, these compounds can easily go through the WWT plants at lower concentration levels and entered into the water bodies. Consequently, these micro-pollutants detected even in the drinking water systems[3,4]. This imposes greater risks to human and even impact adversely the microbiological ecology and the ecological functions as well[5,6]. Therefore, these compounds are known to be emerging pollutants and needs greater attention for its effective and efficient removal from water bodies.

Tetracycline (TC) is one of the widely prescribed antibiotic to human and live stocks to prevent infectious diseases[7]. Animal manure considerably enhanced the tetracycline load in soil since soil readily adsorbs the tetracycline[8]. It is known fact that the bioaccumulation of tetracycline through the food chain showed antibiotic-resistance in microorganisms and having several chronic and acute diseases to human[9]. Further, gastrointestinal distress and skin lesions are the major side effects of tetracyclines[10]. Additionally, a prolonged exposure of tetracycline in human affects liver and kidney[11,12] or cause an acute hepato-nephrotoxicity[13]. TC with four rings fused together has tricarbonylamide, phenolic diketone and dimethylamino functional groups and it is slightly soluble in water[14]. The amino and enone groups are lack of electron whereas phenolic group is rich with electron. Tetracycline possessed three different pk$_a$ values *viz.*, 3.30, 7.7 and 9.7[15–17].

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On the other hand, triclosan (TCS) is an antimicrobial agent which binds the ligase of fatty acids forming stable FAS-NAD$^+$-TCS complex. This effectively blocks the biosynthesis of lipid in cell-membrane and inhibiting the growth of microbe[18]. Therefore, triclosan is a widespread used PPCPs and more than 700 types of PPCPs are made with triclosan[19–21]. Triclosan is an emerging water contaminant because of its geno- and cytotoxicity in aquatic organisms[22]. Moreover, it damages the DNA, hemocyte function with enhanced oxidation stress[23]. Previously it was indicated that the role of soil as in soil nitrogen cycle is extremely impaired when the concentration of triclosan is as high as 5 mg/g[24]. Human urine samples (USA and Asia) showed that 83% of randomly collected samples are contained with high value of triclosan[25]. Triclosan is found to be a potential water contaminant and widely dispersed in the streams, lakes and seawater with significant levels[26]. Therefore, in order to maintain a safe and stable natural environment, it is important and inevitable to devise the newer technologies for safe and efficient elimination of emerging micro-pollutants from effluents of existing water treatment plants[27–30].

The sorption process with advanced functionalized materials are, perhaps, potential implications in tuning the conventional treatment plants to remove efficiently the persistent and residual micro-pollutants[31–33]. Clays are porous materials, employed widely towards the elimination of water pollutants since it possess a large surface area, expandability, high cation exchange capacity, porosity at micro level, low cost and ubiquitous in nature. Moreover, clay minerals are desirable for large-scale operations because of their exceptional strength and are environmentally benign[34]. However, clays are hydrophilic in nature hence, ineffective towards the removal of micro-pollutants[35]. Therefore, advanced and functionalized materials precursors to the natural clays are suitable options for its wide range implications[36,37]. Silane grafted clay has recently shown potential materials, since the silylated clay results from stable confinement of organic functional groups due to the formation of strong bond between clay and organic moieties which further restricted the leaching of organic moieties into the environment[38,39]. Several factors are responsible for the effective immobilisation of silane, including the concentration, type of surface, properties of organosilane and the hydrolytic stability of the bonds formed. However, broken edges of clay minerals is most reactive sites for grafting of silane. Grafting of silane compound within the clay network is, however, challenging [40–43]. Therefore the present study aims to graft the 3-mercaptopropyle trimethoxy silane within the bentonite network as to obtain the novel composite materials. The functionalized bentonite is further, intended to employ in decontamination of water polluted with tetracyclinehydrocloride (TCH) and triclosan (TCS). The insights of removal process under batch and column experiments are extensively studied and real matrix analysis paved the way for real implication of the materials.

Materials and Methods

Materials

Bentonite was obtained from Gujarat, India. Bentonite is washed, dried and crushed to obtain 100 BSS (British Standard Sieve). 3-mercaptopropyle trimethoxy silane and tetracycline hydrochloride are obtained from Sigma, Aldrich, USA. Ethylenediaminetetraacetic acid (EDTA) was obtained from Qualigens, India. Magnesium sulfate heptahydrate is obtained from Loba Chemie, India. Calcium chloride dihydrate, manganese (II) chloride, oxalic acid, di-sodium hydrogen phosphate anhydrous purified and nickel chlorides are obtained from Merck, India. Sodium chloride (Extrapure), glycine and triclosan are obtained from HiMedia, India.

Methodology

Preparation of silane functionalized bentonite clay

Functionalization of bentonite is conducted in a facile one pot method. 12 g of pristine bentonite (BENT) is dispersed in toluene (300 mL) and the mixture is refluxed for 30 min at 60°C under nitrogen atmosphere .In this suspension 3-mercaptopropyle trimethoxy silane (12 mL) is added slowly and again refluxed for 48 h. The slurry is collected and then washed with toluene followed by ethanol. The sample is dried at 100°C for 24 h. The solid is crushed and powder is named as MPTS/BENT. The point of zero charge (pH_{PZC}) of pristine bentonite and composite (MPTS/BENT) is obtained using the known acid/base titration method[44].

Characterization of materials

FT-IR data of solids (BENT and silane grafted bentonite (MPTS/BENT)) is recorded using FT-IR (Affinity-1 Shimadzu, Japan) machine. X-ray diffraction (XRD) analysis is conducted by an X-ray diffraction machine (PANalytical, Netherland; Model X’Pert PRO MPD). The surface morphology of these solids is studied using FE-SEM coupled with EDAX

(Oxford-X-Supreme, Abingdon, Oxfordshire, United Kingdom) machine. The BET adsorption/desorption data was collected using BET Analyzer Macsorb HM machine (Model-1201) Japan.

Batch reactor operations

Tetracycline hydrochloride and triclosan stock solutions (50.0 mg/L) are prepared in double distilled water and the desired concentrations of these pollutants are prepared by simple dilution of stock solutions. Batch reactor studies are conducted for parametric studies *viz*., effect of pH, contact time, co-existing ions, ionic strength, and initial pollutants concentrations. The results could enable to demonstrate suitable mechanism involved at solid/solution interface. 50.0 mL of tetracycline hydrochloride/or triclosan solution is taken into different polyethylene bottles having varied pH values (pH ~2.0 to 10.0) and 100 mg of pristine bentonite/or MPTS/BENT solid is added. The bottles are tightly closed and shaken (Incubator Shaker, TM Weiber, ACMAS Technologies Pvt. Ltd., India) for 24 h at 25°C. The solution mixture is filtered using 0.45 μM filter and the pH is recorded as equilibrium pH. UV–Vis spectrophotometer was employed for analysing the filtrate solution (Shimadzu Model: UV 1800, Japan) at 275 nm and 280 nm for tetracycline and triclosan, respectively. Moreover, the calibration lines of tetracycline/or triclosan was obtained using varied concentrations (1.0, 5.0, 10.0, 15.0, 20.0 and 25.0 mg/L) of these pollutants. The concentration dependent studies on TCH and TCS were performed by changing the initial concentrations from 1.0 to 25.0 mg/L for TCH and TCS at constant pH 4.0. Results were plotted with percentage removal against initial concentrations (mg/L) of micropollutants. The effect of contact time for the elimination of TCH and TCS by MPTS/BENT is conducted at different time intervals (5 to 720 min) at constant pH 4.0 and TCH and TCS concentration of 10.0 mg/L. The effect of background electrolyte (NaCl) in the sorption of these micro-pollutants at constant pH 4.0 was conducted at varied NaCl concentration (0.0001 to 0.1 mol/L). Further, the influence of co-existing cations (Mg (II), Mn (II), Ni (II), Ca (II)) and anions (ethylenediaminetetraacetic acid, glycine, oxalic acid and phosphate) were also studied in the removal of TCH/TCS at pH 4.0. The concentrations of cations/anions were maintained at 50 mg/L. Moreover, the efficiency and applicability of composite material (MPTS/BENT) was evaluated for the sorption of TCH and TCS in the real water samples spiked with TCH or TCS.

Fixed bed column studies

A glass column, 30 cm in height and 10 mm in diameter is employed to conduct fixed-bed column studies. 0.25 g/or 0.5 g of MPTS/BENT solid is taken at the middle of the column and the remaining part of the column is filled by glass beads. Tetracycline hydrochloride or triclosan solution (10.0 mg/L; pH 4.05) is pumped upward using Acuflow Series II, High-Pressure peristaltic pump (flow rate: 1.0 mL/min). The effluent of column was collected by fraction collector and filtered and then analyzed for pollutant concentrations using UV–Vis spectrophotometer.

Results and Discussions

Characterization of materials

FT-IR spectra of BENT and MPTS/BENT are illustrated in (Fig. 1). It is evident from the spectra that weak peaks are appeared 2914 cm^{-1} and 2831 cm^{-1}, with the MPTS/BENT solid, are attributed to the stretching vibrations of -CH$_3$ and -CH$_2$, respectively[45,46]. Similarly, a characteristic peak of methoxy group of silane (MPTS) is appeared at 2914 cm$^{-1,}$ [45,47].The stretching vibration of thiol (–SH) group of 3-MPTS is occurred as very weak peak appeared around 2555 cm$^{-1,}$ [48]. The vibrational peaks at 682 and 1402 cm^{-1} are, perhaps, attributed to the C-H deformation vibration and the C-S stretching of thiol group from MPTS, respectively[49]. These results are clearly indicated that the MPTS is successfully grafted with the bentonite solid. Further, BET adsorption/desorption curves are utilized to estimate surface area, pore volume, and pore size of pristine bentonite and MPTS/BENT. It was observed that the N$_2$ adsorption-desorption isotherms followed type IV

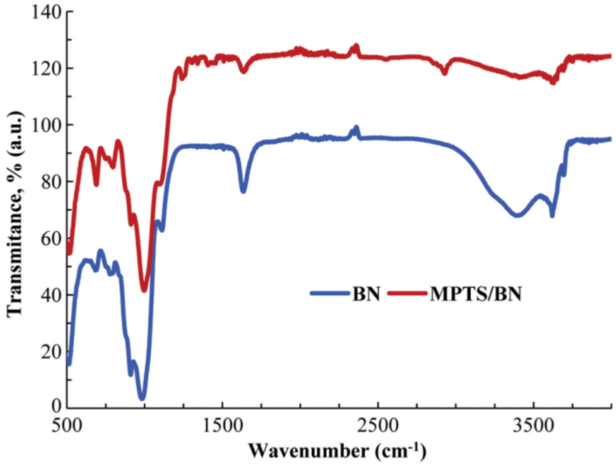

Fig. 1 — FT-IR spectra and obtained for pristine bentonite (BENT) and MPTS/BENT solid materials

isotherm with distinctive H3 hysteresis loop for both these solids. This inferred that BENT and MPTS/BENT materials are possessed with mesoporous structure. Moreover, the pristine bentonite exhibits comparatively wider hysteresis loop having pore size of 8.0 nm and pore volumes of 0.071 cm^3/g. However, the MPTS/BENT showed the pore size and pore volume of 20.15 nm and 0.028 cm^3/g, respectively. Further, the BET specific surface area of BENT was found to be 41.21 m^2/g whereas, MPTS/BENT is 4.72 m^2/g, respectively. It is interesting to note that the surface area of bentonite clay is significantly reduced after modificationsince the incorporated organosilane occupy the mesopores in clay network. This eventually, enhances the organophilicity of solid with enhanced hydrophobic nature. Previously, Tonle *et al*., reported that the functionalization of smectite with MPTS caused for significant decrease in specific surface area of solid[46]. Our previous studies indicated that hybrid materials obtained by incorporating hexadecyl trimethyl ammonium (HDTMA) into bentonite possessed the smaller surface area compared to pristine bentonite[50]. Similarly, the surface area of sepiolite is reduced significantly after the incorporation of MPTS[51,52].

X-ray diffraction data is obtained for the solids BENT and MPTS/BENT and results are included as in (Table 1). It is evident from the XRD data that both the solids are possessed with almost identical crystalline structure. The presence of quartz inboth samples is predominant since the characteristic diffraction peaks are obtained at 2θ values of 20.95, 26.78, 36.68, 50.26, 60, and 68.36[53,54].

The surface morphology of BENT and MPTS/BENT is presented as in (Fig. 2A & B), respectively. The SEM images showed that both the solids exhibited heterogeneous and disordered structure. It is further observed that the pristine bentonite exhibits rather more porosity compared to the silane grafted bentonite. Therefore, the introduction of silane molecules within the clay network reduced significantly the porosity of solid[55]. This finding is in consistent to the textural properties obtained by the BET analysis. Besides, BENT and MPTS/BENT are analysed elemental mapping and results are presented in (Fig. 2C & D)**,** respectively, for BENT and MPTS/BENT. The element composition of bentonite is composed with Si, Al, O, Fe, Na and K. However, the MPTS/BENT solid showed additional peak of sulphur which again confirms the effective introduction of MPTS molecule into bentonite clay. Similarly, previous studies showed that the modification of kaolinite with mercapto (-SH) group shows a pronounced peak of sulphur in the EDX analysis[45,47,56].

Table 1 — XRD peaks of raw bentonite (BENT) and MPTS/BENT

BENT			MPTS/BENT		
Peak position (2 theta)	d-spacing [Å]	Relative Intensity	Peak position (2 theta)	d-spacing [Å]	Relative Intensity
6.3001	14.02961	17.63	6.8127	12.97501	15.19
9.6366	9.17825	7.64	9.6833	9.13404	8.63
12.4995	7.08174	8.48	12.2167	7.24501	6.94
19.8450	4.47397	38.12	19.5763	4.53477	47.58
20.9495	4.24053	35.24	20.7724	4.27627	41.55
24.9889	3.56346	13.32	25.0495	3.55497	25.38
26.7796	3.32911	100	26.5600	3.35614	100
28.0210	3.18438	12.02	-	-	-
30.0445	2.97436	8.48	-	-	-
34.9046	2.57055	23.35	34.8343	2.57557	33.47
36.6833	2.44989	23.46	-	-	-
39.5748	2.2773	8.51	41.9197	2.15518	3.3
45.5118	1.99309	2.79	-	-	-
50.2683	1.81508	16.09	50.0150	1.82368	14.61
54.6967	1.67814	7.71	54.4257	1.68586	12.15
60.0826	1.53995	12.23	-	-	-
61.8523	1.50007	15.6	61.8119	1.50096	22.23
68.3628	1.37223	9.7	67.9788	1.37904	5.96
73.3261	1.29112	5	73.1101	1.2944	6.77

Effect of pH on the removal of TCH and TCS

The effect of pH on the removal of tetracycline hydrochloride (TCH) and triclosan (TCS) is performed at wide pH range (pH 3.0 to 10.0) using the TCH/or TCS concentration 10.0 mg/L. Results are presented as in (Fig. 3). It is shown that increase in pH from *Ca.* pH 3.2 to 7.0 the uptake of TCH and TCS is almost unaffected using the MPTS/BENT solid. However, further increase in pH (pH>7.0), the elimination of TCH and TCS is decreased sharply and reached to a very low removal at *Ca.* pH 10. It is important to analyze the speciation of TCH as varied pH values. Tetracycline (TCH) is having three acid dissociation constants *viz.*, pk_{a1} (3.31), pk_{a2} (7.72) and pk_{a3} (9.71)[9,57]. The speciation analysis is shown as in (Supplementary Fig. 1A) and also discussed previously[58]. Tetracycline is predominantly present in the anionic forms at pH>3.4. On the other hand, the pH_{pzc} of pristine bentonite and MPTS/BENT is 7.82 and 7.65, respectively. Therefore, the surface is positively charged at pH<7.65 (for MPTS/BENT) and pH<7.82 (for BENT). This showed that pH<7.0, the anionic species of TCH is attracted by the positively charged surface of MPTS/BENT, hence, very high uptake of TCH is recorded in this region. The uptake of TCH by the MPTS/BENT is not primarily due to the electrostatic attraction, since almost similar pH_{PZC} is recorded for the BENT solid but the uptake of TCH or TCS is sharply decreased at pH>3.6. This implied that the introduction of silane within the bentonite, enabled the solid more hydrophobic with enhanced organophilic which eventually facilitated the sorption of TCH onto the MPTS/BENT solid. This caused for

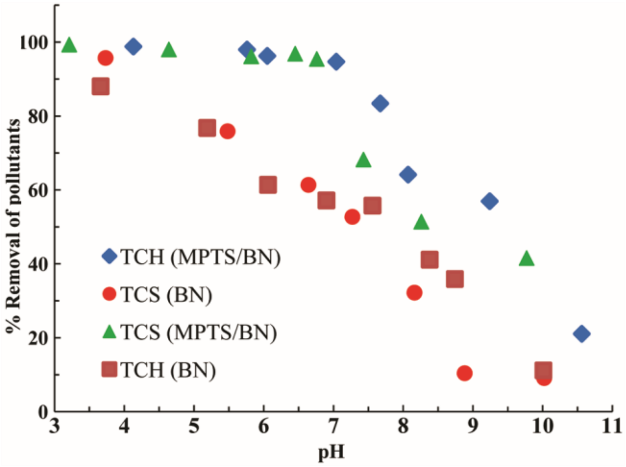

Fig. 3 — Effect of pH in the removal of TCH and TCS by bentonite (BENT) and MPTS/BENT

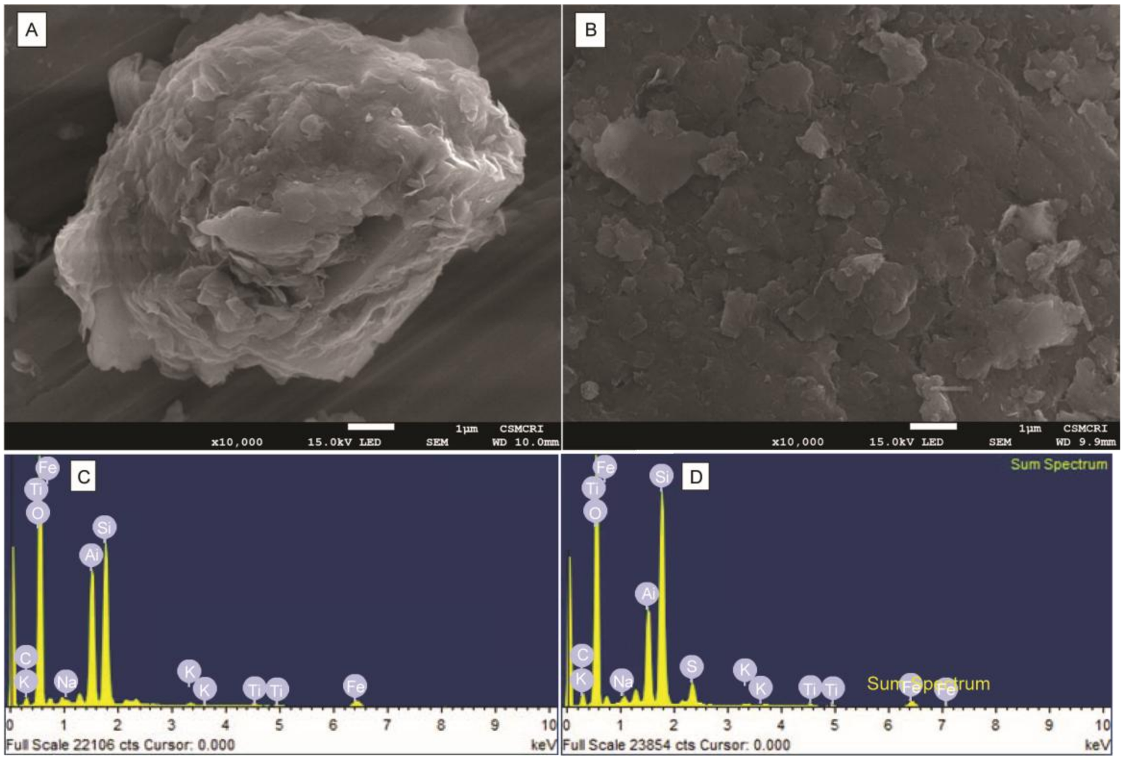

Fig. 2 — SEM images of (A & B) raw bentonite (Inset: EDAX elemental mapping of pristine bentonite); and (C & D) MPTS/BENT (Inset: EDAX elemental mapping of MPTS/BENT solid)

very high uptake of TCH by the MPTS/BENT solid at pH<7.0. However, further increase in pH>7.0, a sharp decreased in percentage uptake of TCH is observed which is due to the fact that strong electrostatic repulsive forces occurred and subsequently hindered the elimination of TCH by MPTS/BENT solid. Similar outcomes are reported on the adsorption of tetracycline onto Fe-Mt[59] and illite[60].

On the other hand, the elimination of TCS is almost constant at pH>7.0. The TCS is having the acid dissociation constant values as pk_{a1}:7.90 and pk_{a2}: 8.1[61]. Therefore, the speciation of TCS is conducted and shown in (Supplementary Fig. 1B) and also reported elsewhere[62]. It is evident from the speciation studies that TCS is predominantly present as uncharged species at pH<7.0. However, at pH>7.0, the dominant species are anionic species (*i.e.*, TCS^{-} or TCS^{2-}). Therefore, very high uptake of TCS at pH<7.0 is primarily due to the hydrophobic and organophilic nature of MPTS/BENT towards the TCS. The strong hydrophobic interaction between the TCS molecules and organo-modified clay had caused for enhanced elimination of TCS[63]. Similar removal behaviour was reported previously in the removal of TCS by kaolinite and montmorillonite[64]. However, further increase in pH above 7.0, a rapid decrease in percentage elimination of TCS by the MPTS/BENT is recorded. This is due to the fact that the anionic species of TCS and negatively charged solid surface caused strong repulsive forces which retarded significantly the sorption of TCS by the solid. Overall, a high elimination percentage of TCS or TCH at neutral pH conditions is providing an optimum pH conditions implying the materials in the treatment strategies for efficient removal of these pollutants from water bodies at neutral pH conditions.

The pristine clay (BENT) showed relatively high uptake at lower pH~3.66, however, further increase in pH, significant decreased in the uptake of TCS or TCH was observed and reached very low removal upto pH~10.0. Therefore, the pristine bentonite showed very limited implications in the elimination of these pollutants from aqueous wastes.

Effect of contact time

The quantity of TCH/or TCS sorbed by MPTS/BENT are obtained at different time intervals (5 to 720 min). The concentration of TCH/or TCS is maintained at 10.0 mg/L at pH 4.05. The time dependent sorption of TCH/or TCS is shown as in (Fig. 4A). A fast uptake of TCH/or TCS by the MPTS/BENT is observed during initial period of contact and more than 60% of TCH/or TCS is sorbed within 5 min. Initially, the rate of adsorption is significantly high which is primarily because of the fact that extent of active sites are relatively more at the MPTS/BENT surface during initial contact time which enabled fast aggregation of TCH/or TCS

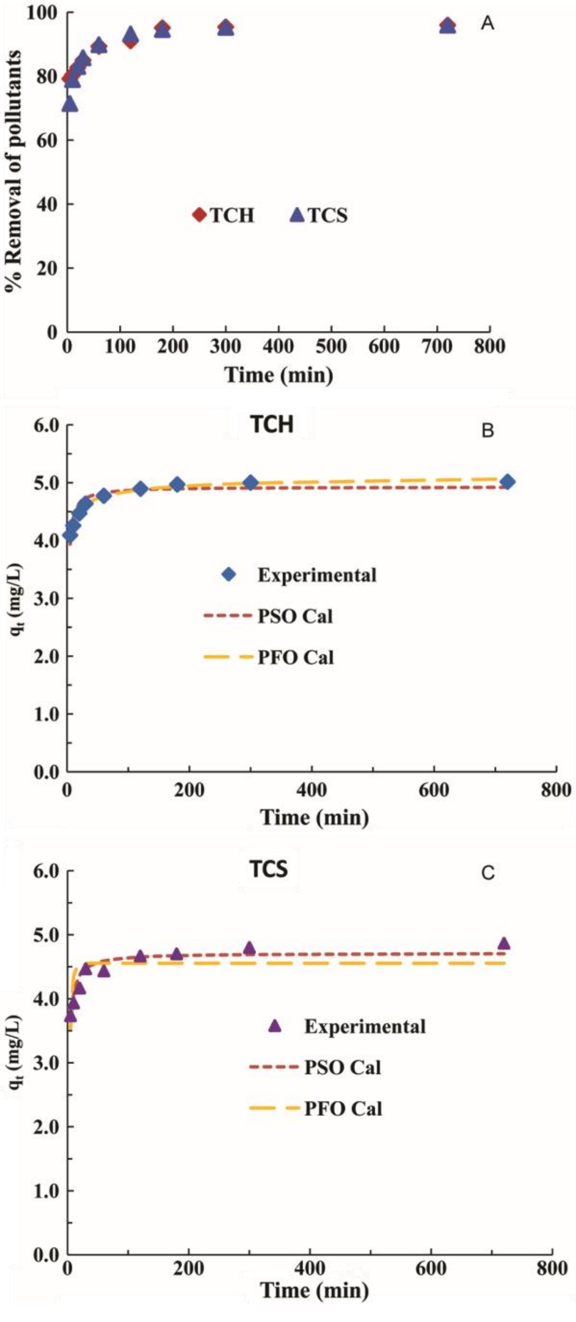

Fig. 4 — (A) Effect of contact time in the removal of TCH and TCS by MPTS/BENT (pH: 4.0; [TCH/TCS]: 10 mg/L; dose: 2 g/L); (B) Plots of PFO and PSO kinetic model for the sorption of TCH; and (C) Plots of PFO and PSO kinetic model for the sorption of TCS by MPTS/BENT

molecules onto the solid surface[65]. However, further increase in time, the rate of sorption slowed down and apparently equilibrium is attained within 180 min of contact for both the pollutants. This signifies that MPTS/BENT is an efficient material for the elimination of TCH/or TCS from aqueous wastes.

Further, the time dependence sorption data of TCH/or TCS is utilized to study the kinetics of sorption by employing pseudo-1st order (PFO) and pseudo-2nd order (PSO) rate kinetics[66]. The simulation results are illustrated graphically in (Fig. 4B & C). Moreover, the estimated parameters are returned in (Table 2). Table 2 showed that the PSO kinetics is more favourable than the PFO model since least square sum is significantly less for PSO kinetics. The removal capacity of TCH and TCS is relatively high which pointed the potential applicability of MPTS/BENT towards the removal of these pollutants from aqueous media. Sorption of tetracycline onto Na-montmorillonite (Na-Mt) modified with carboxymethyl-chitosan is better fitted to the PSO kinetics[67]. It was also reported that the removal of triclosan using *Phaeodactylum tricornutum* follows pseudo-second order kinetic model[68].

Concentration dependent study

The sorption performance of MPTS/BENT towards the elimination of TCH/or TCS is conducted varying the pollutant concentrations1.0 to 25.0 mg/L at pH: 4.05 using solid dose of 2.0 g/L. Results are plotted with initial sorptive concentration against percentage removal of TCH/or TCS and illustrated as in (Supplementary Fig. 2A). It was observed that the percentage elimination of TCH/or TCS is almost unaffected within the studied sorptive concentrations. This implied higher affinity of MPTS/BENT towards these pollutants. Quantitatively, increasing the concentration of TCH from 1.0 to 20.0 mg/L the removal efficiency is decreased from 97.8 to 90.9% (for TCH) and from 95.0 to 90.7% (for TCS).

Furthermore, the result obtained from the concentration dependent study is utilized to obtained the two common adsorption isotherm models *viz*., Langmuir and Freundlich adsorption isotherms[69,70,71] and presented as in (Supplementary Fig. 2B & C). The isotherm constants, *i.e*., Langmuir monolayer sorption capacity (q_o), (a) Langmuir constant (b) and Freundlich constants ($K_f$and $1/n$) are evaluated and returned as in (Table 3). Since higher value of R^2 is obtained for Langmuir adsorption isotherm for TCH and TCS, which inferred the applicability of Langmuir adsorption isotherm for the studied systems.The Langmuir monolayer capacity is found to be 16.64 and 18.87 mg/g, respectively, for the TCH and TCS using the MPTS/BENT solid. Previously, it was reported that the sorption of tetracycline onto different montmorillonite was found to follow the Langmuir adsorption isotherm[16]. Similarly, the adsorption of TCS onto montmorillonite, activated carbon and kaolinite followed Langmuir adsorption isotherm[64]. Moreover, higher values of (*1/n*) and (b), Freundlich and Langmuir constants, respectively, indicated that the material has strong affinity towards TCH/TCS.

Effect of ionic strength

Adsorption with weaker forces are greatly affected in presence of electrolyte species. Therefore, the effect of ionic strength is useful parameter determining the ‘specific’ and ‘non-specific’ adsorption. ‘Specific adsorption’ is unaffected by change of ionic strength while ‘non-specific sorption’ is affected by change in electrolyte concentration[72]. The electrolyte (NaCl) concentrations were varied from 0.0001 to 0.1 mol/L. Further, the sorption of TCH/or TCS by MPTS/BENT is studied at varied ionic strengths and outcome is shown as in (Fig. 5). It is evident that 1000 times increase in NaCl concentration did not affected significantly the removal of TCH/or TCS by MPTS/BENT. This concludes that the TCH/or TCS is forming ‘inner-sphere-complexes’ at surface of solid

Table3 — Langmuir and Freundlich constants estimated for sorption of TCH and TCS using MPTS/BENT

Pollutants	Langmuir			Freundlich		
	q_o (mg/g)	b (L/g)	R^2	$1/n$	K_f (mg/g)	R^2
TCH	16.64	1.019	0.992	0.737	7.925	0.979
TCS	18.87	0.652	0.998	0.764	6.95	0.985

Table 2 — Predicted kinetic parameters for pseudo-first order and pseudo-second order kinetic models in the sorption of TCH and TCS by MPTS/BENT

Material	Pollutants	PFO Model			PSO Model		
		q_e	k_1	s^2	q_e	k_2	s^2
MPTS/BENT	TCH	4.786	0.348	0.429	4.927	0.161	0.101
	TCS	4.555	0.3	0.549	4.713	0.131	0.147

having relatively stronger forces. These results are in conformity with the pH studies in which concluded that the hydrophobic nature of MPTS/BENT attracted TCH/or TCS having stronger forces. Earlier studies reported that increasing NaCl concentration from 0.0 to 0.1 mol/L did not affected significantly the percent removal of TCS by polystyrene microplastic[73]. However, increasing the concentration of NaCl (0.0 to 0.5 mol/L), the amount of tetracycline adsorbed was increased from 132.4 to 172.7 mg/g using activated carbon produced from tomato waste (TAC) which was due to the inability of big tetracycline molecules aggregated at high ionic strength to enter adsorption sites in the pores of TAC in which electrostatic interaction has been overcome by the hydrophobic interaction[74].

Influence of co-ions

The sorption of TCH/or TCS by MPTS/BENT is performed in simultaneous presence of several coexisting ions. The initial concentration of TCH/or TCS is taken as 10.0 mg/L at pH 4.0. The cations are included as Mn(II), Mg(II), Ca(II) and Ni(II) whereas the anions are chosen as ethylenediaminetetraacetic acid, glycine, phosphate and oxalic acid. The concentrations of co-ions were maintained as 50.0 mg/L. The results are presented in (Fig. 6A & B). Results showed that these co-ions have not affected the sorption efficiency of MPTS/BENT for TCH/or TCS, except in presence of EDTA. The presence of EDTA has slightly suppressed the removal efficiency of these two pollutants. Previously, it was reported that presence of EDTA decreased the percentage removal of TCH and TCS[75]. Moreover, Huang *et al*. reported that the presence of 0.01 M (Mg^{2+}, Ca^{2+}, K^+ and Na^+) has a little effect on the removal of TCH by $Fe_3O_4@SiO_2^{-}$chitosan/graphene oxide nanocomposite (MSCG) material[76]. Dou *et al*. also found that the sorption of TCS using MIL-53(Al) and MIL-53(Al)-1 is not affected by the presence of several co-existing ions but only the presence of humic acid (HA) has a little effect on the percentage removal[77].

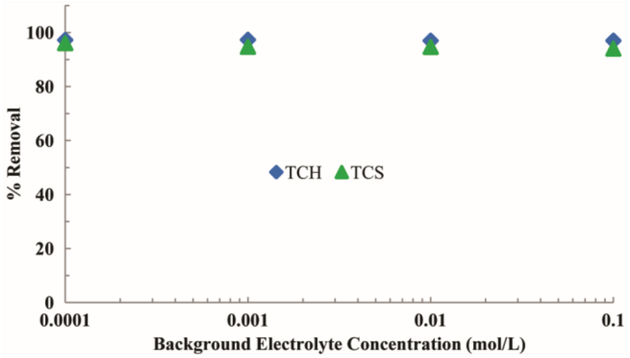

Fig. 5 — Effect of ionic strength in the elimination of TCH and TCS using MPTS/BENT [Initial concentration of TCH/or TCS: 10.0 mg/L (pH: 4.05) at 25°C]

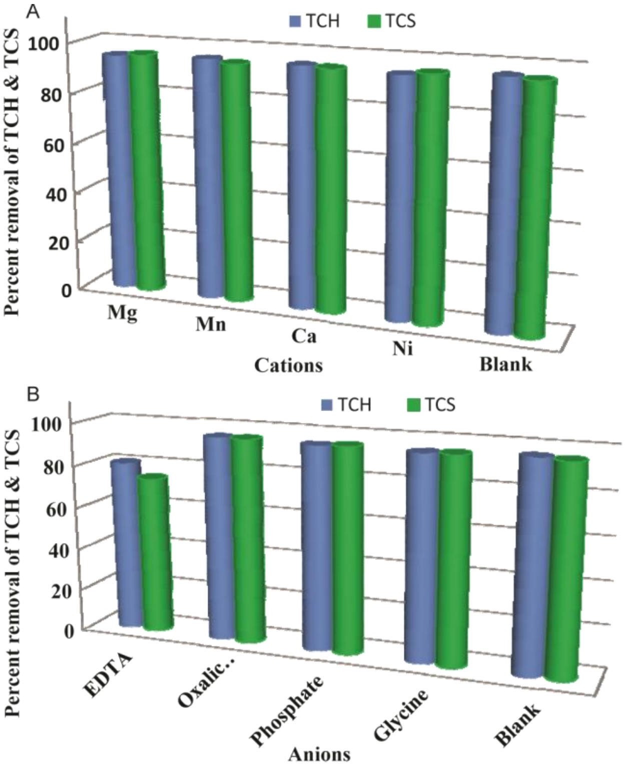

Fig. 6 — Removal of TCH and TCS by MPTS/BENT material in presence of several co-ions (A) cations; and (B) anions [Initial concentration of TCH/TCS: 10.0 mg/L (pH: 4.05); Concentration of co-ions: 50.0 mg/L at 25°C]

Column reactor experiments

Fixed-bed column operations are conducted as to evaluate potential of solid material for the removal of TCH/or TCS under continuous flow system. The breakthrough curves for TCH/or TCS using MPTS/BENT are shown in (Fig. 7). It is noted that a high breakthrough volume were achieved using the MPTS/BENT. The column packed with 0.25 g of the adsorbent show a complete breakthrough volume at throughput volume of 3.01 L for TCH and 2.34 L for TCS. Similarly, a complete breakthrough volume of 6.06 L for TCH and 4.56 L for TCS is obtained using 0.5 g MPTS/BENT solid packed column. Further, breakthrough results are fitted to the Thomas equation[78]. The unknown parameters, Thomas constant K_T, q_0 and least square sum are obtained from the fitting results and shown in (Table 4). The column studies obviously showed that the synthesized composite material (MPTS/BENT) possessed very high loading capacity for the TCH/or TCS under the continuous flow system. Liu *et al*. reported that increasing the bed height of modified silica from 3 to 10 cm for the sorption of TCH in column experiments leads to enhance the removal capacity from 388.5 to 412.7 mg/g[79]. Moreover, hybrid materials precursor to bentonite and local clay *viz*., BH, BAH, LCH and LCAH show high removal capacity 111.979, 97.987, 86.965, 64.996 mg/g of TC under fixed bed column operations[80]. Therefore, the loading capacity of the synthesized materials is comparable to other reported materials and could be efficiently utilized for the removal of TCH and TCS in fixed bed column system.

Removal of TCH/or TCS in real matrix sample

Applicability of MPTS/BENT is performed in the removal of TCH and TCS using real water samples collected from Kawnpui river water, Kolasib District, Mizoram, India. The physico-chemical analysis of river water was conducted and the results are shown as in (Supplementary Table S1).

The pH of river water was found to be 7.45. Analytical results showed that river water contained low levels of Fe, Mn, Ca, and Zn. But, the concentration of Ca is comparatively high and found to be 0.51 mg/L. The concentration of Pb and Cu are negligible. The river water is also subjected to TOC analysis and the data showed that high value of non-purgeable organic carbon (NPOC) and remarkable quantity of inorganic carbon is present. Moreover, very low level of sulfate (1.10 mg) and nitrate (2.0 mg/L) are present in this water sample. River water sample was spiked with the TCH and TCS by maintaining its concentrations at 10.0 mg/L. pH dependent study was conducted and the efficiency of MPTS/BENT is assessed. The percentage removal of TCH/or TCS in real water sample is shown in (Fig. 8). Result showed that the sorption efficiency of TCH or TCS using MPTS/BENT in real water sample is not significantly affected comparing to the removal of these pollutants conducted in double distilled water. Therefore, it can be concluded that the modified material (MPTS/BENT) possessed high selectivity and applicability for elimination of TCH and TCS in real water matrix[34,81].

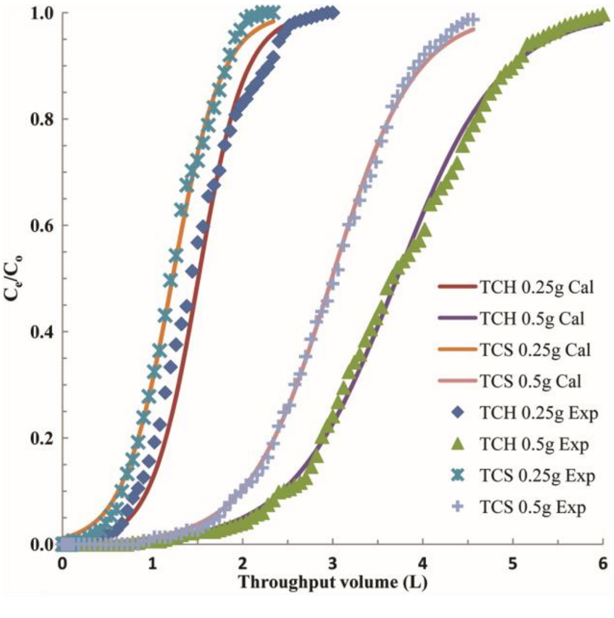

Fig. 7 — Breakthrough curves in the removal of TCH and TCS using MPTS/BENT [Influent concentration of TCH/or TCS: 10.0 mg/L (pH 4.05); Flow rate: 1.0 mL/min]

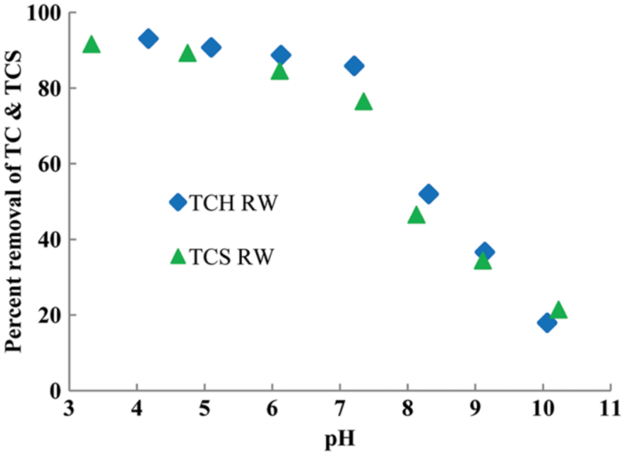

Fig. 8 — Removal of TCH and TCS in real water sample using the MPTS/BENT sample ([TCH/or TCS]: 10.0 mg/L; dose: 2.0 g/L)

Table 4 — Thomas constants for the removal of TCH and TCS by MPTS/BENT material

Weight of the material	Pollutants	Thomas constants		Least square sum (s^2)
		q_o (mg/g)	K_T (L/min/mg)	
0.25 g MPTS/BENT	TCH	60.86	3.82×10^{-4}	1.2
	TCS	49.49	3.6×10^{-4}	1.1
0.5g MPTS/BENT	TCH	75.58	1.69×10^{-4}	1.3
	TCS	60.17	2.16×10^{-4}	1.3

Conclusion

Novel dense composite (MPTS/BENT) material precursor to bentonite and 3-mercaptopropyle trimethoxy silane is synthesized by facile grafting process. The incorporation of organosilane with bentonite is confirmed by FT-IR analysis. SEM images showed the dense and heterogeneous surface of MPTS/BENT and EDX mapping confirmed the presence of sulphur element. Further, BET analysis showed that MPTS/BENT possessed significantly reduced specific surface area compared to pristine bentonite. The MPTS/BENT is employed in the elimination of emerging water pollutants tetracycline hydrochloride and triclosan. The insights of removal process revealed that the uptake of tetracycline hydrochloride and triclosan by MPTS/BENT is primarily preceded through the hydrophobic with enhanced organophilic interactions occurred between pollutants and MPTS/BENT solid. pH dependent sorption of TCH and TCS is almost unaffected within the pH 3.0 to 7.0. Moreover, very high uptake of TCH and TCS is unaffected on increasing the background electrolyte concentration (NaCl) for 1000 times. Rapid uptake of TCH and TCS by MPTS/BENT followed PSO kinetics. Similarly, very high removal efficiency was achieved at wide concentration range (1.0 to 25.0 mg/L) of pollutants. Further, column experiment showed that a significant amount of the pollutants is loaded onto the column. Moreover, the sorption of TCH/ or TCS in real water sample at varied pH values showed that the synthesized MPTS/BENT solid is selective and efficient towards these micro-pollutants.

Conflict of interest

All authors declare no conflict of interest.

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