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Sorptive Removal of Sulphamethoxazole by Modified Clay Materials: Batch and Column Studies

Thanhmingliana¹, C. Lalhriatpuia¹ and Diwakar Tiwari^{2*}

¹Department of Chemistry, Pachhunga University College, Aizawl, Mizoram-796001, (India)

²Department of Chemistry, School of Physical Sciences, Mizoram University, Aizawl, Mizoram-796004, (India)

E-mail: *diw_tiwari@yahoo.com

ABSTRACT—Clay materials were modified using hexadecyltrimethylammonium bromide (HDTMA) or by simultaneous modification with aluminium and HDTMA. The materials were characterized by FT-IR and XRD analytical tools whereas the surface morphology was assessed with FE-SEM images of these solids. The batch data implied that the uptake of SMX by the hybrid materials is slightly reduced at low and high pH within the studied pH range of *ca.* 2.76 - 10.46. The uptake is insignificantly affected by changing the sorptive concentration (from 1.28 mg L⁻¹ to 20.19 mg L⁻¹) and the background electrolyte concentration (0.0001 to 0.1 mol L⁻¹NaCl). Moreover, the sorption of SMX by these hybrid materials is fairly efficient as within 30 mins of contact time, an apparent equilibrium between solid and solution is achieved. The fixed-bed column results showed that relatively high breakthrough volume is obtained for the attenuation of SMX using these hybrid materials, and the loading capacity of SMX is estimated to be 88.99 and 28.87 mg g⁻¹ for the solids BCH and LCH, respectively.

Keywords: Bentonite Clay, Local Clay, Surfactant, Pharmaceutical

INTRODUCTION

The contaminations of aquatic environment by pharmaceuticals products have received increasing attention because of their persistency and toxicity. Many pharmaceutical substances and their metabolites have been recently found at the trace level in the aquatic environment [1]. It is reported that the level of these pollutants is increased significantly in the wastewater treatment plants (WWTPs) effluent, surface water, sewage water, ground water, tap waters or even in the drinking water [2,3]. In addition to the pharmaceutical industries, the human urine and faeces is reported to be additional important and significant sources of increasing the pharmaceutical load in the municipal/ sewage wastewaters since *ca.* 70% of consumed pharmaceuticals are excreted in human urine as active ingredients and metabolites [4]. The level of micro-pollutants in the surface waters is in the range of ng L⁻¹-µg L⁻¹ [5,6]. These micro-pollutants are partially or incompletely degraded/ removed by the WWTPs; therefore, causing a concern of drinking water quality [5,7]. This may results in various direct and indirect toxicological effects

on the environment and on human health. Moreover, many such residual micro-pollutants are found problematic in aquatic ecosystem and potential concern towards human health [8,9].

Sulfamethoxazole (SMX) is a synthetic sulfonamide antibiotic widely applied as a bacteriostatic drug to treat a number of diseases. It is also being used in veterinary practice, aquaculture and livestock breeding both for treating diseases and promoting growth [10]. SMX can persist in the environment for long periods of time because of its low biodegradability, which may result in various, direct and indirect, toxicological effects on the environment and on human health [11]. An increasing number of studies have reported the detection of SMX in ground water, in effluents of WWTPs and in rivers [12,13]. Moreover, the elimination yield of the sulfamethoxazole in WWTPs was only 32-49% when using conventional activated sludge systems and a fixed-bed reactor [1]. SMX has previously been proven by researchers to be persistent to biodegradation [14,15].

In 1999-2000 USGS reconnaissance of US streams, SMX was found at higher concentrations than other sulfonamides (SAs) and was categorized as a persistent anti-biotic [16]. The high frequency of detection and relative persistence of SMX in the water system indicate that this compound is a potential risk to the water supply. Therefore, fundamental research on the elimination of SMX is particularly needed.

In the recent years, diverse technologies have been introduced for the treatment of domestic, municipal and industrial wastewater. The fundamental procedures being used in these innovative wastewater treatment technologies are of physical, chemical and biological in nature [17]. The main priorities for wastewater treatment (WWT) are effluent quality, cost, energy efficiency and nutrient removal/ recovery. A number of technologies are available with varying degree of success to control water pollution. However, most of them require substantial financial input and their use is restricted due to cost factors overriding the importance of pollution control [18]. A number of materials have also been extensively investigated as adsorbents in water pollution control. The choice of adsorbent for the treatment of a specific wastewater with specific chemical pollution characteristics is based on the concentration and type of micropollutants present in the wastewater, the efficiency/ cost ratio and the adsorption capacity of the adsorbent for the pollutant(s) of interest [19].

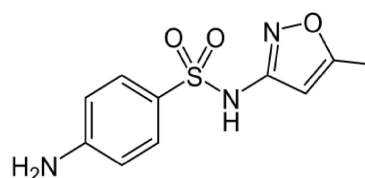
Therefore, modified clays have received widespread attention for their use as adsorbents of organic micropollutants and inorganic ions from aqueous medium because of their easy availability and comparatively less cost. The present study aims to obtain the hybrid materials precursor to the natural bentonite and locally collected clay in an attempt to attenuate the SMX from aquatic environment.

MATERIALS AND METHODS

MATERIALS

Bentonite clay (BC) was obtained from a commercial supplier and it was mined near Bhuj, Gujarat, India. The bentonite clay was not separated anymore and used after simple washing with distilled water and drying at 90°C in a drying oven. Local clay (LC) collected from the field of Phullen, Mizoram, India was having numerous impurities and therefore thoroughly separated using the ISRIC (International Soil Reference and Information Centre) method as detailed elsewhere [20]. The clay samples were crushed in a mortar and sieved to obtain 100 BSS

(British Standard Sieve) mesh size particles (0.150 mm). The cation exchange capacity (CEC) of BC and LC powder were then determined using the USEPA (United States Environmental Protection Agency) method 9080 [21]. The CEC of BC and LC were found to be 69.35 and 46.38 meq/100g of clay, respectively. Hexadecyltrimethylammonium bromide (HDTMA) and Sulphamethoxazole (SMX) were procured from Sigma-Aldrich, USA. Aluminium (III) chloride was obtained from Merck, India. Sodium chloride, Extrapure was obtained from the HiMedia, India. The other chemicals used were of analytical or equivalent grade. The water used was purified using a Millipore water purification system (Milli-Q+).



Structure of SMX

PREPARATION OF ORGANO-CLAY AND INORGANO-ORGANO-CLAY

BC or LC was modified by the usual wet cation exchange process as described earlier [22]. Hexadecyltrimethylammonium bromide (HDTMA) was loaded to saturate 100% of the clay CEC. The HDTMA-modified bentonite and local clay were then labeled as BCH and LCH, respectively. The inorgano-organoclay was prepared by simultaneous pillaring with aluminium and modification with HDTMA to obtain the BC-Al-HDTMA (named as BCAH) or LC-Al-HDTMA (named as LCAH) hybrid materials.

CHARACTERIZATION OF HYBRID MATERIALS

The surface morphology of the materials was obtained by taking the FE-SEM (field emission scanning electron microscope) images of the solids using a FE-SEM machine (Model S-4700, Hitachi, Japan). X-ray diffraction (XRD) data was recorded using an X-ray diffraction machine (PANalytical, Netherland; Model X'Pert PRO MPD). Cu-K α radiations having wavelength 1.5418 Å was used for X-ray diffraction analysis. FT-IR (Fourier Transform-Infra Red) data was collected by using a FT-IR machine (Bruker, Tensor 27, USA by KBR disk method). The pH_{pzc} (point of zero charge) of the materials was determined by the batch pH drift method as detailed elsewhere [23].

BATCH REACTOR EXPERIMENTS

A stock solution (100 mg L⁻¹) of SMX was prepared by dissolving an appropriate amount of SMX into purified water. Further, the required SMX concentration was obtained by successive dilution of stock solution. The pH dependence sorption data was obtained as follows: a series of 10.0 mg L⁻¹ of SMX solution (50ml) was taken into polyethylene bottles and the pH was adjusted by dropwise addition of conc. HCl/NaOH solutions. 0.1 g of the solid sample was introduced into these solutions. The bottles were kept in an automatic incubator shaker (Incubator Shaker, TM Weiber, ACMAS Technologies Pvt. Ltd., India) for 24 hours at 25±1°C. The bottles were then taken out from the shaker and solution mixture was filtered with 0.45 µm syringe filter and the pH was again checked and reported as equilibrium pH. Absorbance of the filtrates was measured using UV-Visible Spectrophotometer (Model: UV1, Thermo Electron Corporation, USA). The absorbance was recorded at 265 nm. Calibration curve was obtained using standard SMX solutions having varied concentrations. Results were presented as percent SMX removed as a function of equilibrium pH. The blank SMX (10.0 mg L⁻¹) solutions were shaken without the hybrid materials in the polyethylene bottles for 24 hours. No decrease in absorbance was observed, which indicated that negligible sorption was occurred to the polyethylene bottles.

The concentration dependence study was performed by varying the SMX concentrations from 1.28 to 20.19 mg L⁻¹ at constant pH ~ 7.0 and at constant temperature 25±1°C. The adsorption process was followed as detailed above. Results were presented as percent SMX removed as a function of initial SMX concentration (mg L⁻¹). Time dependence sorption of SMX by these hybrid materials was obtained at different time intervals. Initial SMX concentration of 10.0 mg L⁻¹ with a solid dose of 2.0 g L⁻¹ was taken as constant and the sorption experiments were conducted at constant pH ~7.0 and temperature 25±1°C. Results were then reported as percent SMX removed as a function of time (min.). Effect of background electrolyte concentration on the sorption of SMX was studied by varying NaCl concentration from 0.0001 to 0.1 mol L⁻¹ with SMX concentration of 10.0 mg L⁻¹. The solution pH (~7.0) and temperature (25±1°C) was kept constant throughout the experiments. Results were presented as percent SMX removed as a function of background electrolyte (NaCl) concentrations.

FIXED-BED COLUMN EXPERIMENTS

Fixed-bed column experiments were conducted using a glass column (1 cm inner diameter) packed with 0.25 g of

hybrid materials (kept middle in the column). Below and above the hybrid material, 1.0 g of sand (14–16 BSS) was placed and the rest of the column was packed with glass beads. SMX (10.0 mg L⁻¹) solution at pH ~7.0 was pumped upward from the bottom of the column using a peristaltic pump (KrosFlo Research I Peristaltic Pump, Spectrum Laboratories Inc., California, USA), at a constant flow rate of 1.0 mL min⁻¹. Effluent solution was collected using a fraction collector (Spectra/Chrom CF-2 Fraction Collector, Spectrum Laboratories Inc., California, USA). The collected effluents were filtered with 0.45 µm syringe filter and absorbance of the filtrate was measured with UV-Vis Spectrophotometer.

Column breakthrough data obtained were further utilized to optimize the loading capacity of SMX by the hybrid materials under the dynamic conditions employing Thomas equation [24]:

$$\frac{C_e}{C_o} = \frac{1}{1 + e^{(K_T(q_o m - C_o V))/Q}} \quad (i)$$

where C_e and C_o are the concentrations (mg L⁻¹) of effluent and influent solutions of SMX, respectively; K_T refer to the Thomas rate constant (L min⁻¹ mg⁻¹); q_o is the maximum amount (mg g⁻¹) of SMX loaded under the specified column conditions; ' m ' is the mass (g) of hybrid materials taken in the column; V is the throughput volume (L); and Q is the flow rate (L min⁻¹) of pumped SMX solution. The column data were fitted to a non-linear Thomas equation using the least square fitting method to estimate the two unknown parameters, K_T and q_o .

RESULTS AND DISCUSSION

CHARACTERIZATION OF MATERIALS

FT-IR data have shown that the hybrid materials, viz., BCH, BCAA, LCH or LCAH possessed prominent IR stretching bands at around the wave numbers 2930 cm⁻¹ and 2850 cm⁻¹ which were considered as -CH₂ asymmetric and symmetric stretching vibrations, respectively. This confirmed the introduction of HDTMA within the clay network for all these hybrid materials. X-ray diffraction analysis showed that both the clay samples contain quartz, smectite, illite and kaolinite minerals with varying composition. The XRD patterns of the modified clay samples are almost identical to the pristine clay, with a slight change in d -values and intensities of the peaks. The FE-SEM images clearly indicated that the organo-modified clay (i.e., BCH or LCH) solids showed more heterogeneous surface structures. BCAA and LCAH solids also showed similar heterogeneous surface structure,

although they contain new particles on the surface which were possibly aggregated/ immobilized aluminium oxide/ hydroxide. Detailed characterization of these materials has been described previously [22,23].

BATCH REACTOR OPERATIONS

EFFECT OF PH

The pH dependence removal of SMX (pH 2.76 to 10.46) by these solids is presented graphically in Fig. 1. It is observed that a very high uptake of SMX is achieved at the studied pH range, although a slightly lower sorption is observed at very low and high pH. The uptake of SMX by these solids could be ascribed with the help of speciation of SMX as well the surface properties of the solids. It is reported that SMX is having the acid dissociation constant (pK_a) of 1.6 and 5.7 [25], which indicated that SMX molecule existed as a neutral molecule almost up to pH ~ 5.7 and carried a net negative charge above this pH. On the other hand, the pH_{pzc} value of these solids is found to be 9.8, 8.2, 6.1, 5.8, 5.1 and 5.1 for the samples BC, BCH, BCAH, LC, LCH and LCAH, respectively. This implied that except BC and BCH solid, other materials possessed a net negative charge at and around neutral pH. Hence, the possible mechanism of SMX uptake by these hybrid materials is primarily demonstrated by the fact that the introduction of organic cation (HDTMA) within the clay network caused to enhance the hydrophobicity organophilic nature of the surface. This enabled SMX to partition at the introduced hydrophobic core. On the other hand; BCAH and LCAH solid showed slightly less uptake of SMX compare to their corresponding HDTMA-modified samples (i.e., BCH and LCH respectively), possibly, due to the screening of the introduced HDTMA molecule by the presence of aluminium oxide/ hydroxide particles onto the solid surface. Hence, this could reduce the hydrophobic core within the clay network. Further, the removal of SMX is decreased to some extent with increasing the solution pH to 10.0 which might be due to acidic dissociation of SMX, which caused for some electrostatic repulsion and hence reduced in partitioning of SMX within the hydrophobic core of the hybrid materials. Further, BC based solids showed lower percent removal compare to LC based solids which is possibly due to lower smectite content in the clay material. It was reported previously that the organoclays prepared with longer chain surfactant molecule were less influenced by the solution pH [26]. Further, hybrid materials obtained by modifying the natural sericite with HDTMA and

alkyldimethylbenzylammonium chloride were used in the remediation of wastewaters contaminated with BPA, and the increase in pH from *ca.* 2.0 to 10.0 did not significantly affect the percentage uptake of BPA by the hybrid materials [23]. It is also noted that the virgin bentonite and local clay showed very insignificant uptake of SMX which is further decreased at low and high pH.

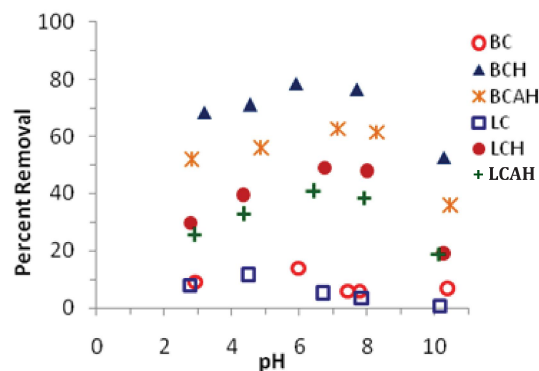


Fig. 1: Effect of pH on the Removal of SMX

EFFECT OF INITIAL SMX CONCENTRATION

Studying the effect of initial sorptive concentration is one of the effective factors for estimating the sorption capacity of the materials. The sorption of SMX obtained as a function of initial sorptive concentrations (1.28 to 20.19 $mg\ L^{-1}$) are presented in Fig. 2. The figure revealed that on increasing the initial concentration of SMX, the percent uptake is not significantly affected. These results again indicated the affinity of the hybrid materials towards the attenuation of SMX. A slightly lower removal of SMX is observed with the local clay based solids. The results are consistent with the pH dependence study.

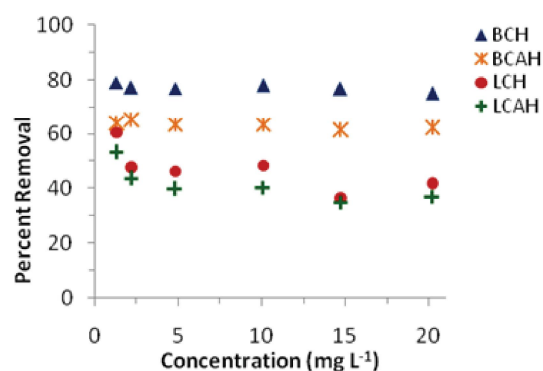


Fig. 2: Effect of Initial SMX Concentration on the Removal of SMX

EFFECT OF BACKGROUND ELECTROLYTE CONCENTRATION

Effect of background electrolytes in the sorptive removal of SMX by the hybrid materials could help to explain the mechanism involved at solid/ solution interfaces. The specific sorption is usually not much influenced by the change in background electrolyte concentrations; whereas the non-specific sorption is greatly influenced by the change in background electrolyte concentrations [27]. The percent removal of SMX obtained as a function of background electrolyte (NaCl) concentrations are shown graphically in Fig. 3. The results showed that increasing the background electrolyte concentrations even up to 1000 times could not significantly affect the percent uptake of SMX by the hybrid materials, i.e., BCH, BCAH, LCH and LCAH. This indicated the affinity of solids towards SMX. Again, this implied that the partitioned SMX is bound with relatively stronger van der Waals forces which retained firmly the SMX molecule onto or within the interspace of hybrid materials. Previously, it was reported that the increase in the NaCl concentration from 0 to 320 mM did not significantly change the adsorption of 17 α -ethinylestradiol (EE2) from landfill leachate onto single-walled carbon nanotubes (SWCNTs)[28].

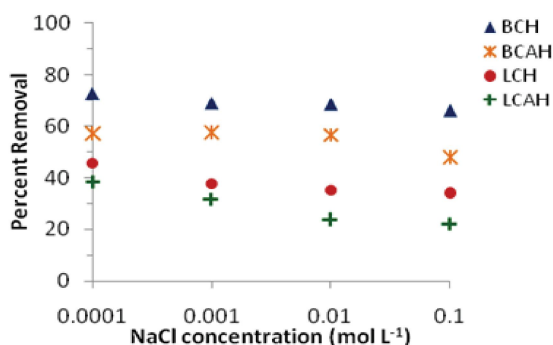


Fig. 3: Effect of Background Electrolyte (NaCl) Concentrations on the Removal of SMX

TIME DEPENDENCE REMOVAL

The percent of SMX removed as a function of time is plotted in Fig. 4. It is evident from the figure that the materials are efficient in the removal of SMX from aqueous solutions since within initial 10-15 mins of contact, the uptake is very fast which is then gradually increased and an apparent equilibrium is achieved within *ca.* 30 mins. This again reaffirmed the affinity of these solids towards SMX. However, it is observed that the uptake of SMX onto the LC based solid is comparatively slower/ lower compare to the other hybrid materials.

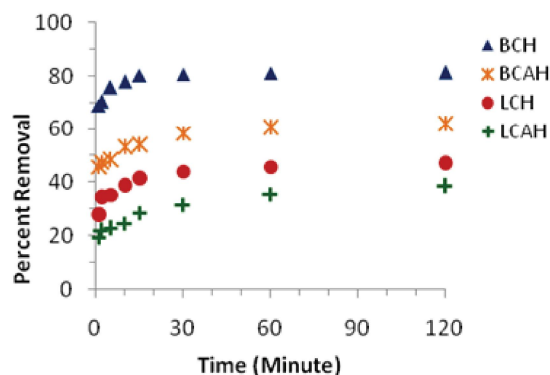


Fig. 4: Effect of Contact Time on the Removal of SMX

FIXED-BED COLUMN REACTOR OPERATIONS

Fixed-bed column operations were performed to assess the loading capacity of the hybrid materials BCH and LCH for SMX under the dynamic conditions. The column experiments were carried out with the stated column conditions. The breakthrough curves obtained are presented graphically in Fig. 5. This revealed that relatively high breakthrough volume is obtained for SMX by these solids. A complete breakthrough is achieved at the throughput volume of 3.18 L and 1.20 L, respectively for the BCH and LCH solids. The relatively high values of breakthrough volumes indicated the high removal capacity of SMX by the modified solids under the dynamic conditions. This further showed that the modified solids could be potential and promising sorbing materials for the removal of SMX.

Further, the non-linear least square fitting is conducted with the breakthrough column data employing the Thomas equation (Eq. i). The fitting is performed to simulate the two unknown parameters, i.e., K_T and q_o . The values of Thomas constants along with the least square sum are estimated and returned in Table 1. These results indicated that a high loading capacity is achieved for SMX by these solids under the dynamic conditions. Relatively, BCH showed higher removal capacity for SMX compare to the LCH solid. It is further noted that although LCH showed lower removal capacity for SMX, the locally collected clay could be a useful natural material to be exploited in the efficient and effective remediation of wastewater contaminated with SMX. These results are similar to the findings of batch reactor experiments. Also, the results are in a line of other reports in which the Thomas equation is utilized to demonstrate the loading capacity of different sorbing materials [22,29].

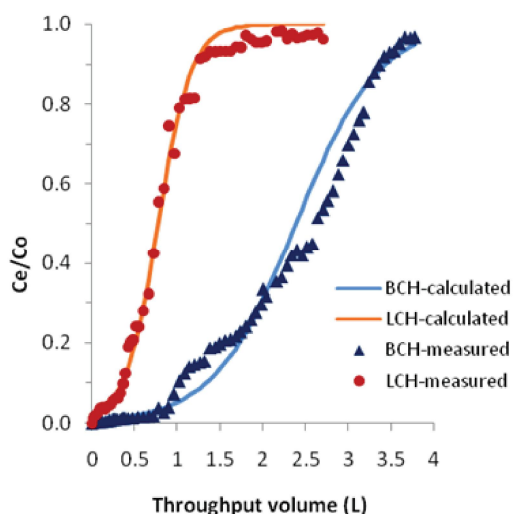


Fig. 5: Breakthrough Curves for the Removal of SMX

Table 1: Thomas Constants (along with the Least Square Sum) Estimated for the Removal of SMX by BCH and LCH

Materials	Thomas Constants		Least Square Sum (s ²)
	$K_t \times 10^{-4}$ (L min ⁻¹ mg ⁻¹)	q_0 (mg g ⁻¹)	
BCH	88.99	2.25	12.0
LCH	28.87	5.57	10.0

CONCLUSION

The organo-modified clay and inorgano-organo-modified clay materials, precursor to the natural bentonite and local clay was synthesized and characterized by the IR and XRD analysis. The IR data show that the HDTMA is well introduced within the clay network. The XRD analysis indicates the presence of quartz, smectite, kaolinite and illite (having varied percentage) with these two clay samples, i.e., bentonite and local clay. SEM images of the modified solids show the heterogeneous structures of HDTMA modified clay materials whereas Al-pillared solids show that additional fine particles of aluminium hydroxides or Al₂O₃ are aggregated onto the clay surface. Further, the materials are utilized for the remediation of SMX contaminated waters under the batch and column reactor operations. The batch data implies that the uptake of SMX by the hybrid materials is slightly reduced at low and high pH within the studied pH range of 2.76 -10.46. The uptake is insignificantly affected by changing the sorptive concentration (from 1.28 mg L⁻¹ to 20.19 mg L⁻¹) and the background electrolyte concentration (0.0001 to 0.1 mol L⁻¹ NaCl). Moreover, the attenuation of SMX by these hybrid materials is fairly efficient as within 30 min of contact time, almost an apparent equilibrium

between solid and solution is achieved. The fixed-bed column results show that relatively high breakthrough volume is obtained for attenuation of SMX using the hybrid materials. Further, the breakthrough data are fitted well to the Thomas equation and hence, the loading capacity of SMX is estimated to be 88.99 and 28.87 mg g⁻¹ for the solids BCH and LCH, respectively. Therefore, this investigation suggests that the hybrid materials obtained from bentonite and local clay must be an useful material in the remediation of water contaminated with SMX.

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