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## ORIGINAL ARTICLE

# Preparation of organophilic montmorillonite-based dimethylamino benzaldehyde-Schiff-base as antibacterial agents

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## KEYWORDS

Antimicrobial activities;  
Montmorillonite;  
*p*-N,N-dimethylamino  
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Water treatment;  
Schiff bases

**Abstract** New antibacterial composites were synthesized by modification and functionalization of montmorillonite (MMT). The antibacterial composites were synthesized by the reaction of MMT clay with the quaternary salt of *p*-N,N-dimethylamino benzaldehyde which produced modified functionalized montmorillonite composite in the form of Schiff bases. The Schiff bases (**4–11**) were obtained by the reaction of functionalized montmorillonite with various amines namely *o*-anisidine, anthranilic acid, *p*-carboxy aniline, *p*-methyl aniline, *p*-methoxy aniline, *p*-hydroxy aniline, *p*-nitro aniline and *p*-phenylene diamine. The structures of the newly prepared composites were elucidated by Fourier transform infra red (FT-IR), thermal gravimetric analysis (TGA) and X-ray diffraction (XRD). The antibacterial activities of these composites were investigated by the ‘cut plug’ method against Gram-negative bacteria such as *Escherichia coli*, *Serratia marcescens*, *Enterobacter cloacae*, *Shigella dysenteriae*, *Salmonella enterica* and *Proteus vulgaris*, and Gram-positive such as *Bacillus subtilis* and *Staphylococcus aureus* which showed high antimicrobial activities at relatively low concentrations (2.5–20 mg/mL). These promising results pave the way in the future to use the newly synthesized composites as antibacterial agents for water treatment against pathogenic bacteria which exist in polluted water courses.

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## 1. Introduction

Montmorillonite (Sodium MMT) is an aluminosilicate clay with layer structure of a 2:1 (molar ratio) containing exchangeable cations Na<sup>+</sup> and Ca<sup>2+</sup>. MMT has been used as a carrier for functional materials because it is well known that it has high exchange capability, swelling behavior, high surface area, and excellent absorptivity. MMT silicate layers are separated by a van der Waals gap, occupied by hydrated alkaline or alkaline-earth metal cations. The hydrophilic MMT

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becomes hydrophobic or organophilic when the metal cations are replaced with onium such as alkyl ammonium cation through ion exchange reaction (Zanetti et al., 2000; Lebaron et al., 1999).

In the last years, academics and industries gave great attention to organocatalyst (Bergaya and Lagaly, 2001; Ray and Okamoto, 2003; Vijayalekshmi, 2015; Salahuddin et al., 2012; Xu et al., 2011; Melinte et al., 2015; Xie et al., 2011; Abreua et al., 2015; Sedaghat et al., 2014; Yu-shan et al., 2010). The antibacterial activities of organic modified MMT have attracted the attention due to the advantages of this system. Some results showed that natural layered silicates have little antibacterial effect. However, these systems have dual functions of adsorbing and killing bacteria specially when interacted with materials having antimicrobial activity.

Schiff bases are produced from the condensation of primary amines with carbonyl groups and they have broad spectrum of biological activities (Singh and Pandey, 2012; Ceyhana et al., 2011; Patel et al., 2014; Siddique et al., 2013; Bedia et al., 2006; Bagihalli et al., 2008).

The present work reports the synthesis of Schiff bases of the modified MMT hoping to develop antibacterial activities of the prepared composites. The MMT-Schiff bases (4–11) were obtained by the reaction of MMT composite with various amines namely *o*-anisidine, anthranilic acid, *p*-carboxy aniline, *p*-methyl aniline, *p*-methoxy aniline, *p*-hydroxy aniline, *p*-nitro aniline and *p*-phenylene diamine.

The biological activities of the newly synthesized composites were tested against *Escherichia coli*, *Serratia marcescens*, *Enterobacter cloacae*, *Shigella dysenteriae*, *Salmonella enterica* and *Proteus vulgaris* as Gram-negative bacteria, and *Bacillus subtilis* and *Staphylococcus aureus* as Gram-positive bacteria, at concentrations (2.5–20 mg/mL) using the 'cut plug' method.

## 2. Experimental

### 2.1. Materials

Montmorillonite with cation exchange capacity (CEC) of 114.8 meq/100 g was obtained from Southern Clay Products, Texas, USA, and *o*-anisidine, anthranilic acid, *p*-carboxy aniline, *p*-methyl aniline, *p*-methoxy aniline, *p*-hydroxy aniline, *p*-nitro aniline and *p*-phenylene diamine were purchased from Sigma-Aldrich (USA).

Bacteria used in this study were obtained from Bacteriology Unit, Faculty of Science. Gram-negative bacteria used in this study were *Escherichia coli* (NCIM2065), *Serratia marcescens* (W1765), *Enterobacter cloacae* (NCTC10005), *Shigella dysenteriae* (Type1), *Salmonella enterica* (DT104BN9181) and *Proteus vulgaris* (CIP103181T). Gram-positive bacteria used were *Bacillus subtilis* (PC1219) and *Staphylococcus aureus* (ATCC25292).

### 2.2. Characterization techniques

Bruker (Tensor 27) spectrophotometer using KBr Pellet was used to record the FT-IR spectra with a spectrum of wave number range of 4000–600  $\text{cm}^{-1}$ . GNR, APD 2000 PRO step scan X-ray diffractometer was used to record the XRD pattern at room temperature using Cu-K radiation (generator setting of 40 kV and 30 mA), scanning range of  $2\theta$  (5–35°). The thermal gravimetric analysis (TGA) was carried out using Perkin-Elmer simultaneous thermal analyzer (TG/DTA), and the samples were heated from 40 °C to 820 °C with a heating rate of 10 °C  $\text{min}^{-1}$ .

### 2.3. Modification of MMT clay with quaternized *p*-N,N-dimethylamino benzaldehyde

MMT (5 g) was dispersed into hot distilled H<sub>2</sub>O (200 mL) with stirring for 3 h at 60 °C. A solution of *p*-N,N-dimethylamino benzaldehyde (1 mol, 5.76 g) in methyl iodide (2 mol, 5 mL) was added to the swelled MMT for 36 h at 70 °C with stirring. The obtained composite was filtered and then washed by water to yield aldehyde functionalized MMT (Scheme 1).

### 2.4. Synthesis of Schiff bases of the quaternized *p*-N,N-dimethylamino benzaldehyde modified MMT with various amines (4–11)

Aldehyde functionalized MMT (10 m mole) was stirred and heated for 3 h with various amines (10 m mole) in ethanol and piperidine as a catalyst, and the precipitate was filtered, and washed by ethanol to give the Schiff base products.

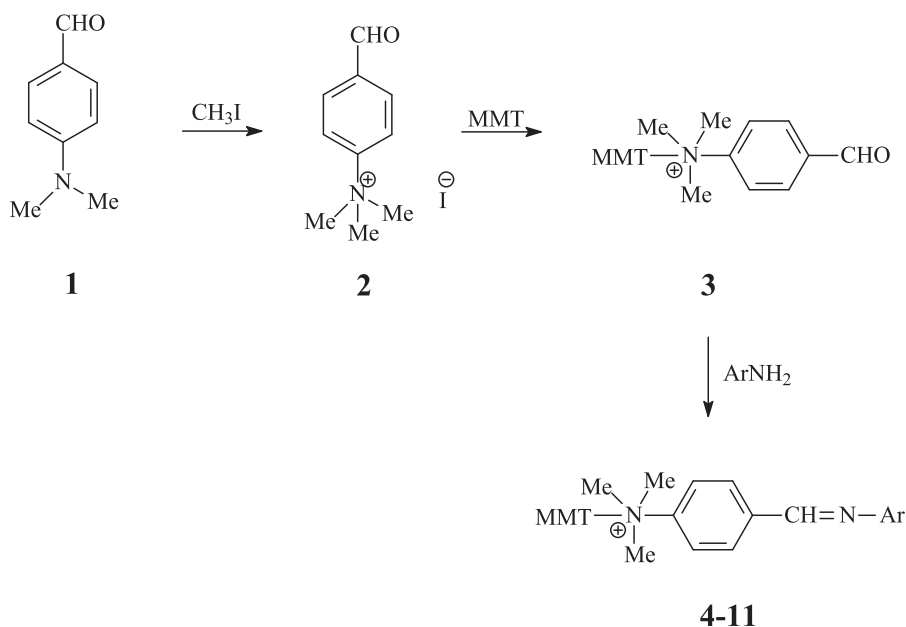
### 2.5. Antibacterial activities evaluation

Antibacterial activities of the synthesized composites were determined according to 'cut plug' method previously described in the literature (Pridham et al., 1956). Cultures were grown on nutrient agar containing the following: peptone (10 g L<sup>-1</sup>), NaCl (5 g L<sup>-1</sup>), beef extract (5 g L<sup>-1</sup>) and agar (20 g L<sup>-1</sup>). Plates were seeded with the test microbes, and filled the wells with composites (20 mg) and then incubated at 37 °C for 24 h. Inhibition zone diameters were measured and compared with two reference antibiotics (Ampicillin and Gentamicin 5 µg/mL).

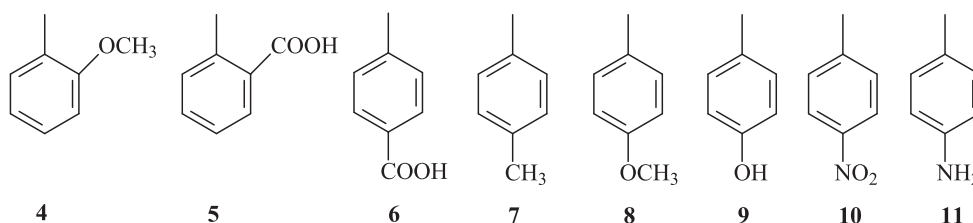
Composites that produced relatively high inhibition zones were quantified by their inhibitory effects (MIC) at different concentrations.

Antibacterial activities of the synthesized composites were assessed using the previously described method (Nakashima et al., 1987), where a loop full of each culture was placed in 10 mL of tenfold diluted broth, which was then incubated overnight at 37 °C. These liquid cultures were then used for the antibacterial testing. The prepared composites were suspended in sterilized nutrient broth medium in the concentration 0.05 g L<sup>-1</sup>. 0.5 mL was then transferred to flasks containing sterilized nutrient broth, diluted 10 $\times$ , to give the concentrations of 0.0, 2.5, 5.0 and 10.0 mg/mL. The culture (0.2 mL) containing 6  $\times$  10<sup>6</sup> bacterial cells/mL was added to the above biocide suspension (10 mL) which was shaken at 37 °C.

Diluted nutrient broth (10 mL) was added to the same culture (0.2 mL), and the spread plate method was used to count the starting number of cells. After 24 h, aliquots (1.0 mL) were removed and mixed with the diluted nutrient broth (9.0 mL) and then decimal serial dilutions were made from these dilutions and the surviving was counted. Plates were inoculated at 37 °C and the number of colonies was counted after 24 h. The ratio was made in triplicate every time. The ratio of colony numbers for the media containing the composites (*M*) and those without these compounds (*C*) was taken as surviving cell number.



Where Ar:



**Scheme 1** Schiff base synthesis of the modified MMT with *p*-N,N-dimethyl benzaldehyde.

### 3. Results and discussion

#### 3.1. Modification of MMT

Recently, we reported the synthesis and antimicrobial activity of a series of biologically active compounds such as  $\alpha$ -aminophosphonates and modified chitosan (Abdel-Megeed et al., 2012a, 2012b, 2012c, 2012d, 2013; Kenawy et al., 2015, 2005; El-Newehy et al., 2014).  $\alpha$ -aminophosphonates are analogous to  $\alpha$ -amino acids in which the carboxylic group is replaced by phosphonic acid group and can be integrated in the microbial metabolism as a substitute for amino acids, and as they are in a different shape they cause the destruction of microbial cells. Similarly modified chitosan, which is biocompatible and biodegradable, showed a similar activity to the  $\alpha$ -aminophosphonates. Following these results we reasoned that clays such as sodium montmorillonite (MMT), currently used in the absorption of heavy metal and organic contaminants, could be modified to increase the antibacterial activity.

Sodium montmorillonite (MMT) clay was functionalized by introducing aldehyde group on MMT by reacting it with the quaternary salt of *p*-N,N-dimethylamino benzaldehyde to yield aldehyde functionalized-MMT. The latter was reacted with various amines namely *o*-anisidine, anthranilic acid, *p*-carboxy aniline, *p*-methyl aniline, *p*-methoxy aniline,

*p*-hydroxy aniline, *p*-nitro aniline and *p*-phenylene diamine to give Schiff bases (4–11) (Scheme 1).

The structures of the newly synthesized composites were confirmed by Fourier transform infra red (FT-IR), X-ray diffraction (XRD) and thermal gravimetric analysis (TGA).

The FT-IR spectrum of Na-MMT is characterized by the absorption band at  $3452\text{ cm}^{-1}$  due to the stretching vibration of Al–OH. The band at  $1048\text{ cm}^{-1}$  is due to symmetrical Si–O–Si. Other characteristic bands at 919 and  $524\text{ cm}^{-1}$  are due to the stretching vibration of Al–Al–O and Si–O–Al respectively (Abdeen, 2014).

The FT-IR spectrum of the modified clay with *p*-N,N-dimethyl amino benzaldehyde showed the band at  $2906\text{ cm}^{-1}$  due to the stretching vibration of C–H bond of the N–CH<sub>3</sub> group and the absorption band at  $1662\text{ cm}^{-1}$  due to C=O group.

The FT-IR spectra of the Schiff bases (4–11) are characterized by the presence of absorption bands within the region  $1606\text{--}1587\text{ cm}^{-1}$  corresponding to the stretching vibrations of the azomethine (C=N group) groups (Table 1).

The interlayer spacing of the silicate layers was confirmed using X-ray diffraction (XRD). The intercalated structure should result in an increase in the *d* spacing and a decrease in the  $2\theta$  value. The XRD patterns of composites (3–11) show that the basal spacing increased in comparison with Na<sup>+</sup>-MMT. The XRD pattern of Na<sup>+</sup>-MMT appeared at

**Table 1** IR spectral data of Na<sup>+</sup>-MMT and composites (3–9) (KBr, cm<sup>-1</sup>).

Compound	Band assignment					
	$\nu$ Al–OH	$\nu$ C–H	$\nu$ C=N	$\nu$ Si–O–Si	$\nu$ Al–Al–O	$\nu$ Si–O–Al
Na <sup>+</sup> -MMT	3452	–	–	1048	919	524
3	3444	2911	–	1046	921	521
4	3415	2943	1598	1027	939	517
5	3448	2929	1587	1046	918	521
6	3423	2924	1600	1039	927	521
7	3444	2922	1589	1046	918	522
8	3423	2925	1606	1044	919	521
9	3423	2926	1597	1043	917	521
10	3480	2927	1596	1046	919	522
11	3426	2932	1605	1046	919	521

**Table 2** The XRD pattern data of Na<sup>+</sup>-MMT and composites (3–11).

Sample	2 $\theta$ (°)	<i>d</i> spacing (Å)
Na <sup>+</sup> -MMT	6.90	12.80
3	6.39	13.83
4	6.42	13.76
5	6.14	14.37
6	6.15	13.90
7	6.35	13.91
8	6.40	13.79
9	6.06	14.56
10	6.54	13.50
11	6.84	12.91

**Table 3** The total mass loss of Na<sup>+</sup>-MMT and composites (3–11).

Sample	Mass loss (%)
Na <sup>+</sup> -MMT	17
3	40
4	65
5	36
6	37
7	40
8	25
9	34
10	33
11	35

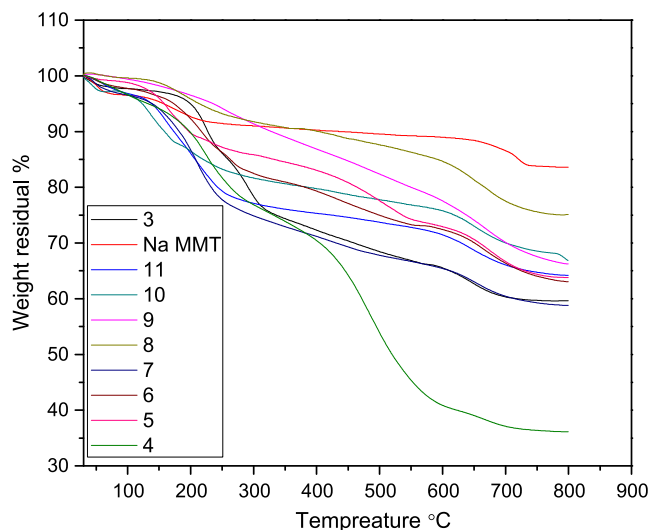
$2\theta = 6.90^\circ$  and this peak in composites (3–11) was shifted to a lower angle for all the compounds. The *d* spacing was also increased with composites (3–11) over than that of Na<sup>+</sup>-MMT (Table 2).

The thermal gravimetric analysis (TGA) for pure Na-MMT showed two significant reductions in weight, the first at 120–140 °C, presumably due to evaporation of the free water. The second was observed between 510 and 730 °C which was assigned to the OH group release from different positions of the MMT structure (Abdeen, 2014).

Three stages of weight loss were observed for the modified clay (3). The first, below 125 °C, demonstrated the release of free water molecules. Between 180 and 590 °C is associated with the decomposition of the intercalated quaternary salt of *p*-N,N-dimethylamino benzaldehyde in the clay mineral. In the last stage of weight loss in the temperature range of 640–750 °C, the structural water that is bound with the hydroxyl groups starts to be released on decomposition of the hydroxyl groups. Pure Na-MMT is the most stable; it showed total low mass loss of 17% compared to other composites. The total mass loss of the modified clay Schiff base (4–11) is listed in Table 3 and Fig. 1.

### 3.2. Antibacterial activity of the modified MMT

The following microorganisms were selected for investigation because of their effect on water and human health. These included the Gram-negative bacteria, *Escherichia coli*, *Serratia marcescens*, *Enterobacter cloacae*, *Shigella dysenteriae* (shigellosis), *Salmonella enterica* (salmonellosis) and *Proteus vulgaris*.

**Figure 1** TGA plots of Na<sup>+</sup>-MMT and composites (3–11).

The Gram-positive bacteria that were used in this study were *Bacillus subtilis* and *Staphylococcus aureus*.

#### 3.2.1. Inhibition zone testing of the modified MMT clays

The synthesized composites (4–11) were screened for their antibacterial activities and the inhibition zones were recorded as listed in Table 4.

**Table 4** Antibacterial activity (inhibition zones mm) of Na<sup>+</sup>-MMT and composites (3–11)<sup>a</sup>.

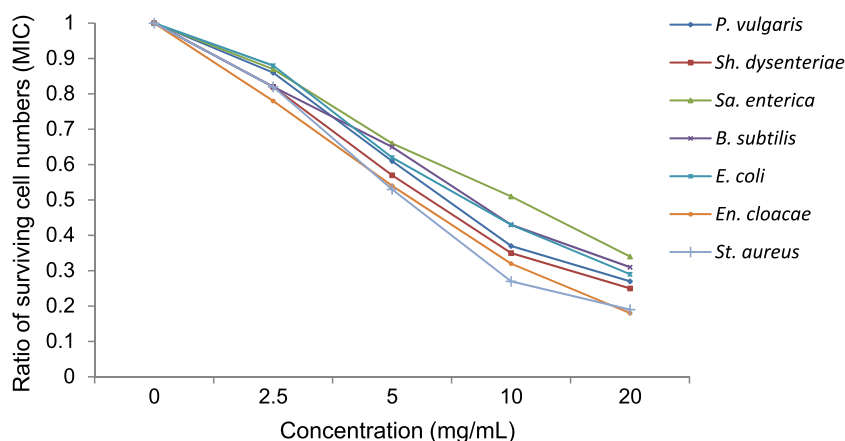
Cpd.	<i>P. vulgaris</i>	<i>S. dysenteriae</i>	<i>S. enterica</i>	<i>B. subtilis</i>	<i>E. coli</i>	<i>S. marcescens</i>	<i>E. cloacae</i>	<i>S. aureus</i>
1	–	–	–	–	10.0 ± 0.0	10.0 ± 0.0	18.0 ± 0.0	–
2	0	–	–	–	16.0 ± 0.0	–	–	–
3	17.7 ± 2.1	17.3 ± 0.6	–	–	15.0 ± 0.0	–	23.7 ± 0.3	17.7 ± 1.1
4	–	–	–	–	16.0 ± 0.0	–	17.3 ± 0.7	12.7 ± 0.3
5	–	–	22.0 ± 0.0	–	18.0 ± 0.0	24.0 ± 0.0	26.7 ± 1.5	20.7 ± 0.3
6	32.5 ± 1.0	22.0 ± 1.5	23.9 ± 0.7	24.3 ± 1.0	21.2 ± 0.5	26.2 ± 0.5	24.5 ± 0.2	29.5 ± 0.4
7	–	–	18.3 ± 1.1	23.0 ± 0.0	–	–	17.0 ± 0.2	16.5 ± 0.6
8	22.0 ± 0.2	–	16.6 ± 0.3	22.6 ± 0.2	19.5 ± 0.4	24.7 ± 0.7	18.4 ± 0.4	18.8 ± 0.2
9	22.1 ± 1.1	15.8 ± 0.2	22.8 ± 0.1	23.9 ± 0.2	17.3 ± 0.0	–	16.4 ± 0.7	15.0 ± 0.0
10	20.7 ± 0.3	16.6 ± 1.1	20.7 ± 0.3	16.7 ± 0.5	22.4 ± 1.5	17.7 ± 0.4	31.6 ± 1.8	16.1 ± 0.6
11	19.3 ± 1.1	19.3 ± 1.5	19.3 ± 1.1	21.7 ± 0.3	19.7 ± 0.4	23.5 ± 1.1	18.8 ± 0.6	19.5 ± 0.7
Gentamicin	35.0 ± 0.0	34.0 ± 0.0	25.0 ± 0.0	25.0 ± 0.0	24.0 ± 0.0	25.0 ± 0.0	26.0 ± 0.0	30.0 ± 0.0
Ampicillin	34.0 ± 0.0	26.0 ± 0.0	–	–	–	–	–	30.0 ± 0.0

<sup>a</sup> DMSO was added to different organisms as control and showed no inhibition zone.

The results showed that unmodified MMT has no antibacterial activity, and it seems clear that it has become a necessity to be tailored to become rightfully lethal to pathogenic bacteria. It seems clear from the range of activity observed, that the Schiff base is not basically antibacterial, while all modified MMT compounds showed reasonable antibacterial activity. Apparently, composites **6**, **10** and **11** have established outstanding inhibition zone against all the studied Gram-negative and Gram-positive bacterial strains. The highest inhibition zone diameter, possessed by these composites, was obtained with *Proteus vulgaris* (32.5 mm) and *Enterobacter cloacae* (31.6 mm) for the preceding composites on succession. The mentioned composites showed an inhibition zones similar to what was produced by the control antibiotics: Gentamicin and Ampicillin. Composites **8** showed broad spectrum antibacterial activity against all the studied strains, except *Shigella dysenteriae*. The highest inhibition zone diameter was obtained with the bacterium *Serratia marcescens* (24.7 mm). Also, composites **9** showed antibacterial activity against all the studied strains, except *Serratia marcescens*. The highest inhibition zone diameter was obtained against the bacterium *Bacillus subtilis* (23.9 mm). Composites **5** and **7** showed no antibacterial effect

against *Proteus vulgaris* and *Shigella dysenteriae*. In addition, composite **7** has no antibacterial activities against *Escherichia coli* and *Serratia marcescens*. The highest inhibition zone diameter achieved by composite **5** was against *Enterobacter cloacae* (26.7 mm) and by composite **7** was against *Bacillus subtilis* (23.0 mm).

The majority of the modified clays were effective against *Escherichia coli*, *Staphylococcus aureus* and *Enterobacter cloacae*. However, the composites showed lower antibacterial activities against *Shigella dysenteriae* and *Serratia marcescens*. In spite of the different cell wall structures of the gram-negative bacteria, the composites **6**, **10** and **11** showed reasonable antibacterial activities as they were against the Gram-positive strains. Increasing charge density of the antimicrobial polymers, comparable to that of monomers, enhances adsorption onto the negatively charged bacterial cell surfaces (Fan et al., 2004). The repulsion between negatively charged clay and bacteria cell surface prevents their association. This necessitates the modification of clay by cationic polymers to be positively charged with various degrees of hydrophobicity to increase the electrostatic interactions with bacteria. It could be concluded that the mechanism of action comprises

**Figure 2** MIC of compound **6**.

uncoupling of oxidative phosphorylation; inhibition of active transport across the membrane; inhibition of catabolic and anabolic pathways; disruption of cell division; loss of membrane integrity and leakage of essential intracellular constituents (Abdeen, 2014).

### 3.2.2. MIC of the modified MMT clays

The minimum inhibitory concentration (MIC) is the lowest concentration of a chemical that prevents visible growth of a bacterium. To assess the level of antibacterial activity, the ratio of surviving cell numbers was then examined (Harder et al.,

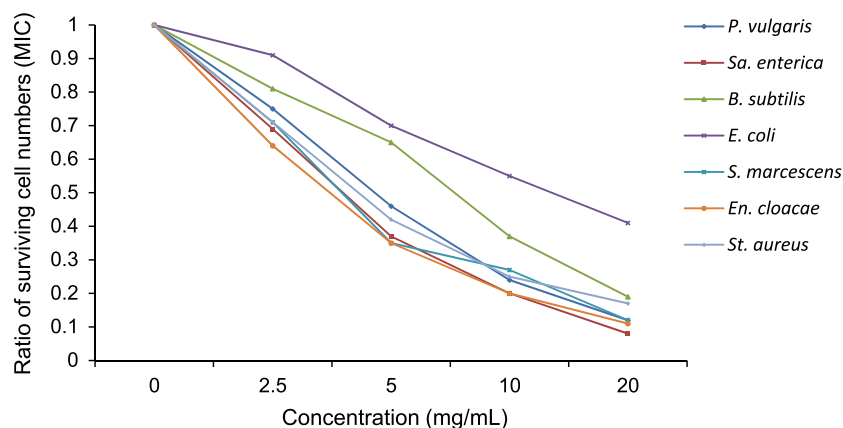


Figure 3 MIC of compound 8.

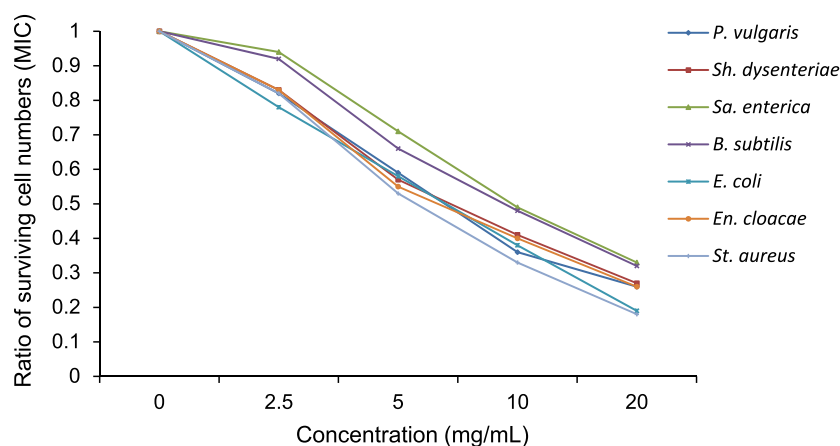


Figure 4 MIC of compound 9.

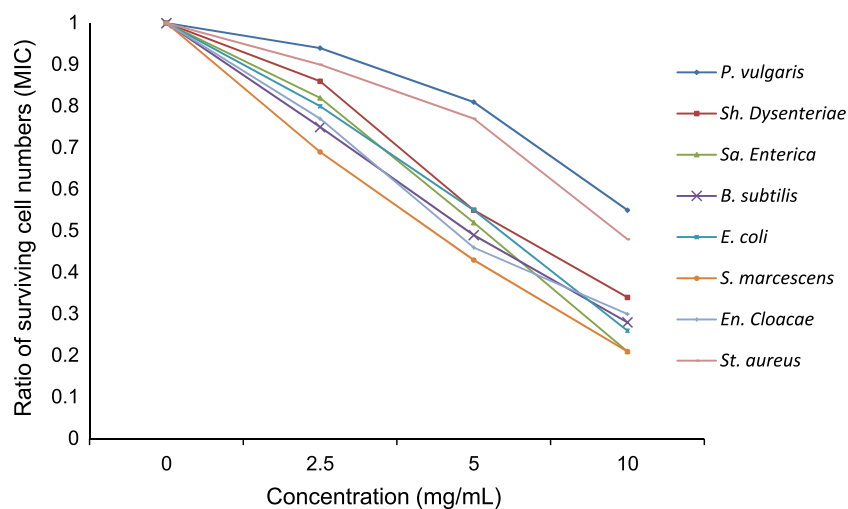


Figure 5 MIC of compound 10.



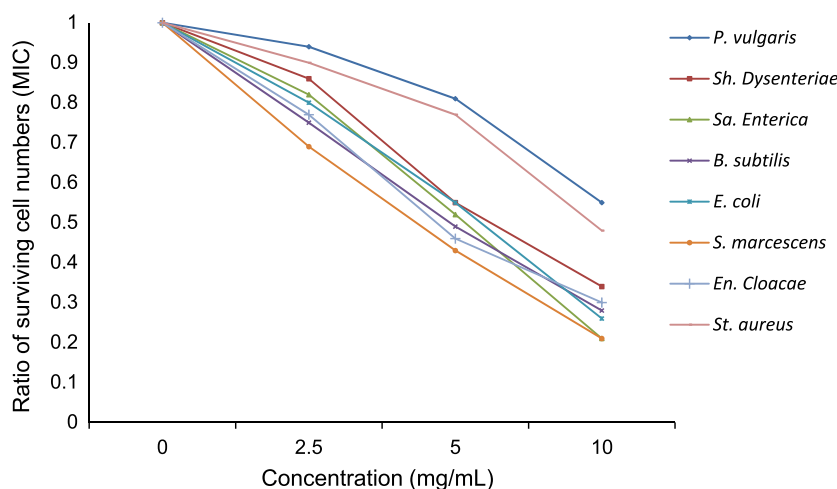


Figure 6 MIC of compound 11.

1997). The majority of the composites demonstrated some biocidal activities against the Gram-positive bacteria. Composite 6 showed high inhibition zone against the Gram positive bacterium *Staphylococcus aureus*; however, it showed relatively lower activities against the Gram negative bacterium *Salmonella enterica* at the highest used concentration (20 mg/mL) (Fig. 2). Composite 8 showed relatively higher antibacterial activity against the Gram negative bacteria *Salmonella enterica* and *Enterobacter cloacae*; nevertheless, it has showed relatively lower activity against *Escherichia coli* (Fig. 3). Composite 9 showed high inhibition zone against the Gram positive bacterium *Staphylococcus aureus* and lower activities against the Gram negative bacterium *Salmonella enteric* (Fig. 4). Composite 10 showed high inhibition zone against the Gram negative bacterium *Serratia marcescens* at all the used concentrations (2.5–20 mg/mL) and lower activities against the Gram negative bacterium *Proteus vulgaris* (Fig. 5).

Composite 11 showed high inhibition zone against the Gram-negative bacterium *Serratia marcescens*. However, this composite showed relatively lower antibacterial activity against the Gram-negative bacterium *Proteus vulgaris* even at higher concentration as 20 mg/mL (Fig. 6).

#### 4. Conclusion

Montmorillonite clays are widely used for the absorption of organic and inorganic waste water contaminants. In this study, the clays were modified with *p*-N,N-dimethylamino benzaldehyde to produce a range of clays that also demonstrated high antibacterial activity. All the modified composites demonstrated relatively high biocidal activity against all the screened strains in comparison with the non-substituted clay. Modified MMT clays could have a dual function in being able to remove contaminants through absorption and act as a biocidal agent for pathogenic bacteria. The future work will focus on using modified clays in water treatment applications, as these compounds are easily prepared, inexpensive, and safer, as well as, they poses broad spectrum against water contaminating bacteria.

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