

Simultaneous action of surfactant modified clinoptilolite: Adsorbent of dyes and antibacterial agent

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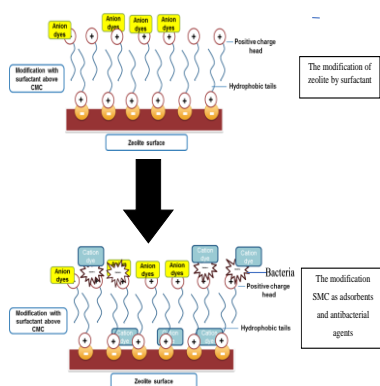
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Article history

Received 3 May 2018
Revised 25 August 2018
Accepted 11 September 2018
Published Online 25 October 2018

Graphical abstract



Abstract

In this study, the simultaneous action of surfactant modified clinoptilolite (SMC) as adsorbent for dyes and its antibacterial activity was investigated. Methylene blue (MB) and acid orange 7 (AO7) represent cationic and anionic dyes, respectively were used as adsorbate in this study and the antibacterial activity was studied against Gram-negative (*Escherichia coli* ATCC 11229) and Gram-positive bacteria (*Staphylococcus aureus* ATCC 6538 and *Enterococcus faecalis* ATCC 2921). Initially, natural zeolite clinoptilolite was modified with 3 different concentrations (0.1, 1.0 and 4.0 mM) of cationic surfactant hexadecyltrimethyl ammonium bromide (HDTMA-Br). The SMC samples were characterized by Fourier transform infrared (FTIR) spectroscopy, X-ray diffraction (XRD), amount of HDTMA adsorbed and dispersion behaviour. Result from XRD shows that the HDTMA-Br molecules caused no effect on primary structure of the clinoptilolite since the clinoptilolite structure remained the same after modification with HDTMA-Br. Compared to the unmodified clinoptilolite, FTIR spectra of the SMC shows peak corresponds to C-H stretches which proved the attachment of HDTMA onto the clinoptilolite surfaces. In the dispersion behaviour study, SMC samples were located at the adjacent phase between the water and oil mixture. The amount of HDTMA-Br adsorbed onto the clinoptilolite increased with the increasing concentrations of the surfactant. The use of SMC as adsorbent and antibacterial agent were further studied against the ionic dyes and bacteria simultaneously. The results show that the adsorption capacity of SMC towards both ionic dyes increase with the increasing HDTMA-Br concentration. While for the antibacterial activity, the number of colony forming unit of bacteria seem to be highly reduced at the highest concentration of the HDTMA (4.0 mM) attached on the clinoptilolite. Hence, this study had shown that SMC has high adsorption capacity towards the ionic dyes at the same time reducing the growth of both Gram positive and negative bacteria in aqueous solution.

Keywords: Clinoptilolite, Surfactant Modified Zeolite, Methylene Blue, Acid Orange 7, Antibacterial Agent

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INTRODUCTION

Nowadays, the advanced technology in the industrial application has led to various products to meet the needs of people. However, the improper use of chemicals in most of the products causes the world to suffer. The presence of many contaminants such as heavy metals, colouring dyes and harmful microorganisms in the wastewater and other aqueous solutions can seriously affect the environment and human health (Yang *et al.*, 2012). There are several processes to remove these contaminants from wastewater such as desalination (Humpalik *et al.*, 2011), oxidation technology (Ebrahiem, Al-Maghrabi, & Mobarki, 2017), photocatalytic degradation (Li *et al.*, 2016) and adsorption (Sadeh *et al.*, 2017). Although many methods have been applied to overcome these problems, adsorption technique is the best approach compared to other techniques in term of their economical (Onundi *et al.*, 2011), effectiveness for dye removal in wastewater (Li *et al.*, 2002) and sludge free operation (Sadon *et al.*, 2012). There are many nanomaterials that have been introduced as nanosorbent of heavy metals including mesoporous silica (Vojoudi *et al.*, 2017), magnetic sulfide (Patel *et al.*, 2018), carbon nanotubes (Coa *et al.*, 2017) and zeolite (Goyal *et al.*, 2018). In this paper, natural zeolite which is clinoptilolite was chosen as an adsorbent as it is the most abundant and low cost. The unique physical properties like

high surface area, negatively charged structure, high cation exchange capacity, high adsorption for certain pollutants (Armağan *et al.*, 2004) and able to be modified with cationic surfactant (Apreutesei *et al.*, 2008) without changing the structure has made it the best candidate for this research.

The modified zeolite that was treated with cationic surfactant hexadecyltrimethylammonium-bromide (HDTMA-Br) is able to attract the anionic compounds from the wastewater due to its positively charged bilayer formation on the zeolite surface (Malek and Yusof, 2007). Therefore, the surfactant-modified zeolite clinoptilolite (SMC) could adsorb the anionic dye in water. Research from Malek *et al.* (2014) proved that the SMC has antibacterial properties when combined with another cationic surfactant which is cetylpyridinium chloride (CPC).

The aim of this study was to modify the clinoptilolite with the cationic surfactant HDTMA-Br and characterized using X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), HDTMA-Br adsorption and dispersion behaviour. The natural zeolite clinoptilolite and SMC were tested for the adsorption of methylene blue (MB) and acid oranges 7 (AO7) dyes. MB dye was chosen as it represented cationic compound while AO7 represented anionic compounds. For the antibacterial activity, Gram-negative (*Escherichia*

coli) and Gram positive (*Staphylococcus aureus* and *Enterococcus faecalis*) bacteria were used in this study.

EXPERIMENTAL

Materials

The natural zeolite clinoptilolite was imported from Indonesia and supplied by Provet Group of Companies Sdn. Bhd, located in Serdang, Selangor. Cationic surfactant reagent (HDTMA-Br), was supplied by Qrec (Asia) Sdn. Bhd.

Preparation of surfactant modified clinoptilolite

The clinoptilolite was modified with three different initial concentrations of HDTMA-Br (0.1, 1.0 and 4.0 mM). The HDTMA-Br surfactants were prepared by dissolving 0.03645 g, 0.3645 g and 1.458 g of the HDTMA-Br powder into 1 L of distilled water in 1 L volumetric flasks. Accurately, 2 g of the clinoptilolite was then added in 200 ml of the surfactant solution in a 250 ml conical flask and stirred for 16 hours using magnetic stirrer at room temperature. The resulting SMC was separated from the HDTMA-Br solution by single filtration through Macherey-Nagel filter paper (125 mm) and dried at 80°C in a universal oven (model UF30, Memmert, Germany) overnight. The dried filtrate was ground into a fine powder by using mortar and pestle and sieved using #40 American Society for Testing and Materials (ASTM) sieve and the samples were kept in a suitable plastic container for characterization and adsorption study.

Characterizations

Fourier Transform Infrared Spectroscopy (FTIR)

All samples were characterized with a Thermo Scientific Nicolet iS5 with Smart iTR Diamond crystal FTIR (Fourier Transform-Infrared) spectrometer. The instrument was used for the solid sample using attenuated total reflectance (ATR) method. The solid sample was ground using a mortar to obtain powder form. About 1-2 mg powder sample was then placed on the sample platform for the FTIR scanning spectrum and it was recorded using OMNIC software in the range of 400 to 4000 cm^{-1} .

X-Ray diffraction technique

The phase identification of natural zeolite and SMC were determined using X-ray diffraction (XRD) method on a Bruker AXS GmbH (German) machine. X-ray diffraction patterns of all samples were recorded with a $\text{CuK}\alpha$ radiation at $\lambda = 1.5418 \text{ \AA}$ at 40 kV and 20 mA in the range of $2\theta = 5^\circ$ to 50° with a scanning speed of 0.05° per second.

Amount of HDTMA-Br adsorbed on zeolite

The amount of surfactant adsorbed onto clinoptilolite was determined according to the method described by Yusof et al. (2008) Approximately, 25 mL distilled water, 5 mL sulfuric acids 2 M (RCI Lab Scan, Thailand), 10 mL chloroform (QReC, New Zealand) and 2 mL acid orange 7 1 mM (Sigma-Aldrich, USA) were mixed and shaken in a separating funnel. Following this, 1 mL from the sample solution was added to the mixture and was shaken vigorously. As a result, the colourless chloroform at the bottom layer from the mixture become light orange. The light orange layer was then separated and inserted into the bottle sample according to each concentration and analysed using visible spectrophotometer (model NANOCOLOR® VIS, Macherey Nagel, Germany) at $\lambda 487\text{nm}$.

Adsorption of acid orange 7 (AO7) and methylene blue (MB) on surfactant modified clinoptilolite

The different concentrations of dye at 100, 200 and 400 ppm were prepared. Then, 100 mg of all the samples were accurately weighed and placed into 50 mL plastic tubes containing 25 mL of each concentration of dye solution. The mixture of dyes and samples were shaken constantly at 200 rpm for 2 hours under room temperature.

The samples were separated from dye solutions by single filtration through Macherey-Nagel filter paper (125 mm) and the absorbance of the resulting filtrates were measured using Visible spectrophotometer (model NANOCOLOR® VIS, Macherey Nagel, Germany) at a wavelength of 487 nm for AO7 while 661 nm for MB dye adsorption.

Dispersion behaviour

In order to study the relative position in an oil-water mixture of unmodified and modified clinoptilolite an approximately 0.06 g of the sample was added in the mixture of distilled water (2 mL) and n-hexane (2 mL) in a 10 mL glass bottle with stopper. The relative positions of the particles in the mixture were compared. After that, the samples were shaken for 2 hours at room temperature. The suspension formed were then left at static conditions. The images of all the samples were captured at an appropriate time before shaking, after shaking for 2 hours, static condition after shaking for 30 minutes and 24 hours

Simultaneous action of zeolite and SMC

The simultaneous action of clinoptilolite and SMC as adsorbent and antibacterial agent were studied against AO7 (Sigma-Aldrich, USA) and MB (Sigma-Aldrich, USA) for adsorption of dyes (Malek et al., 2016), while *E. coli* ATCC 11229 for Gram-negative bacteria and *S. aureus* ATCC 6538 and *E. faecalis* ATCC 2921 for Gram-positive bacteria were used for antibacterial activity.

Bacteria culture that reached the OD reading between 0.6–0.8 (1.5×10^8 CFU/mL) at 4000 rpm, 4°C, for 15 min was centrifuged. The supernatant was discarded and the pellet was washed twice using distilled water. Following this, 50 ml of the 10 ppm dye solution were added into falcon tubes. Then, the falcon tubes were vortexed to suspend and disperse the bacterial pellet in the dye solution. After that, 0.1 g of the sample was weighed accurately into 50 ml falcon tube and mixed with 20 ml of the prepared dyes solution and bacterial culture. All the samples were incubated in an incubator shaker at 27°C (200 rpm) for 30 min. After shaken for 30 min, the sample was separated from mixed bacteria and dye solutions by single filtration through Macherey-Nagel filter paper (125 mm) and the absorbance of the resulting filtrates were measured using Visible spectrophotometer (BUCK 100 Vis Spectrophotometer, Jenway) to determine the concentration of AO7 (Sigma-Aldrich, USA) and MB (Sigma-Aldrich, USA) dyes at wavelengths of 487 nm and 661 nm, respectively.

The number of bacteria presented after 30 mins of treatment with the natural zeolite, SMC0.1, SMC1.0, and SMC4.0 were determined by a serial dilution technique together with dropped plate (DP) method with slight modifications (Malek et al., 2014). In this study, the nutrient agar (NA) plate was divided into four quadrants, which each quadrant was reserved for one dilution factor of filtrates solution. Each quadrant was dropped with 10 μL of the bacterial suspension from each falcon tube. After the drops on the agar dried, the plates were kept in an incubator at 37°C for 18 h and the reduction number of bacteria in Colony forming unit (CFU) in dye solution were calculated.

RESULTS AND DISCUSSION

Adsorption of HDTMA-Br onto zeolite

Based on Fig. 1, the result shows that the amount of HDTMA-Br adsorbed onto clinoptilolite increased with the increasing concentration of the surfactant. According to Erdogen and Ulku (2013), the adsorption occurred due to the formation of electrostatic interaction and hydrogen bonding between the surfactant and the clinoptilolite surface. As the HDTMA-Br molecules positively charged, increasing the concentration of HDTMA-Br resulted in a higher affinity towards the negatively charged surface of clinoptilolite at the solid-liquid interface (Mi-Na et al., 2006). The adsorption of cationic surfactant onto negatively charged surface of clinoptilolite is attributed by two mechanisms which are ion exchange and hydrophobic bonding (Li et al., 1998).

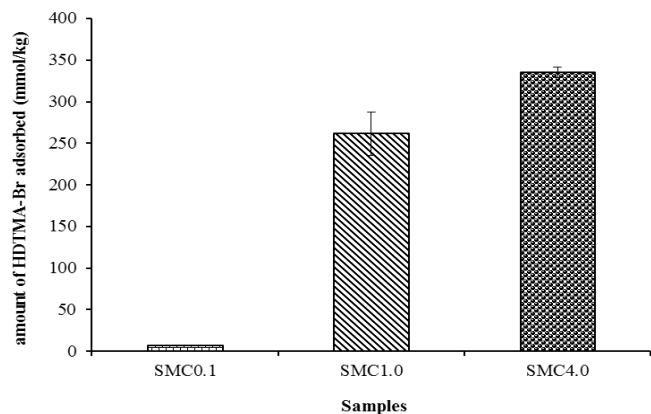


Fig. 1 : Amount of surfactant adsorbed by different concentration of HDTMA-Br SMZ0.1 (0.1mM), SMZ1.0 (1.0mM) and SMZ4.0 (4.0 mM) on clinoptilolite

The critical micelle concentration (CMC) plays an important role in the adsorption behaviour of HDTMA-Br molecules onto clinoptilolite. According to Cifuentes *et al.*, (1997) the CMC value of HDTMA is 0.93 mM. At lower CMC, the surface tension of clinoptilolite changes strongly with the concentration of the surfactant where the surfactant molecules exist as monomers and retained on the surface of the adsorbent via ion exchange interaction (Li *et al.*, 1998). At this stage, the SMC will have a low affinity or weak adsorption towards anion compound. After reaching the CMC or slightly increase from the CMC, the surface tension remains relatively constant or changes with lower slopes that resulted in bilayer formation of micelles on the clinoptilolite surface. The internal layer of the micelle is attached on the adsorbent surface through ion exchange and the outer layer is anchored by hydrophobic interactions (Li *et al.*, 1998). With the increasing concentration of surfactants, the bilayer formation of micelles on the clinoptilolite surface tends to reverse the negatively charge into positive charge surface and, therefore, this allow the SMC to adsorb anionic compounds (Zhu *et al.*, 2014).

Physicochemical properties of Zeolite and SMC

X-Ray diffraction

X-ray diffraction was used to identify and verify the compounds and crystalline structure in the clinoptilolite and SMC (Torres-Pérez *et al.*, 2008). XRD patterns of the raw clinoptilolite and surfactant modified clinoptilolite (SMC) are shown in Fig. 2.

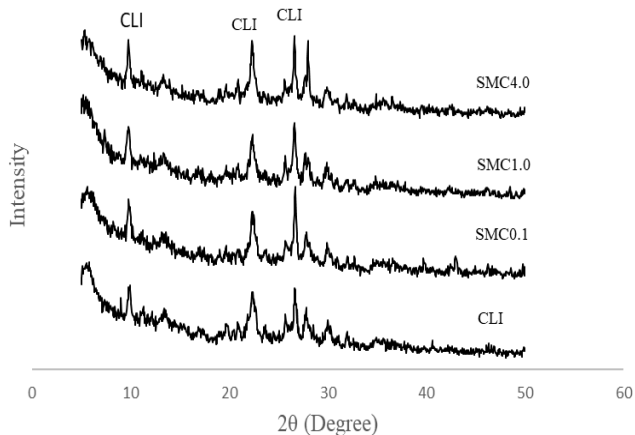


Fig. 2 : XRD pattern of the prepared samples.

Based on the patterns, it was observed that the main crystalline phase in the sample is clinoptilolite as the position of the intensities peaks were correspond to the clinoptilolite structure (Vassileva and Voikova, 2009). It was seen that clinoptilolite and quartz were the primary components in the natural zeolite samples and no present of

clay minerals were detected (Torres-Pérez *et al.*, 2008). It was also observed that SMC samples showed no significant changes in the position of the intense peak. Hence, the results showed that cation surfactant HDTMA-Br caused no effect on primary structure of clinoptilolite after modification process.

Fourier transform infrared spectroscopy (FTIR)

The FTIR spectroscopy was used for chemical identification in the samples of unmodified clinoptilolite and SMC (Kaushik *et al.*, 2009). The comparison between both FTIR spectra of FTIR is shown in Fig. 3.

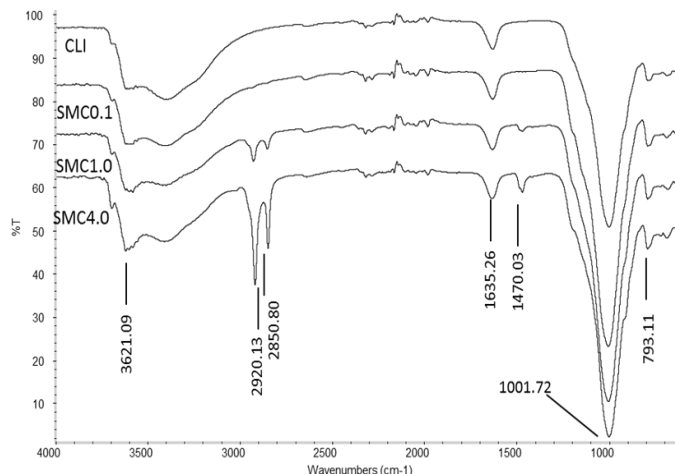


Fig. 3 : FT-IR spectra of the prepared samples.

FTIR spectroscopy was used to determine the presence of surfactant molecules on the clinoptilolite structure at around 3000 to 2800 cm^{-1} . This is important region to identify two significant peaks when cationic surfactant was successful loaded onto the clinoptilolite (Li and Bowman, 2001). Based on the FTIR spectra, three additional peaks which are at 2920, 2850 and 1470 cm^{-1} are found for SMC1.0 and SMC4.0 which confirms the loading of HDTMA-Br on the clinoptilolite surfaces. The peaks found on the SMC represent the symmetric and asymmetric vibrations of the C-H stretching modes, respectively, in the hydrocarbon chain of the HDTMA-Br compound (Malek and Ramli, 2015).


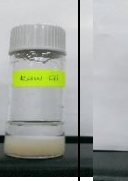

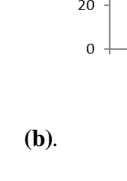



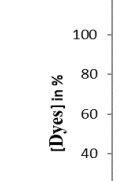



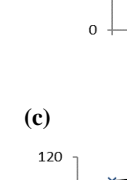
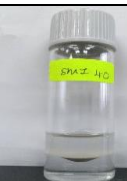


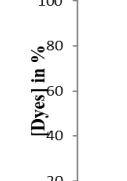
The presence of small peaks at 1470 cm^{-1} is assigned to the primary amino groups (NH_2) of the HDTMA-Br structure. Furthermore, the assignment of the Si-O or Si-O-Al molecules that built up the structural framework of clinoptilolite can be seen from the corresponding wavelength within 600 to 1200 cm^{-1} . The intense band at 1001 cm^{-1} is subjected to the internal T-O bonds in TO_4 tetrahedral (T = Si and Al) stretching vibration (Tijani *et al.*, 2013). Generally, the FT-IR spectra of SMC show that the clinoptilolite structure is not changed and remains intact after modification.

Dispersion behaviour

Dispersion behaviour of SMC and clinoptilolite was conducted to observe the relative position in which clinoptilolite would be occupied. This test can also demonstrate the changes in the surface properties of the SMC in comparison to unmodified clinoptilolite. This is because the surface of modified clinoptilolite may transform from hydrophilic to hydrophobic due to the attachment of hydrophobic molecules (surfactant) on its surface. Table 1 shows the optical images of the distribution of samples in hexane and water mixture. The sample of unmodified clinoptilolite was located at the lower layer of aqueous phase while the SMC sample is located at the adjacent phase between the water and oil mixture in the beginning. After shaking for 2 hours, both of the samples dispersed well in the water phase which is called colloidal dispersion. After static condition for 30 minutes and 24 hours, the unmodified clinoptilolite seems to locate at the lower layer of water phase while SMC samples still dispersed well in the water. These results support findings from other

characterization results that the clinoptilolite surface is successfully modified by the surfactant molecules.

Tab. 1 : Dispersion behaviour studies of raw clinoptilolite and SMC in hexane and water mixture.

Sample	Time			
	At beginning	After shaking for 2 hours	After 30 hours	After 24 hours
CLI				
SMC 0.1				
SMC 1.0				
SMC 4.0				

The organic phase of oil (upper layer) in SMC samples appears cloudy due to the presence of hydrophobic surfactant, while the organic phase in unmodified clinoptilolite appears to be clear. Surfactant contains hydrophobic and hydrophilic moieties which enable it to accumulate between fluid phases and thus, it can reduce surface and interfacial tension. This property contributes to the application of surfactant in various industries such as in agriculture, food and petroleum industries (Negin, Ali, & Xie, 2017). Therefore, the attachment of surfactant onto clinoptilolite may change the surface property of clinoptilolite.

Clinoptilolite are originally hydrophilic in nature due to its high aluminium content (Chaouati *et al.*, 2013). Attachment of surfactant as a monolayer onto clinoptilolite may change the surface of hydrophilic clinoptilolite to hydrophobic which is created by the surfactant tail groups (Li *et al.*, 2001). This hydrophobic or organic coating on the surface of the clinoptilolite causes the clinoptilolite particles to avoid contact with the aqueous phase or water and partition itself in the organic phase (Bowman., 1991). This causes the position of the solid sample of raw clinoptilolite where the solid sample are positioned at the aqueous phase of the mixture.

Simultaneous action of SMC: Antibacterial and adsorption

The adsorption of both ionic dyes on the samples was analysed using visible spectrophotometer while the reduction of a number of bacteria in colony forming unit (CFU) in the dye solution was analysed for the antibacterial properties of the samples. Fig. 4, 5 and 6 show results of the simultaneous action of the prepared samples towards the dye solution and bacteria.

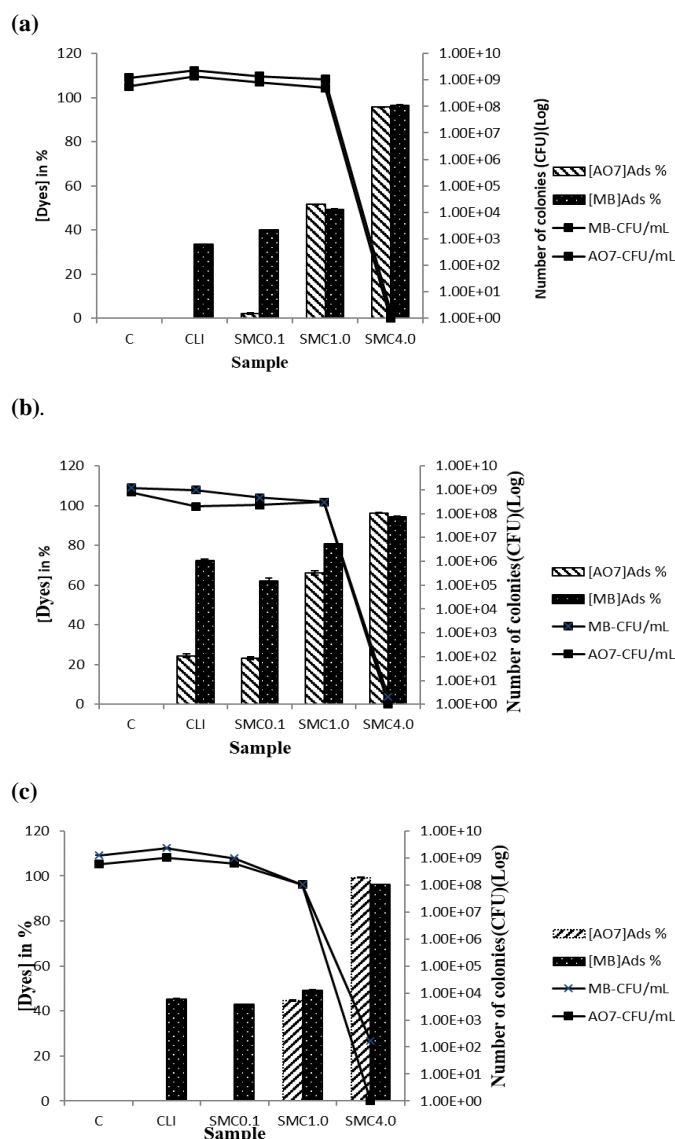


Fig. 4: Simultaneous action of SMC against AO7, MB dye adsorption and inhibition amount of (a) *E.coli* (b) *S. aureus* (c) *E. faecalis*.

Based on Fig. 4, the simultaneous actions of SMC against ionic dyes and bacteria showed better adsorption capacity and antibacterial activity with increasing concentrations of HDTMA-Br on clinoptilolite. The highest adsorption of AO7 and MB was found for SMC4.0 while for the antibacterial activity, there was no general trends could be observed. However, it was shown that the number of bacteria was reduced as the concentration of surfactant increased. The highest antibacterial activity by the samples towards both Gram positive and Gram negative bacteria was for SMC4.0.

The highest adsorption of AO7 by SMC4.0 was due to the presence of more HDTMA-Br molecules on the clinoptilolite. Clinoptilolite structure consists of a three dimensional framework having a negatively charge lattice. The negative charge that can be balanced by cations make it suitable to be modified with cationic surfactant HDTMA-Br (Qiu *et al.*, 2009). Hence, modification of clinoptilolite surface with cationic surfactant can enhance the number of positive sites and eventually increase the adsorption capacity toward anionic dye. This can be due to the high electrostatic attraction between the positively charge surface of adsorbent (SMC) and AO7 dye molecules which are negatively charge. Furthermore, the degree of hydrophilicity plays an important roles in which the bilayer formation of admicelles positively charged group has a strong influence on the anionic dye uptake rather than monolayer formation (Torres-Pérez *et al.*, 2008). Thus, by increasing the concentration of surfactant, it definitely increases the adsorption site of SMC towards

anionic dyes through increasing positive charge on the surface. This was proven by the increasing percentage removal of anionic dyes by the SMC. While for the MB, the highest adsorption was also observed by SMC4.0. As the dye solution contains the presence of bacteria, it seems that SMC4.0 forming electrostatic interaction with the negative charge of bacterial protein. Since it was reported that bacteria cells have a tendency to adsorb certain cation pollutants (Luke et al., 2015), hence the bacteria could act as the intermediate between the SMC4.0 and MB in order to adsorb the cationic dye. However, this study are not evaluate the reaction between dye with just the bacteria cells

For the antibacterial activity, the reduction of number of both bacteria by the samples were the highest for SMC4.0. The antibacterial activity is related to chemical properties of the cationic surfactant that are capable to reduce the surface tension, form ionic aggregates, changes the conductivity and solubility of bacteria in water (Block, 2001). Furthermore, due to the positive charge of HDTMA, the high affinity to attract the negatively charged bacterial protein caused stresses in the cell wall which led to cell lysis and disruption of cell wall permeability of the bacteria.

CONCLUSION

Natural zeolite clinoptilolite has been modified with different concentrations of HDTMA-Br and the characterization results showed that the HDTMA molecules adsorbed on the clinoptilolite without distorting the zeolite structure although there is some changes in their physical characteristics mainly its dispersion behavior. The SMC with the highest amount of HDTMA (4.0 mM) showed the ability in adsorbing dyes and killing the bacteria simultaneously. Therefore, it can be concluded that the surfactant modified zeolite has two simultaneous actions which is as adsorbent and antibacterial agent which can be used for many beneficial purposes in the future.

ACKNOWLEDGEMENT

This work was financially supported by the Universiti Teknologi Malaysia under the Research University Grant (Vot 18H87) and Ministry of Higher Education Malaysia.

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