Review of modified Zeolites by surfactant and Silver as antibacterial agents

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ABSTRACT

The emergence of the bacterial resistance towards current used antibiotics and antibacterial agents trigger scientists and researchers to develop new or improved antibacterial agents. Zeolite can be used as a reservoir material of the antibacterial agents of cationic surfactant or silver ions, providing their gradual released and resulting in a sustained antibacterial action on the infected sites topically or applying as a coating material for medical devices. These materials can be a promising candidate in pharmaceutical and biomedical applications. This paper reviewed the development of the surfactant modified zeolites and silver loaded zeolites as the antibacterial agents in terms of their advantages and setbacks as the antibacterial agents.

Keywords:
Zeolite, Surfactant, Silver, Antibacterial agent

1. Introduction

Antibacterial agents are chemical compounds that have the capability to inhibit (bacteriostatic) or killed (bactericide) the bacteria [1]. The physical or chemical process used to completely removed or killed all forms of microbial life is termed as sterilization, whilst the prevention of multiplication of microorganisms is termed as preservation [2]. Antibacterial agents compose of antibiotics and biocides [1]. Antibiotics are organic substances which are naturally occurring (e.g. penicillin) or synthetically produced (e.g. sulfonamide) that could destroy or inhibit selective microorganisms [2]. The antibiotics are antibacterial agents which are applied for systemic purposes (used in the body) in human beings and animals [3] as they have a specific action in treating the infections and they are used in low concentration [2].

Due to the outbreak of the pathogenic bacteria which resistance to the currently used antibiotics [1], there were several works have been done by medical scientists and researchers to improve the effectiveness of the agents such as producing semisynthetic antibiotics by the attachment of other functional groups to the conventional antibiotics [4-6]. Besides, some works have been done to extract antibiotics from other sources such as from plants [7] and animals [8] which are known as...
antimicrobial peptides [1-9]. On the other hand, antibiotic could be combined with other antibiotic to treat osteoarticular infections on osteoblast viability [10]. The combination of the antibiotics/drugs which enhanced the effectiveness of the antibiotics/drugs is term as synergistic [11-13]; whilst the combination of the antibiotics/drugs which lower the effectiveness of the antibiotics/drugs term as antagonistic [14]. Although antibiotics have special properties (e.g. specific activity, used in low concentration) in treating the infection [2]; they still have drawbacks to the body as consuming antibiotics can cause side effects such as liver [15] and kidney failure [16]. Furthermore, the antagonistic effect of drug combination could affect the biological system in the host [17]. Ultimately, the bacterial resistance problems still occurred [18-19].

Biocides are synthetic chemical agents (e.g. disinfectants, antiseptics and preservatives) that used to inhibit or kill the microorganisms; they usually have a broad spectrum activity [2] and used for topical purposes (used outside the body) with varying concentrations [1]. Biocides are used in many purposes. Disinfectants are used on the inanimate objects or surfaces; antiseptics are applied to living tissues; whilst, preservatives are used to preserve pharmaceuticals and foods [2]. Quaternary ammonium compounds (QACs) are usually used as antiseptics and disinfectants, whereas inorganic silver is antimicrobial agent used in burn and eye infections, and destroy warts [2]. Conventional biocides are usually used in the form of solution (elutable biocides) on the surfaces and infected sites [20]. Using elutable biocides as the antibacterial agents possess several problems such as: (1) exposure to high concentration of biocides could cause cytotoxicity; (2) inconvenient due to short time effectiveness as it would easily dry by time and need to be applied frequently to achieve the expected antibacterial activity [21]. Using biocides as the alternative antibacterial agents are worth action to cope with the resistance problems as biocides having a broad spectrum of antimicrobial action (attacked several sites) [1] and thus, it would give hurdles to the bacterium in order to become resistant.

2. Zeolites as a Carrier System for Surfactant and Silver Ions

Zeolite is an inorganic crystalline material with three-dimensional framework structure consists of aluminosilicates as its backbone, comprising cations and water molecules in its framework [22]. The cations are from group I or group II in the periodic table (e.g. Na\(^+\), K\(^+\), Mg\(^{2+}\), Ca\(^{2+}\)) located in the zeolite framework to stabilize the negative charges of exchangeable sites [22]. The cations are mobile and can be exchanged with other cations that presence in the solution while the intra-crystalline zeolitic water can be removed reversibly [22]. For instance, cationic surfactant QAC such as cetyltrimethyl ammonium bromide (or hexadecyltrimethyl ammonium bromide) (CTAB) molecules having positively charge surfactant head and silver ions (Ag\(^+\)) could be adsorbed onto zeolite by ion exchange with the cations which are presented on zeolite surface and in the zeolite frameworks. In term of the attachment of surfactant molecules adsorbed on zeolite, the surfactant molecules are too large to enter the small pore of zeolite and thus, they are attached on zeolite surfaces. Specifically, cationic surfactant CTAB molecules having a head diameter of 0.694 nm [23] are unable to penetrate the average pore diameter of NaY zeolite (0.74 nm) [24]; thus, they would occupy the exchangeable active sites at the exterior of NaY zeolite framework. On the other hand, the small size of cationic silver ions would be adsorbed on the zeolite surface as well as inside its framework [25].

The conventional antibacterial agents can be improved by immobilizing the biocides in the carriers; thus, it can release a low concentration of biocides in the long term [26-28]. The flexibility of zeolites (e.g. NaY zeolite) as the adsorbent materials could reduce the cost of the preparation. Furthermore, zeolite has been approved by the Food and Drug Association (FDA) as Generally Regarded as Safe (GRAS).
Inorganic materials possess several advantages over conventionally used organic compounds as they have high chemical stability, thermal resistance, safe to the user, long lasting action period and others [29]. As the inorganic materials, zeolites and clays are widely used as the adsorbent of antibacterial agents [30-40] because they possess high ion exchange capacity, high surface area and sorption capacity, negative surface charge, chemical inertness and low or null toxicity [29]. Although clays have several properties similar to zeolite, due to its shrink-swell properties when contacted with water attributed from its two-dimensional structure [22] limits its application as the adsorbent materials. When the clays was applied as the antibacterial materials in water filter, it would clog the system [41]. Whereas, zeolite structure is more rigid and tough as it possess a three-dimensional framework structure [22]. Besides, zeolites have higher cation exchange capacity compared to clays and thus, it would adsorbed more cationic compound/ions at the exterior and within its frameworks [22].

Silver ions have a broad spectrum antimicrobial properties, showed high thermal stability and low volatility, display cytotoxicity to animal cells (dependent of the silver concentration), relatively inert and safe [32]. Despite, precious properties of silver as the antimicrobial agents, Ag-based products generally have two main drawbacks: (1) bacterial resistance to silver [42]; and (2) formation of insoluble precipitates (e.g. AgCl or Ag₂S) which occurred due to the reaction of Ag⁺ from Ag-zeolite with electrolytes (e.g. chloride and sulphur anions) in bacterial solution [43]. This will reduce the antibacterial activity of Ag-zeolite [44]. Bacterial resistance to silver can occur when the bacterium was rendered in a sublethal concentration of silver for long periods of time [45]. This problem can be solved by increasing the concentration of silver in solution for an instant antibacterial activity [45]. As silver ions are less stable in aqueous solution, they tend to reduce to metallic silver (Ag⁰) upon light [46] or heat exposure [47] and forming insoluble precipitates by reaction with anions in solution [48]. Thus, the incorporation of silver ions in the suitable support material could solve the problem as silver ions would slowly release into the solution containing bacteria [49]. According to Ferreira et al. [32], silver ions are preserved in its ionic state in AgY zeolite. Moreover, Lalueza et al. [50] claimed that silver ions in Ag-zeolite would release into the solution if only the Ag⁺ sites are exchanged with other cationic ions in the solution that would take Ag⁺ place and pump out Ag⁺. In addition, Matsumura et al. [49] claimed that in water condition, Ag⁺ may be released from zeolite when bacterial cells are present. Thus, the incorporation of Ag⁺ in zeolite would preserve the silver remained in ionic form (Ag⁺) [32] and slow release Ag⁺ progressively into the medium containing bacteria [49]. On the other hand, the incorporation of Ag⁺ into zeolite could solve the problem occurred with AgNO₃ which is inconvenient for handling as well as can be used for limited purposes [51]. Compared to other transition metals (e.g. Zn, Cu), silver ions displays higher antibacterial activity [52] and zeolites possess better selectivity for Ag than for Zn and Cu [53]. Furthermore, Ag-zeolite displays similar antibacterial activity to AgNO₃ [49] and thus, it is expected that the incorporation of Ag⁺ in zeolite did not reduce the antibacterial activity of Ag⁺.

2.1 Bacteria

Bacteria are unicellular forms of microorganisms which inhabit soils, water stream, plants, food and others. There are certain bacteria which can inhabit in radioactive waste [54]. Generally, bacteria are categorized into two groups namely Gram-negative and Gram-positive bacteria, according to the characteristics of their cell wall [1]. Several bacteria can give benefit to human in many processes such as normal flora in the digestive system of human [1]. In contrary, there are also several bacteria which are harmful to human. The presence of these bacteria in human body or on skin can cause problems and diseases. The antibiotics, biocides, disinfectants or antimicrobial agents have been
developed to combat against the pathogenic bacteria. Biocides are chemical agents which are applied in suspension on surfaces to inhibit or kill the microbes, whilst antibiotics are organic compounds whether naturally synthesized by a living organism (e.g. penicillins) or chemically produced in a laboratory (e.g. sulphonamides) which have a specific activity against a limited number of organisms [1]. Currently, most pathogenic bacteria are resistant to the antibiotics, and thus the production of new or improved antibacterial agents are greatly desired.

2.2 Surfactant Modified Zeolites as Antibacterial Agents

Surfactant is an organic compound of an amphiphilic molecule which is a molecule having hydrophilic and hydrophobic properties in one molecule. The positive charged of ammonium group contributes to the hydrophilic property in surfactant head, while the hydrophobic property of the surfactant is due to its hydrocarbon tail. Due to the unique structure of surfactant, it is soluble in both organic solvents and water [55]. The surfactant can be categorized in four groups which are non-ionic, cationic, anionic and amphoteric considering the charge present in each surfactant molecule and the difference of the characteristic brought by each other. Since zeolite has a negative charge on its surface as well as in its framework, therefore the cationic surfactant molecules are suitable type of surfactant in the modification of zeolite surfaces.

The cationic surfactants are included in the group of quaternary ammonium compounds (QAC). They consist of a positively charged hydrophilic ammonium group in their head and long chain hydrophobic of hydrocarbon tail/tails. In medical area, QAC is used as disinfectant which is applied on the hard surface, hand sanitizers and moisturizers [56] as well as applied on non-critical surfaces and unbroken skin as antiseptics, and also applied in mucous membranes [57]. For example, CTAB is used as one of the ingredients in the Cetrimide drug which is a topical antiseptic agent (British Pharmacopoeia). The hydrophobic hydrocarbon tails of the QACs would act on the hydrophobic part of the phospholipid bilayer at the inner cytoplasmic membrane of the bacteria [2] by hydrophobic interaction.

In general, the QACs molecules would affect the membrane of the cells by reacting with the cell membrane and cause disruption to the cell membrane followed by a leakage of the cytoplasmic content of the cell [58]. When the bacterial cells exposed to a low concentration of the QACs, QACs start the autolysis [59-60], followed by disruption and denaturation of structural proteins and enzymes [61]. When the cells are exposed to a high concentration of the QACs, the QACs would solubilize in the hydrophobic cell membrane components into mixed micellar aggregates [62]. QACs would act on the carboxylic groups in the cytoplasm causing general coagulation in the bacterial cytoplasm. QACs could affect bacteria, fungi, yeasts, protozoa and certain viruses [63]. The emergence of the bacterial resistant trigger problems in food processing industry, health and medicine [63].

Due to the broad spectrum of antibacterial characteristics, the QACs have also been applied in pharmaceutical, water treatment and antifungal treatment for the crops [56]. In general, QACs are chemically stable at pH 3 to pH 9 [64] and show antimicrobial activity with chain length composed of 8 to 18 carbon atoms [65]. A study carried out by Jono et al. [66] showed that the antimicrobial property of QACs decreased when the hydrocarbon chain is longer than C18 due to the increased in the hydrophobic interaction with the lipid bilayer of the bacterial cell wall. Meanwhile, when the hydrocarbon chain less than C8 was used as the antimicrobial agent, the hydrophobic interaction between the QACs and the bacterial cell wall was generally low and thus, reduced the chances of penetration of the alkyl chain into the bacterial cell wall [67]. QACs are cationic surface active agents
(surfactant) that have antimicrobial properties as they attack the microbial cells by disrupting the cell membrane of the bacterial cells [65, 68, 69].

![Diagram of surfactant attachment on zeolite surfaces at low and high concentrations.](image)

**Fig. 1.** Schematic diagram of the attachment of surfactant molecules on zeolite surfaces at low and high concentrations of the surfactant.

The attachment of the cationic surfactant onto the zeolite surface is through the ion exchange reaction (electrostatic attraction) of the positively charged ammonium group in the surfactant molecules head one-to-one with the cations situated on the zeolite surface [70]. The attachment of cationic surfactant molecules on the zeolite creates hydrophobic condition on the zeolite surface and subsequently reverses the negative charge of zeolite to positive charge due to the formation of surfactant bilayer on the zeolite which is balanced by the counter ions [71]. Figure 1 shows the schematic diagram of the attachment of cationic surfactant on zeolite surfactant at lower and higher concentration of surfactant and figure 2 shows the ability of surfactant modified zeolite in adsorbing cation, anion and organic compounds.
This unique condition gives special property to the surfactant modified zeolite (SMZ) as it can be used as the adsorbent of cations, anions and non-polar (organic) molecules. The SMZ can adsorb bacteria through electrostatic attraction between the positive charge of surfactant head which located from surfactant bilayer formation on the zeolite and the negatively charge bacterial surface [58]. Meanwhile, the hydrophobic interaction could occur between the hydrocarbon tails of the surfactant molecules which are attached on the zeolite to the hydrophobic part of the phospholipid bilayer of the bacteria [58]. At a concentration of surfactant below the Critical Micelle Concentration (CMC), the surfactant molecules will exist in the form of monomers in the solution. The bilayer of surfactant (micelles) starts to form at the increasing surfactant concentration above its CMC value and keep increasing in the numbers as the concentration of surfactant in the solution increases. The electrostatic attraction is strong and almost irreversible [72]. Meanwhile, the hydrophobic bonding is weaker as the surfactant from the second layer of SMZ tends to desorb into the solution [73], mainly solution with low ionic strength [71].

Figure 4 displays the overview of the previous researches on SMZs and surfactant modified clays that have been applied as antibacterial agents. The researches regarding the production of SMZs as an antibacterial agent is still small in numbers. Research based on the production of SMZ as an antibacterial agent was done by Malek and Malek [77] where the synthetic zeolites NaA, NaX and NaY attached with HDTMA and benzalkonium chloride (BKC) were tested against Bacillus subtilis.
study showed that the Si/Al ratio of zeolite and the zeolite framework structure contributed to the antibacterial activity of the materials. Zeolite having low Si/Al ratio tends to adsorb more cationic surfactants and thus, exhibit high antibacterial activity against the bacteria. However, the zeolite which has a rigid framework structure such as NaA zeolite adsorbs low concentration of surfactant molecules, and subsequently exhibits low antibacterial activity against the tested bacteria.

Most of the researches regarding the production of surfactant based antibacterial materials used clays as the adsorbent materials of the antibacterial agent. There are some limitations that occur when using clays as the adsorbent material for the antibacterial agent. Herrera et al. [41] studied the production of the surfactant based antibacterial material tested against Salmonella enteritidis. When the materials were used in the water filter, the system was clogged by time. This condition occurred due to the properties of the clay which expand when the material absorbed water attributed by its two-dimensional framework structures [22]. In addition, clays have lower cation exchange capacity (CEC) compared to the zeolites [22] and thus, able to adsorb lower amount of other compounds. Additionally, zeolite structure is more rigid and stable upon water treatment attributed by its three-dimensional framework structures [22]. Therefore, the use of zeolite as the adsorbent materials of the antibacterial agents is more flexible and effective compared to the clay. To solve the problem, Herrera et al. [91] then combined surfactant modified clay minerals with sand to give the hydraulic effect to the antibacterial material.

Although the attachment of the surfactant onto the support materials has reduced the antimicrobial activity of the agents compared to the free surfactant in the solution [98, 106], the immobilized surfactant on the support materials (e.g. natural zeolite [74, 79], synthesized zeolites [77] and clay minerals [72, 92]) still exhibit significant antibacterial properties. In addition, the SMZ with bilayer or patchy bilayer surfactant coverage showed bactericidal effect against phosphate accumulating bacteria [81].

A study carried out by Shulze-Makuch et al. [79] on the antimicrobial activity of the SMZ on the viruses and E. coli present in the groundwater and sewage effluent showed that the SMZ was able to remove about 99% viruses and 100% E. coli from the solutions. They suggested that the positive charge of the bilayer surfactant coverage on the SMZ adsorbed microorganism through positive-negative interaction. Besides, Abbaszadegan et al. [74] also studied a QAC-treated zeolite which was applied in pilot filter against E. coli, Klebsiella terrirena, Chlorella vulgaris and Cryptosporidium parvum oocysts. The study showed that the reduction of the microorganisms occurred after the SMZ was applied in the filters. Besides that, benzalkonium chloride modified natural zeolite clinoptilolite has been used as a salicylate carrier for the salicylate delivery system and its antibacterial activity against E. coli and S. aureus and showed that the material was potentially used as the anti-inflammatory and antibacterial material [80]. Other than zeolites and clays, the cationic surfactant has been loaded onto other materials such as on porous glass surface for water disinfection [107], in a resin matrix for oral cavity [21], loaded onto poly (vinyl alcohol) hydrogels for wound dressings [108], bonded onto the silicon as antibacterial material [65], and functionalized silica nanoparticles and inhibited bacterial adhesion [109].

2.3 Silver Loaded Zeolites as Antibacterial Agents

Silver ions are “evergreen antibacterial agents” which have been used since the ancient time [110]. Hitherto, they are still famous antibacterial agents and have been used worldwide. After antibiotic was introduced in 1940s, the use of silver ions has suddenly decreased since the antibiotic action was more specific in treating bacterial on the infected cell compared to the silver ions [1]. However, due
to the current emergence of antibiotic resistant bacteria, silver ions were retrieved again to battle such problems.

**Fig. 4.** An overview of the SMZs and surfactant modified clays as the antibacterial agent
As a broad spectrum antibacterial agent, silver ions are incorporated in various adsorbent materials or carriers, such as incorporation in mesoporous silica nanoparticles [111] and microspheres [112]. Silver has also been incorporated in sodium alginate composites [113], polymer [114], cellulose-graphene oxide nanocomposite [115], potato starch nanocapsules [116], silica hybrid particles on air filtration [117], cellulose nanocrystal [118], polypropylene [119], TiO$_2$ composite [120], poly(N-vinyl pyrrolidone)-grafted graphene oxide [121], coating Ti metal for biomedical applications [122], doped onto calcium phosphate ceramics [123], functionalized graphene oxide [124, 125]; as well as impregnated onto zeolites and act as antibacterial material [126-129]. Silver exists as a metallic form (Ag$^0$) in these materials.

The outer membrane permeability increases as Ag$^+$ attached to the thiol groups (-SH) of enzymes and proteins on the bacterial membrane [130]. Besides, Ag$^+$ also triggers the production of hydroxyl radicals in bacteria, causing denaturation of proteins, and also affects the lipids and DNA of the bacteria which ultimately kill the bacteria [131, 132]. The cell envelope and contents of bacteria are damaged as Ag$^+$ interacts with nucleic acids of the bacteria [133]. Based on the study of antibacterial activity of Ag against *E. coli* and *S. aureus* that was carried out by Feng et al. [134], Ag$^+$ reacted with DNA and proteins thiol groups which led to the loss of replication abilities of the DNA molecules and caused inactivation of bacterial proteins. Both of the bacteria exhibited similar morphological changes after the treatment with Ag$^+$. However, compared to Gram-negative bacteria (*E. coli*), the Gram-positive bacteria (*S. aureus*) showed stronger defence system.

In medical applications, silver ions are loaded onto zeolites by ion-exchange with the cationic ions in the zeolites frameworks and exist as silver ions [135-137]. Figure 5 shows the schematic diagram of the silver modified zeolite and its antibacterial action. Currently, silver zeolite materials are combined with other antibacterial agents such as sulfadiazine [138, 139], 3-aminopropyltriethoxysilane (APTES) [140] and other metals (e.g. copper, zinc) [32], to act as a drug carrier and an antibacterial material. Silver zeolite-loaded silicone elastomers recently can act as a good antibacterial material, where the presence of organic functionalization of the zeolite prior to blending with the matrix has improved the composite mechanical properties and reduced the colour development in silver zeolite containing the silicone elastomers without affecting the antibacterial performance of the materials [30]. Silver zeolite is incorporated with hydroxyapatite and can be potentially used as bone implants [141]. The production of various silver based antibacterial materials promotes the advantages of silver as a broad spectrum antibacterial agent.

The use of Ag-modified zeolites as an antibacterial agent is not new since Hagiwara et al. [51] published their silver zeolites patent in 1990. However, there are a few researches have been done on the antibacterial properties of silver nanozeolites [126, 142-144], one research studied the biomedical properties of silver nanozeolite [141] and another one research studied the electrocatalyst properties of Ag-loaded ZSM-5 nanozeolites which was synthesized from bagasse [145]. In the latest study based on the application of Ag$^+$/Ag$^0$ loaded onto the nanozeolite, it was used as a coating material on a membrane surface as the Ag-nanozeolite was grafted on a membrane with polyvinyl alcohol (PVA) and polydopamine (PDA) [144]. Another research carried out by Wu et al. [143] based on the incorporation of Ag-nanozeolites onto the commercial polyamide nanofiltration membrane to prevent biofouling in long term membrane applications. Tosheva and her co-workers [142] studied the antibacterial properties of Ag and Cu loaded nano- and micro-sized FAU-type zeolite, but the nanozeolite used in her study was synthesized using different methods ((1) preparation of highly reactive gels at room temperature [146]; (2) using a three-stage temperature control synthesis procedure [147]; and (3) using 2$^3$ factorial methods for optimization of the experimental conditions [148]) and they used different silica source which is fly ash in the preparation of the materials. Dong and his co-workers [126] studied the antibacterial properties of EMT-type
nanozeolite comparing the antibacterial properties of two types of silver Ag⁺-EMT and Ag⁰-EMT against *E. coli* ATCC 8739. Whilst, Kaur and her co-workers [141] studied the biomineralization of hydroxyapatite in silver ion-exchanged nanocrystalline ZSM-5 zeolite using simulated body fluid; where the materials were considerable potential for biomedical applications such as for bone implant; and Rostami et al. [145] studied the application of Ag-loaded ZSM-5 nanozeolites synthesized from the bagasse as electrocatalyst in electrode, as the Ag-loaded zeolite was added onto the carbon paste electrode (Ag/ZSM-5/CPE) used for electrooxidation of oxalic acid. The reduction of the size of zeolite crystals from micron- to nano-dimensions lead to an increase in the external surface area, short diffusion paths and can increase lifetime [142]. The nanozeolites which are used for the catalytic purposes have particle size of less than 100 nm [149-151]. However, this small sized zeolite (< 100 nm) is not convenient for the application as the antibacterial materials because they are toxic to the cells which could enter the lung through respiration [152]. The size ranges of zeolite between 500-1000 nm have the properties of the microsized zeolite, which is known as the ‘nanosized materials’ [153]. Meanwhile, zeolite with particle size of 5-500 nm is termed as ‘nanosized crystals’ which exhibits the properties of the nanosized zeolite [153]. An overview of the previous researches of Ag-modified zeolites and Ag-modified clays are given in Figure 6.

![Fig. 5. Schematic diagram of formation of Ag-modified zeolite and its mechanism as antibacterial agent.](image)

### 3. Summary

Quaternary ammonium compounds (QACs) cationic surfactant having number of C with C8 to C18 in the hydrocarbon tail has the antibacterial properties. For instance, CTAB with C16 of hydrocarbon tail has a broad spectrum of antibacterial properties effective against Gram-negative and Gram-positive bacteria [58]. Additionally, Ag has broad spectrum antimicrobial properties which are effective against Gram-negative and Gram-positive bacteria [153]. Both QACs and cationic metal Ag⁺ have a broad spectrum activity. They attacked the pathogenic bacterial on several sites and thus, decrease the probability of bacterial resistance. Surfactant can be used as skin antiseptics and disinfectants [58] and Ag is used as an antibacterial agent in burns [184]. They were applied to the infected sites or on surfaces in the form of solution (elutable biocide).
Fig. 6. An overview of the Ag-modified zeolites and Ag-modified clays as the antibacterial agent.
Elutable biocides having some disadvantages such as short time effectiveness thus need to be applied frequently on the infected sites and possibility to cause toxicity to the surrounding tissues [25]. Moreover, silver ion (Ag\textsuperscript{+}) is less stable in solution as it tends to reduce to metallic silver (Ag\textsuperscript{0}) when exposed to the light or heat. Only Ag\textsuperscript{+} has the antibacterial property [185]. By loading Ag\textsuperscript{+} onto the zeolite, the Ag state can be preserved as Ag\textsuperscript{+} in the zeolite [170] and only released into the solution when other cationic ion has exchanged with Ag\textsuperscript{+} in zeolite [50] and only when the bacteria are present [49]. Thus, the antibacterial activity of Ag-modified zeolites can last longer.

Although Ag is an expensive metal, but due to the oligodynamic effect of the metal, only a small amount of metal is needed in order to exhibit high antibacterial property [186]. Low concentration of Ag\textsuperscript{+} can be preserved in the zeolite framework in the form of Ag\textsuperscript{+} [170]. High concentration of Ag\textsuperscript{+} loaded onto zeolite could cause the loosely bound Ag\textsuperscript{+} on the zeolite surface reduced to Ag\textsuperscript{0} upon light or heat exposure [166]. Thus, in order to produce effective Ag-modified zeolite antibacterial material, only a low concentration of Ag is needed. Also, the attachment of surfactant in the forms of partial monolayer and monolayer coverage on the zeolite through ion exchange reaction with the Na\textsuperscript{+} on the zeolite surface [187] is via electrostatic attraction. This bonding is strong and almost irreversible [72]. Thus, surfactant modified zeolite (partial monolayer and monolayer coverage) can become a long lasting antibacterial agent [26]. The antibacterial agents mainly consist as antibiotics and biocides [1]. There were several improvements have been done with the antibiotics to cope with the bacterial resistance problems. Biocides were used as the alternative antibacterial agents. Immobilizing the antibacterial agents (e.g. surfactant, Ag) onto a support material could improve the properties of the antibacterial agents such as prevent cytotoxicity and prolonged the antibacterial activity of the agents.

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