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Preparation and antibacterial characteristic of water-insoluble antibacterial material QPEI/SiO_2

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Abstract Polyethyleneimine (PEI) was grafted onto micron-sized silica gel particles via the coupling action of γ-chloropropyl trimethoxy silane, and grafting particles PEI/SiO_2 was prepared. Then, polymeric reactions of two steps, tertiary amination reaction and quaterisation, were conducted for the grafted PEI. After quaterisation of the grafted polyethyleneimine, a composite particle, QPEI/SiO_2, was obtained. QPEI/SiO_2 is a water-insoluble antibacterial material. In this work, the antibacterial characteristic of QPEI/SiO_2 was mainly investigated using *Escherichia coli* (*E. coli*) as a disease-leading bacterium and adopting a colony count method. The effects of quaterisation degree of PEI and pH of the medium on the antibacterial ability of QPEI/SiO_2 were examined. The antibacterial mechanism of QPEI/SiO_2 was explored profoundly by using two enzyme activity determination methods, β-D-galactosidase activity determination and TTC-dehydrogenase activity determination. The experimental results indicates that the water-insoluble antibacterial material QPEI/SiO_2 possesses strong antibacterial ability, for the bacterial suspension with a concentration of 10^9 CFU/ml, the antibacterial ratio of QPEI/SiO_2 can reach about 100% only with a dosage of 15 g/l and only for a contact time of 10 min. The main factors influencing the antibacterial ratio of QPEI/SiO_2 are the quaterisation degree of the grafted PEI and pH value of the medium. QPEI/SiO_2 with higher quaterisation degree has stronger antibacterial ability. In a certain range of pH value, the higher the pH value of the medium is, the stronger the antibacterial ability of QPEI/SiO_2 is. Enzyme activity determination results show that the antibacterial mechanism of the water-insoluble antibacterial material QPEI/SiO_2 is based on a sterilization process and not only is a bacteriostasis action.

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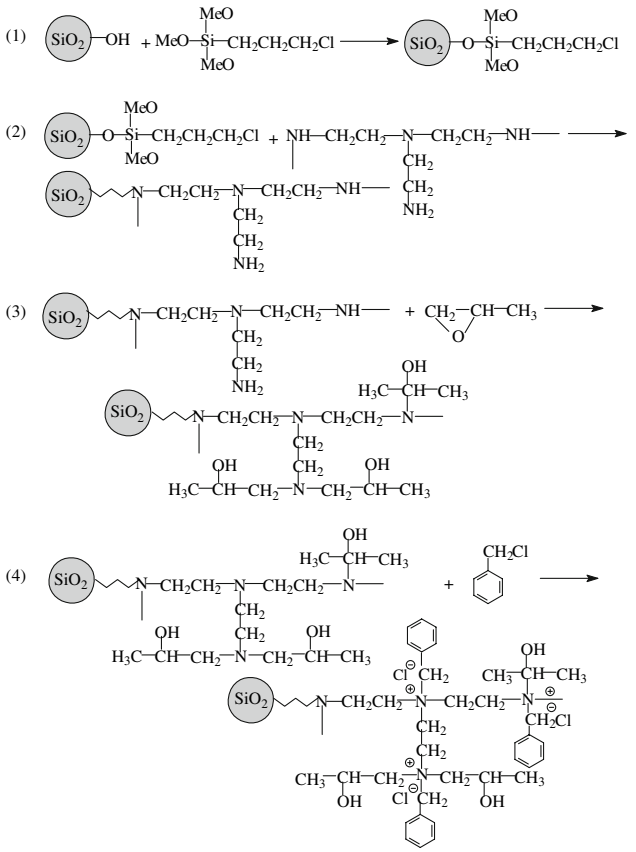
1 Introduction

At the present time, the most commonly used antibacterial agents in disinfection are small molecular agents, such as chlorine, chlorine dioxide, organic biocide and so on. However these small molecular agents are highly toxic to the environment and their residues will react with organic substances in water to yield disinfection by-products [1–4] that have mutagenic and/or carcinogenic activity [5–8]. Besides, their effects are short-lived due to the difficulty of controlling the rate of diffusion [9, 10]. In order to overcome these shortcomings, water-insoluble antibacterial materials have been developed [11–14]. For water-insoluble antibacterial materials, antibacterial groups are chemically immobilized on water-insoluble carriers, and sterilization is carried out via contacting with water medium without releasing any reactive agent. Several water-insoluble antibacterial materials have been synthesized, such as crosslinked polystyrene on which quaternary ammonium groups are bond [15], clay-polyvinylpyridinium material [16], pyridinium-type resin [17] and polyvinylpyridinium-grafted silica gel [18]. During using the water-insoluble antibacterial materials, not only disinfection by-products are avoided effectively, but also because the antibacterial groups are concentrated on carrier surfaces, the "collecting effect" will lead to high antibacterial efficiency in a short disinfection time and with a smaller dosage. Thus, the water-insoluble antibacterial



Scheme 1 Schematic representation of preparing process for QPEI/SiO_2

material is a kind of environmentally friendly disinfection materials, and it has been attracted much attention.

Polyethyleneimine (PEI) is a kind of water-soluble polyamine, and there is a mass of nitrogen atoms of amine groups on its macromolecular chains. The commercial PEI always is a branched macromolecule which chemical structure is given in Scheme 1, and the ratio of primary, secondary and ternary amine groups on PEI macromolecules is equal to 1:2:1 approximately. In this work, polyethyleneimine was firstly grafted onto micron-sized silica gel with the manner of "grafting onto" [19, 20] and grafting particles PEI/SiO_2 were prepared. Afterward, the grafted PEI on SiO_2 was quaterised via two polymeric reaction steps, tertiary amination reaction and quaterisation. Finally, water-insoluble antibacterial particles QPEI/SiO_2, on which a great deal of quaternary ammonium groups were supported, were obtained. The antibacterial mechanism of QPEI/SiO_2 was also profoundly studied. This water-insoluble antibacterial material has very strong antibacterial activity because of the concentration of the antibacterial groups on the surfaces of silica gel particles. QPEI/SiO_2 particles combine well the antibacterial activity of polymeric quaternary ammonium salt and multi-advantages of silica gel particles, such as high specific area, excellent mechanical strength, thermal stability, innocuity and low cost. Therefore, QPEI/SiO_2 is a functional composite particle material with high property. It is a promising route for preparing water-insoluble antibacterial materials to graft functional polymer with antibacterial activity onto inorganic particle carriers. To our knowledge, the similar study has not been reported.

2 Experiments

2.1 Materials and instruments

Silica gel (120–160 mesh, about 125 μm of diameter, Ocean Chemical Limited Company, Qingdao, in China) was received, and γ-chloropropyl trimethoxysilane (CPMS, Yongchang Chemical Limited Company, Naking in China) was of analytical grade. Polyethyleneimine (Mr = 2×10^4 to 5×10^4, aqueous solution with a content of 35%, Qianglong Chemical Limited Company, Wuhan in China) was of chemical grade and its concentration was determined accurately with UV spectrophotometry before use. Epihydrin (Beijing chemical reagent company) was of analytical grade. Benzyl chloride was of analytical grade and was purchased from Chinese reagent companies. *Escherichia coli* (*E. coli*) was supplied by a microorganism institute of Shanxi Province of China. The culture medium components contained beef cream, peptone, agar and NaCl, and they were all of commercial grade. *O*-nitraphenyl, β-D-galactopyranoside (ONPG, Aldrich), 2, 3, 5-triphenyl-2H-tetrazolium chloride (TTC, Shanghai Reagent Factory), Tri-hydroxymethyl aminomethane (Tris, Beijing Chemical Factory) and Glucose were all of analytical grade. Phosphate buffered solution (PBS) was prepared by ourselves. Water used here was sterilized water.

Used instruments were as follows: 8400S Shimadzu FTIR spectrometer, Unic-2602 UV spectrometer (American Unic Company), and PHS-2 acidimeter (The Second Analytical Instrument Factory of Shanghai). 250B biochemical culture box, pressure stainless steel sterilizing boiler and THZ-82 constant temperature shaker equipped with water bath were all made in China.

2.2 Grafting polyethyleneimine on surface of silica gel

2.2.1 Surface-modifying silica gel with CPMS

Silica gel particles activated with the aqueous solution of methane sulfonic acid were added into xylene (as solvent), and a certain amount of γ-chloropropyl trimethoxysilane (CPMS) and a little of water was also added. The mixture was allowed to react at 80°C for 6 h, and the filtrated product particles were extracted in a soxhlet for 24 h to

remove free CPMS. The separated product was dried under vacuum and the surface-modified silica gel particles were obtained. Chloro-propyl groups were attached chemically on the surface of the modified silica gel particle, so the particle was denoted as CP-SiO_2.

2.3 Preparation and characterization of grafting particle PEI/SiO_2

Five grams of CP-SiO_2 particle and 50 ml of concentrated PEI solution were added in a glass reactor, and the content was allowed to react at a refluxing temperature of 95°C for 8 h. After ending the reaction, the product was washed repeatedly with a great quantity of water to remove unreacted PEI, filtrated, dried under vacuum, and the grafting particles PEI/SiO_2 were gained. The PEI grafting degree of PEI/SiO_2 (g/100 g) was determined with acid–base titration method, in which the aqueous mixture containing fully swollen PEI/SiO_2 was titrated using HCl standard solution. The used PEI/SiO_2 in this work has a PEI grafting degree of 15.65 g/100 g. The chemical structure of PEI/SiO_2 was characterized with infrared spectrum with KBr pellet method.

2.4 Preparation and characterization of composite particle QPEI/SiO_2

Firstly, tertiary amination reaction was performed. Five grams of PEI/SiO_2 was added into a glass reactor and swollen in ethanol for 4 h, and the content of the primary and secondary amine groups was approximatively calculated according to the grafting degree. Epihydin was used as alkylation agent. Epihydin was added and its amount (mol) is 10 times more than the amount of primary and secondary amine groups of PEI. The content was allowed to react under stirring for 8 h on an ice-water bath because of the strong exothermic reaction. After finishing the tertiary amination reaction, the product particles (TPEI/SiO_2) were filtrated, washed with water and dried under vacuum.

Secondly, quaterisation was carried out. Particles TPEI/SiO_2 swollen in ethanol for 4 h were allowed to be quaterised with benzyl chloride as quaterisation agent at 50°C for a certain period of time. The product particles were filtrated, washed with ethanol and dried under vacuum. By controlling reaction time (in a range of 1–7 h), the composite particles QPEI/SiO_2 with different quaterisation degrees (mmol/g) were obtained. The quaterisation degree (mmol/g) implies the millimole number of the quaternary ammonium groups per gram of QPEI/SiO_2, and it was determined by using silver nitrate titration method in which the aqueous mixture containing fully swollen QPEI/SiO_2 was titrated with $AgNO_3$ standard solution (Cl^- anions of quaternary ammonium salt were reacted with Ag^+ cations). The titration was performed three times and the mean deviation was ±0.1%. The chemical structure of QPEI/SiO_2 was characterized with infrared spectrum.

2.5 Measuring the antibacterial ability of QPEI/SiO_2 against *E. coli*

2.5.1 Determining concentration of original cell suspension

The viable cell count was carried out using the serial dilution and spread plate technique. Activated *E. coli* was taken and inoculated into liquid culture. The culture was incubated at 37°C for 16 h on a rotary shaker at 300 rpm. One milliliter of original cell suspension was taken and serial dilutions were prepared with sterile water. About 0.2 ml of cell suspension of the grads of 10^{-8} and 10^{-9} were taken and spread on nutrient agar plates, respectively. The plates were incubated at 37°C for 24 h and then the number of viable cells (the number of colonies) were manually counted and the result were expressed as mean colony forming units per ml (CFU/ml). The concentration of original cell suspension was about 10^9 CFU/ml.

2.5.2 Determining antibacterial activity of QPEI/SiO_2 under different contact time

One milliliter of original cell suspension of *E. coli* with bacterium age of 16 h and concentration of about 10^9 CFU/ml was added into several clean tubes, respectively, in which 9 ml of water and 0.15 g of QPEI/SiO_2 had been added and QPEI/SiO_2 had been swollen for 4 h. These suspensions were shaken, and after contacting of different time, were allowed to stand statically for 2–3 min until the QPEI/SiO_2 settled. The various supernatants were taken, and the viable cell concentrations were measured using the serial dilution and spread plate technique as described above. The antibacterial ratios of the QPEI/SiO_2 samples under different contact time were calculated according to Eq. 1

$$\text{Antibacterial ratio} = \frac{\text{Number of original cell} - \text{Number of viable cell}}{\text{Number of original cell}} \times 100\%. \quad (1)$$

2.5.3 Determining antibacterial activity of QPEI/SiO_2 under different dosages

One milliliter of original cell suspension of *E. coli* with bacterium age of 16 h and concentration of about 10^9 CFU/ml was added into several clean tubes, respectively, in which 9 ml of water and different masses of QPEI/SiO_2 had been added and QPEI/SiO_2 had been swollen for 4 h.

These mixtures were shaken, and after contacting of 10 min, these suspensions were allowed to stand statically for 2–3 min until the QPEI/SiO_2 settled. The various supernatants were taken, and the viable cell concentrations were measured also using the serial dilution and spread plate technique as described above. The antibacterial ratios of the QPEI/SiO_2 samples with different dosages were still calculated according to Eq. 1.

2.6 Examining effects of various factors on antibacterial activity of QPEI/SiO_2

2.6.1 Effect of quaterisation degree of QPEI/SiO_2

One milliliter of original cell suspension of *E. coli* with bacterium age of 16 h and concentration of about 10^9 CFU/ml was added into several clean tubes, respectively, in which 9 ml of water and different masses of QPEI/SiO_2 sample with a certain quaterisation degree had been added. After the contacting of 10 min, the antibacterial ratios were determined. For QPEI/SiO_2 samples with different quaterisation degrees, the same experiments were conducted.

2.6.2 Effect of pH value of medium

Five milliliter of original cell suspension of *E. coli* with bacterium age of 16 h and concentration of about 10^9 CFU/ml was added into several clean conical flasks, respectively, in which 44 ml of water and 0.75 g of QPEI/SiO_2 samples had been added. The pH value of these mixtures was adjusted by adding dilute solution of HCl and NaOH, so that they had different pH values. After shaking these mixtures for 10 min, the antibacterial ratios for various QPEI/SiO_2 samples in those mediums with different pH values were measured.

2.7 Exploring antibacterial mechanism of QPEI/SiO_2

2.7.1 Measuring activity of β-D-galactosidase

The substrate of ONPG can be hydrolyzed to produce onitrophenol (ONP) under catalysis of β-D-galactosidase which is produced by alive cell. So it is possible to estimate whether the cell membrane of *E. coli* is disrupted through examining the extent of the above enzyme-accelerating reaction [21]. About 0.75 ml of cell suspension with a concentration of 10^9 CFU/ml and 0.75 ml of ONPG solution with a concentration of 25 mmol/l were added into 8.5 ml of PBS buffer solutions (pH = 7.4). After shaking of 15 min, a certain amount of QPEI/SiO_2 was added and the mixture was shaken rapidly. After standing for 2 min, the measurements of the supernatant absorption at 420 nm began to be carried out on a spectrophotometer, and the measurements were continuously performed with time prolonging. By varying the added amount of QPEI/SiO_2, the same measurements were curried out repeatedly.

2.7.2 Measuring activity of TTC-dehydrogenase

TTC as an acceptor of hydrogen can be reduced to form triphenylformazane (TF) under the catalysis of dehydrogenase produced by viable cells, so the sterilizing situation of QPEI/SiO_2 against *E. coli* can be estimated by examining the amount of the product TF [22]. QPEI/SiO_2 samples with different masses were added into several clean tubes, respectively, in which 5 ml of water was added, and then 1 ml of cell suspension was added. After contacting of 10 min, 2 ml of Tris–HCl buffer solution (pH = 8.5) and 2 ml of TTC-glucose standard solution were added into these tubes, respectively. These mixtures were placed in culture box at a constant temperature of 37°C for 2 h. When these mixtures colored, 5 ml of toluene was added to extract the product TF from water phase. Statically placed, these mixtures were demixed, and the absorptions of various organic phases at 485 nm were measured by using toluene as blank liquid.

3 Results and discussion

3.1 Reaction process to prepare composite particles QPEI/SiO_2

After activation of silica gel particles, a great deal of hydroxyl (silanol group) was produced on the surfaces of silica gel particles. γ-Chloropropyl trimethoxy silane (CPMS) was selected as coupling agent to link chemically silica gel with polyethyleneimine. CPMS was reacted with the silanol groups and the surface-modified silica gel is formed (CP-SiO_2). In turn, CP-SiO_2 was reacted with PEI and the grafting particles PEI/SiO_2 were obtained. The primary and secondary amine groups on PEI chains were transferred into tertiary amine groups by using epihydrin as tertiary amination agent [23]. In the tertiary amination reaction, ring-opening addition reaction occurs for epihydrin and alkylation reaction occurs for the primary and secondary groups of PEI. Then those tertiary amine groups were transferred into quaternary ammonium groups via quaterisation with benzyl chloride as quaterisation agent [23]. All the reaction processes are expressed in Scheme 1.

3.2 Surface structure of QPEI/SiO_2

Figure 1 shows the infrared spectra of four particles, SiO_2, CPMS-SiO_2, PEI/SiO_2 and QPEI/SiO_2. After modification by coupling agent CPMS for silica gel, the vibration

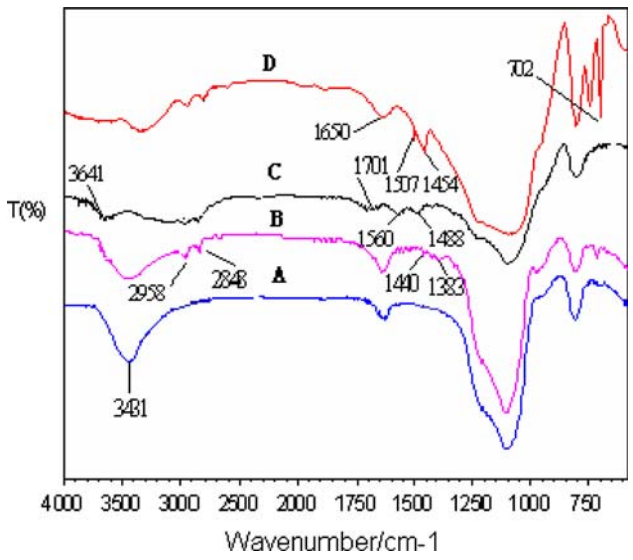


Fig. 1 FTIR spectra of various particles (**A**) SiO_2; (**B**) CP-SiO_2; (**C**) PEI/SiO_2; (**D**) QPEI/SiO_2

absorption of C–H bond at 2,958 cm^{-1} and 2,848 cm^{-1} as well as in the range of 1,383–1,440 cm^{-1} have appeared. They indicate that $–CH_2$ and $–CH_3$ groups have been produced on the surface of silica gel, the reaction between CPMS and silanol groups has occurred and particles CP-SiO_2 has formed. After the reaction of CP-SiO_2 with PEI, the stretch vibration and bending vibration absorptions of N–H bond appear at 3,641 cm^{-1} and 1,701 cm^{-1}, respectively. Besides, the bands at 1,488 cm^{-1} and 1,560 cm^{-1} are ascribed to the stretch vibration absorption of C–N bond. The appearances of these bands reveal that the macromolecular chains of PEI have chemically linked onto the surface of silica gel in coupling manner, and the grafting particles PEI/SiO_2 have been formed. In the spectrum of QPEI/SiO_2, the characteristic absorptions of benzene ring have been produced at 1,650 cm^{-1}, 1,507 cm^{-1}, 1,454 cm^{-1} and 702 cm^{-1} which are attributed to the linked benzyl chloride molecule. The appearances of these bands confirm that the quaterisation of PEI grafted on silica gel has occurred and the composite particles QPEI/SiO_2 has been obtained.

3.3 Antibacterial activity of QPEI/SiO_2 for *E. coli*

Figure 2 gives the variation of the antibacterial ratio of QPEI/SiO_2 with the contact time with a fixed dosage of 15 g/l and Fig. 3 displays the variation of the antibacterial ratio of QPEI/SiO_2 with the dosage in a fixed contact period of 10 min. Obviously, QPEI/SiO_2 enable the number of viable cells of *E. coli* to decrease rapidly in a shorter time (about 5 min) and with a smaller dosage (about 10 g/l). For the sample with a quaterisation degree of 1.57 mmol/g, the antibacterial ratio can reach about100% in 10 min of

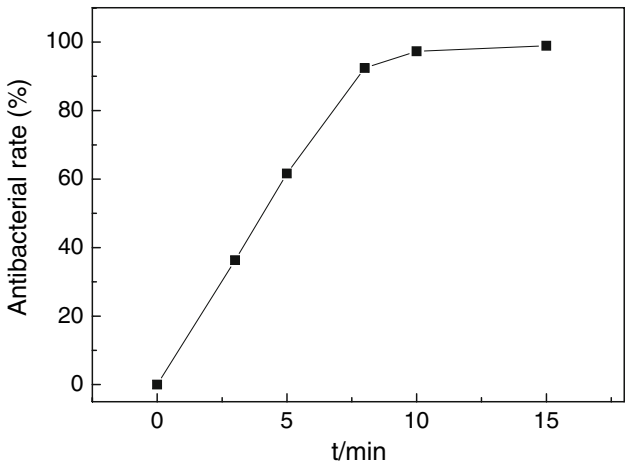


Fig. 2 Variation of antibacterial ratio of QPEI/SiO_2 with contact time. Content of QPEI/SiO_2: 15 g/l; Quaterisation degree of sample: 1.57 mmol/g

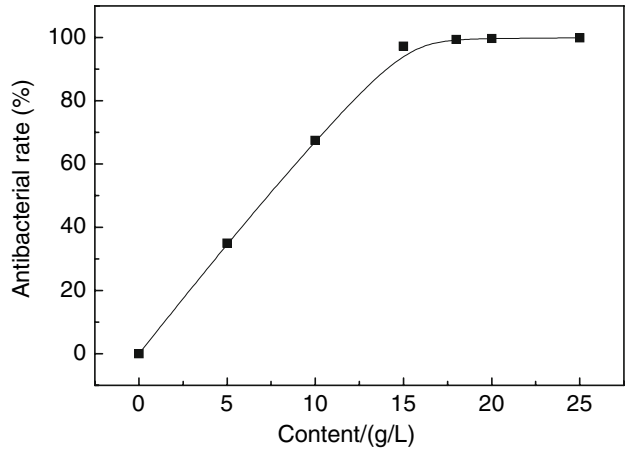


Fig. 3 Variation of antibacterial ratio of QPEI/SiO_2 with dosage. Contact time: 10 min; Quaterisation degree of sample: 1.57 mmol/g

contact time and 15 g/l of dosage. Thus, the experiment results show clearly that the water-insoluble antibacterial material QPEI/SiO_2 has a strong antibacterial ability against *E. coli*. A great deal of polymeric quaternary ammonium salt are supported on the surface of QPEI/SiO_2, and the concentrating effect of quaternary ammonium groups leads to high antibacterial activity of QPEI/SiO_2. The comparison of antibacterial efficiency is demonstrated in Fig. 4 as different dosages of QPEI/SiO_2 were used.

3.4 Effect of quaterisation degree on antibacterial activity of QPEI/SiO_2

QPEI/SiO_2 samples with different quaterisation degrees were used, and the variations of antibacterial ratio with dosages in a fixed contact period of 10 min for the various

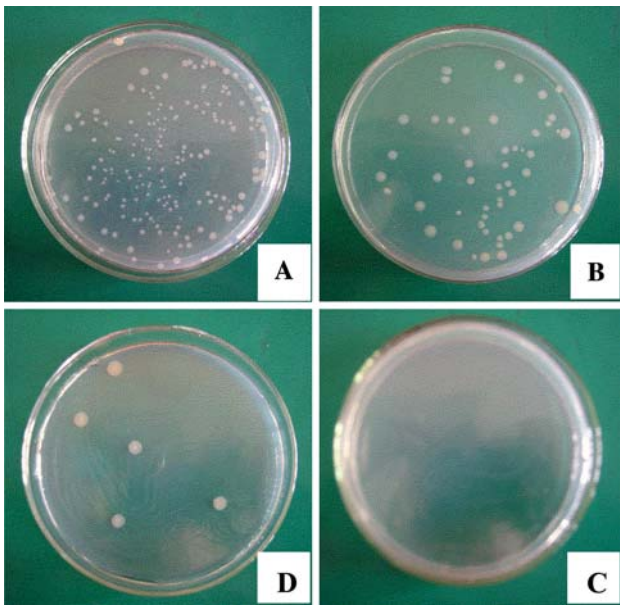


Fig. 4 Antibacterial efficacy of QPEI/SiO_2 against *E. coli* (**A**) without QPEI; (**B**) 10 g/l of dosage (**C**) 15 g/l of dosage; (**D**) 15 g/l of dosage. Contact time: 10 min; Quaterisation degree of sample: 1.57 mmol/g

samples are shown in Fig. 5. Taken the data of a dosage of 15 g/l from Fig. 4, the relationship curve between the antibacterial ratio and quaterisation degrees can be obtained and it is displayed in Fig. 6. It is can be seen clearly that the antibacterial ratio of QPEI/SiO_2 is strengthened with the increase of the quaterisation degree. Quaternary ammonium groups are charged positively, whereas the bodies of the microorganisms are charged negatively, so the particles QPEI/SiO_2 will strongly attract microorganisms by right of strong electrostatic interaction. Thus, the QPEI/SiO_2 sample with higher quaterisation

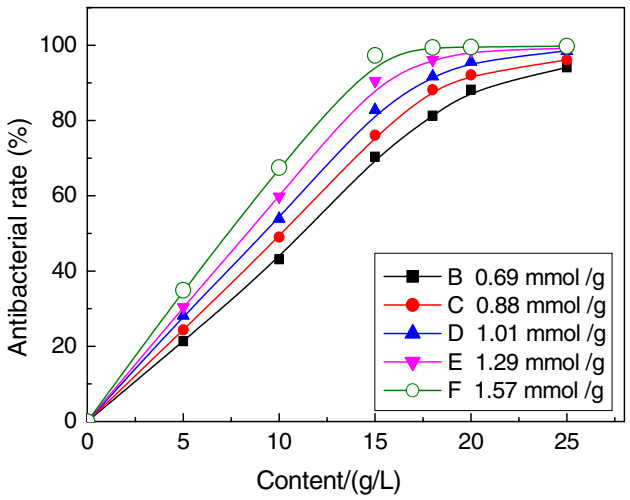


Fig. 5 Variation of antibacterial ratio of QPEI/SiO_2 with dosage for QPEI/SiO_2 samples with different quaterisation degrees. Contact time: 10 min

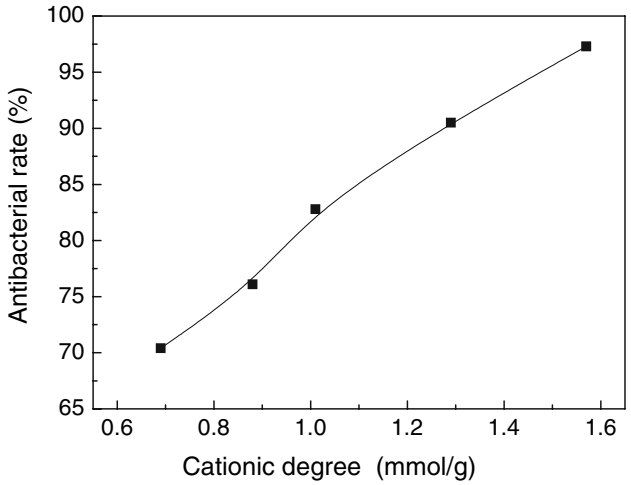


Fig. 6 Effect of quaterisation degrees on antibacterial ratio. Content of QPEI/SiO_2: 15 g/l; Contact time: 10 min

degree will have stronger adsorption towards microorganisms and will produce stronger antibacterial activity owing to higher density of positive charge on its surface.

3.5 Effect of pH value of medium on antibacterial activity of QPEI/SiO_2

The antibacterial activities of QPEI/SiO_2 at different pH values were tested, and Fig. 7 shows the changes of the antibacterial activity of QPEI/SiO_2 with pH value. It can be found that there is a lowest point on the curve, and the corresponding pH value is 4.5. It can be speculated that the lowest point is probably corresponding to the isoelectric point of the protein of *E. coli* cells. So the adsorption force between QPEI/SiO_2 and cells exists no longer because the cells of *E. coli* are not charged at pH = 4.5, and the antibacterial ability of QPEI is the weakest. Over the

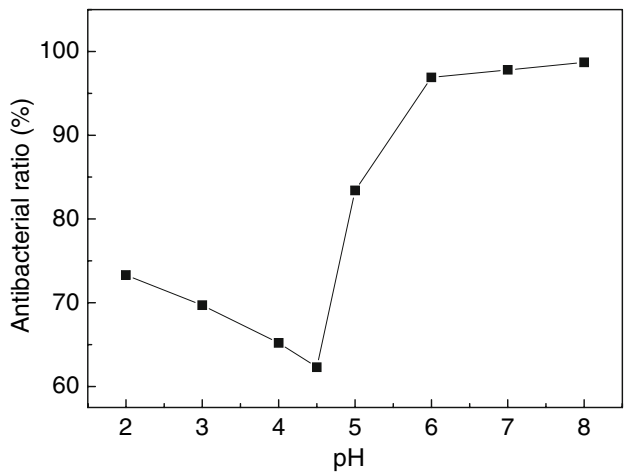


Fig. 7 Effect of pH value on antibacterial ratio. Content of QPEI/SiO_2: 15 g/l; Contact time: 10 min; Quaterisation degree of sample: 1.57 mmol/g

isoelectric point (on the right of this point), the antibacterial activity of QPEI increases with enhancing of pH value, and the antibacterial activity reaches about 100% as pH value increases to 6. The reason for this is that the neutralized degree of the carboxylic groups of amino acid of cell protein generally increases with enhancing of pH value, negative electricity on surface of cells increases, and the adsorption interaction between QPEI and cells strengthens, resulting in the increase of the antibacterial activity of QPEI. To the left of the isoelectric point, the cells are charged positively, and mutual repulsion of the congeneric electricity is disadvantageous to the adsorption interaction between QPEI and cells, so the antibacterial activity of QPEI should be very low. However, the apparent antibacterial activity of QPEI increases slightly with the decrease of pH value. This is probably caused by the antibacterial effect of H^+ ions.

3.6 Antibacterial mechanism of QPEI/SiO_2

3.6.1 Result of measuring activity of β-D-galactosidase

β-D-galactosidase has special hydrolyzing activity for *β*-D-galactose glycoside bond. Especially, *β*-D-galactosidase from *E. coli* has substrate specificity for the hydrolysis of ONPG [24]. If the *E. coli* cells break, *β*-D-galactosidase will leak out, and further will catalyzes the hydrolysis of ONPG in the solution. The product of ONPG hydrolysis, onitrophenol (ONP), has a characteristic absorption at 420 nm, so whether the cells of *E. coli* are disrupted can be examined with spectroscopy method. Different dosages of QPEI/SiO_2 were added into the cell suspensions containing ONPG, respectively, and the changes of absorption with time were measured. For comparison, the absorption of blank system into which QPEI/SiO_2 was not added also was measured. The experimental results are given in Fig. 8. It can be found that the absorption of blank system at 420 nm is nearly equal to zero and does not change with time. This shows that the membrane of *E. coli* cell is intact and no *β*-D-galactosidase is released. However, for the cell suspensions into which QPEI/SiO_2 was added, the absorption at 420 nm increases with time. Furthermore, for the cell suspension into which more QPEI/SiO_2 was added, the absorption increases more rapidly. This experimental result reveals clearly that after adding QPAV/SiO_2, cell membrane of *E. coli* is disrupted and the intracellular contents including *β*-D-galactosidase are released. The more the added amount of QPEI/SiO_2 is, the stronger the destroying action against the cell membrane is. The breaking of cell membrane implies the death of bacterium. So the antibacterial effect of QPEI/SiO_2 is based on a killing bacteria process.

3.6.2 Result of measuring activity of TTC-dehydrogenase

TTC is a small molecular substance, can be incepted by viable bacteria, and passes through cell wall and membrane. Furthermore, under the action of dehydrogenase in viable cells, TTC will be reduced into the product TF, which is colored and has characteristic absorption at 485 nm. The more the number of alive cells is, the more vigorous the metabolism is, resulting in the stronger ability to transform TTC for the alive cells, and leading to forming more amount of TF. So the survival amount of viable bacteria can be estimated by measuring the produced amount of TF. Figure 9 shows the relationship between the absorption of TF at 485 nm and the amount of QPEI/SiO_2 added into the cell suspensions. It is obvious that absorption of TF decreases markedly with the increase of the

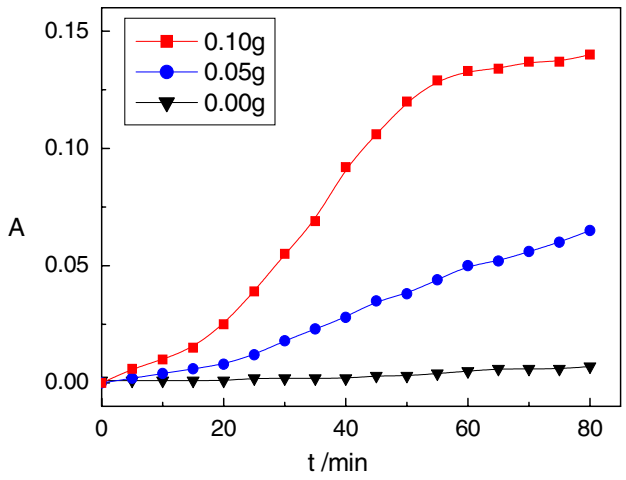


Fig. 8 Variation of absorption of ONP at 420 nm with time under different used amounts of QPEI/SiO_2

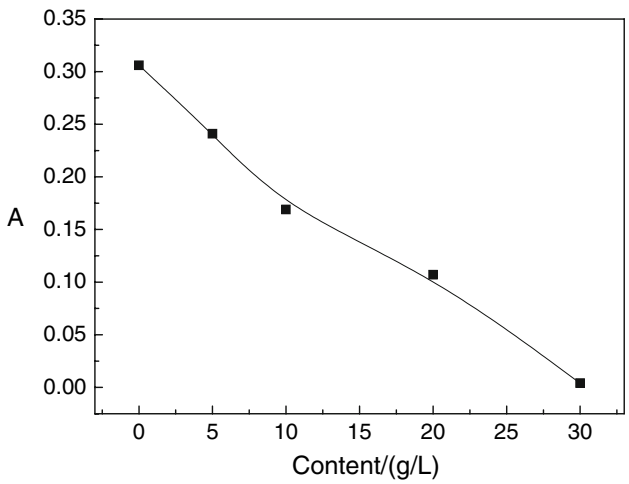


Fig. 9 Absorption of TF vs. the added amount of QPEI/SiO_2

added amount of QPEI/SiO_2. This experiment result once more shows clearly that the water-insoluble antibacterial material QPEI/SiO_2 exerts a killing action against microorganism in the disinfection process.

To sum up, the antibacterial mechanism of QPEI/SiO_2 is the same as that of small quaternary ammonium salts. QPEI/SiO_2 also exerts a sterilizing action during contacting with viable bacterium. The only difference is that QPEI/SiO_2 is a kind of water-insoluble antibacterial material and some advantages are resulted in. The antibacterial mechanism of QPEI/SiO_2 can be explained as follows: (1) firstly, the macromolecular chains of polymeric quaternary ammonium on QPEI/SiO_2 are swollen in water and fully stretch inner water; (2) bacteria cells are adsorbed onto the surfaces of QPEI/SiO_2 particles relying on electrostatic interaction; (3) further, the quaternary ammonium groups penetrate through cell wall of bacteria; (4) the quaternary ammonium groups combines with the cytoplasmic membrane and disrupts the cytoplasmic membrane; (5) intracellular contents are leaked, such as K^+ ions, DNA and RNA; (6) finally, the death of bacteria cells is led to.

4 Conclusions

Polyethyleneimine as a polyamine was grafted onto the surfaces of silica gel particles in the manner of "grafting onto", and then tertiary amination reaction and quaterisation were conducted in turn for the grafted PEI. Finally, the water-insoluble antibacterial material QPEI/SiO_2 was successfully prepared. QPEI/SiO_2 has strong antibacterial ability due to the concentrating of antibacterial groups on the surface. QPEI/SiO_2 with higher quaterisation degree has stronger antibacterial activity. The antibacterial mechanism of QPEI/SiO_2 is based on a process of killing bacterium. The water-insoluble antibacterial material QPEI/SiO_2 combines well the antibacterial function of polymeric quaternary ammonium salt QPEI with various excellent properties of inorganic support silica gel, such as high specific area, strong mechanical property and fine chemical and thermal stability and low cost. If QPEI/SiO_2 is used in disinfection treatment of water, there will be a great variety of advantages, such as strong antibacterial activity, without residues, without disinfection by-products and avoiding recontamination of water. In conclusion, it is an effective way for preparing water-insoluble antibacterial materials to graft functional macromolecules onto inorganic particle carriers.

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