CHAPTER IV
RESULTS AND DISCUSSION

In this study, two types of alumina used as support material were alumina balls and alumina powder. These two types of alumina were chosen in order to determine the effect of specific surface area on the killing efficiency. Appendix A shows how to calculate the bacterial destruction efficiency, and the contact time. The experimental data of this study are shown in appendix B.

4.1 Silver catalysts

4.1.1 Characterization of alpha-Alumina Balls

Table 4.1 gives physical properties of the alumina balls used for this study. Figure 4.1 shows the alumina balls having α-form as a result from XRD analysis. The average paticle size was about 5 mm, and the specific surface area was 4.236 m^2/g. This material had a very low surface area.

From the SEM picture of the alumina ball surface as shown in Figure 4.2, it shows the smoothness of the surface. This result is also confirmed from the low values of BET surface area and total pore volume as shown in Table 4.1. This low surface area was a result from using high temperature in producing alumina balls.

Table 4.1 Physical properties of alumina balls used as support

Property	Description
Alumina structure[1]	α-Al_2O_3
Alumina shape	sphere
Average diameter, mm	4.995
BET surface area[2], m^2/g	4.236
Average pore diameter[3], °A	2.028
Total pore volume[4], cc/g	1.13×10^{-4}
Alumina content , %	90
Density, g/cm^3	3.55
Hardness (ROCKWELL 45 N)	75
Bending strength, kg/cm^3	3,000
Compressive strength, kg/cm3	20,000
Colour	white

1 from XRD characterization

2, 3 from surface area analyzer

4 total pore volume for pore with Radius less than 8.1 at P/P0 = 0.1113

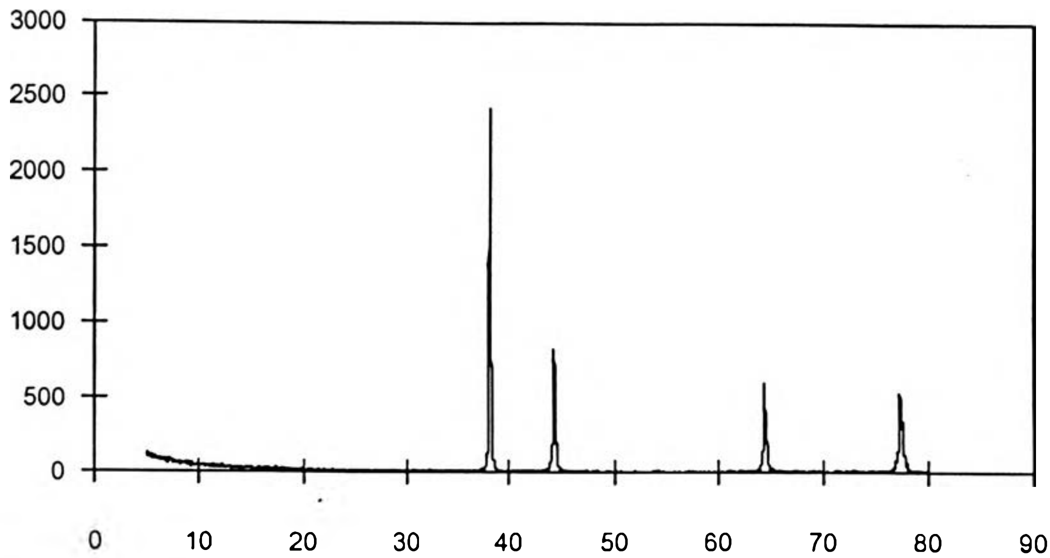


Figure 4.1 XRD result of alumina balls.

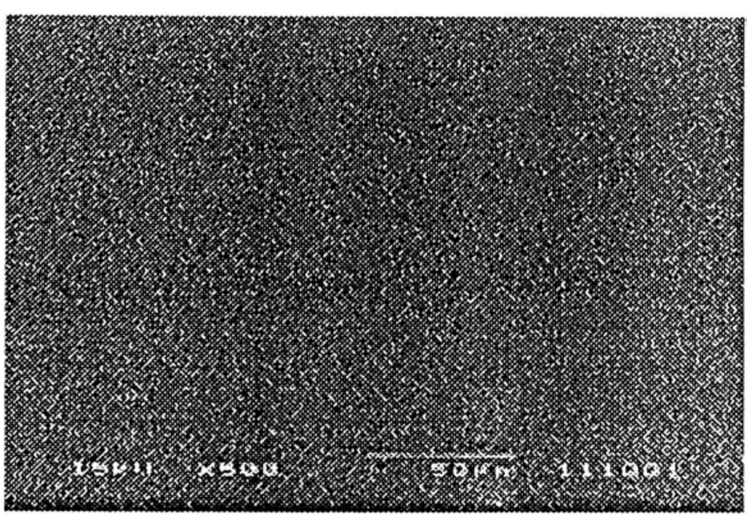


Figure 4.2 Alumina ball surface taken by SEM (X500)

4.1.2 Characterization of Silver Catalyst Supported on Alumina Balls

Thermal reduction was used to prepare silver catalyst on the alumina balls. This technique was carried out by dipping alumina balls into the solution of silver nitrate precursor and followed by drying and calcining. This process was repeated several times. Silver nitrate was converted to metallic silver. It was expected to obtain strong adhesiveness on the alumina surface because of high calcination temperature of 800 °C that is near the melting point of silver metal about 960 °C.

SEM pictures of three different silver loadings on alumina balls are shown in Figures 4.3 to 4.5. The three different silver loadings prepared for this study were 0.73%, 2.77%, and 6.45%. As can be seen from Figures 4.3 to 4.5, for all three silver loadings, granules of metallic silver form throughout the alumina surface. The size of silver particles ranged 10-30 μm. In addition, the formation of some large particles resulted from fusion of nearby silver particles. For the highest loading of 6.45%, it was found that there was more number of large particles in comparison to the other two lower loadings. This was due to fusion of nearby silver particles. These granules identified as metallic silver according to the XRD result as shown in Figure 4.6.

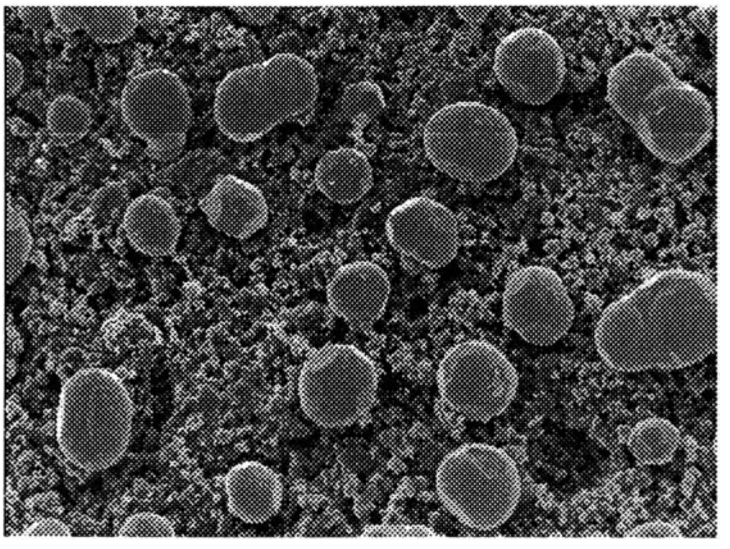


Figure 4.3 SEM picture of 0.73% Ag loading on alumina ball surface, X750.

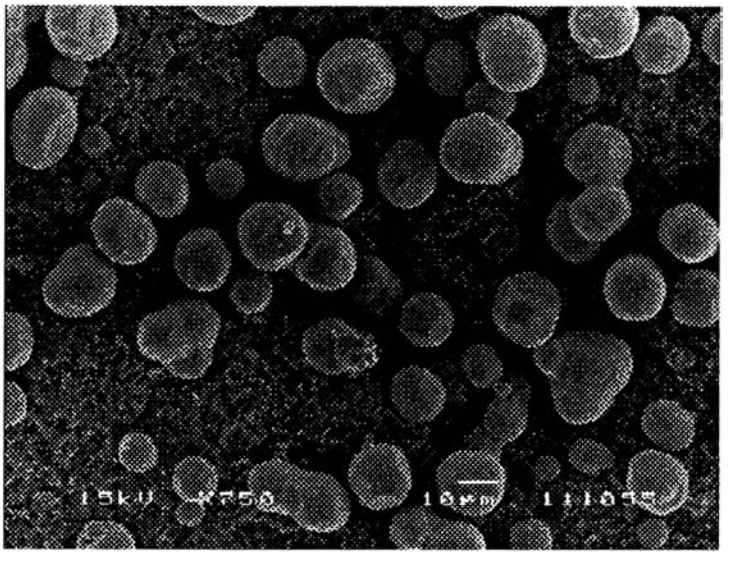


Figure 4.4 SEM picture of 2.77% Ag loading on alumina ball surface, X750.

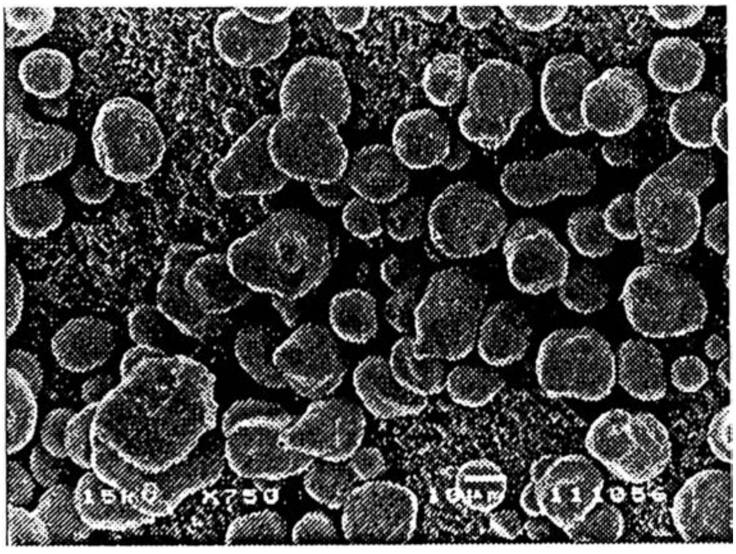


Figure 4.5 SEM picture of 6.45% Ag loading on alumina balls surface, X750.

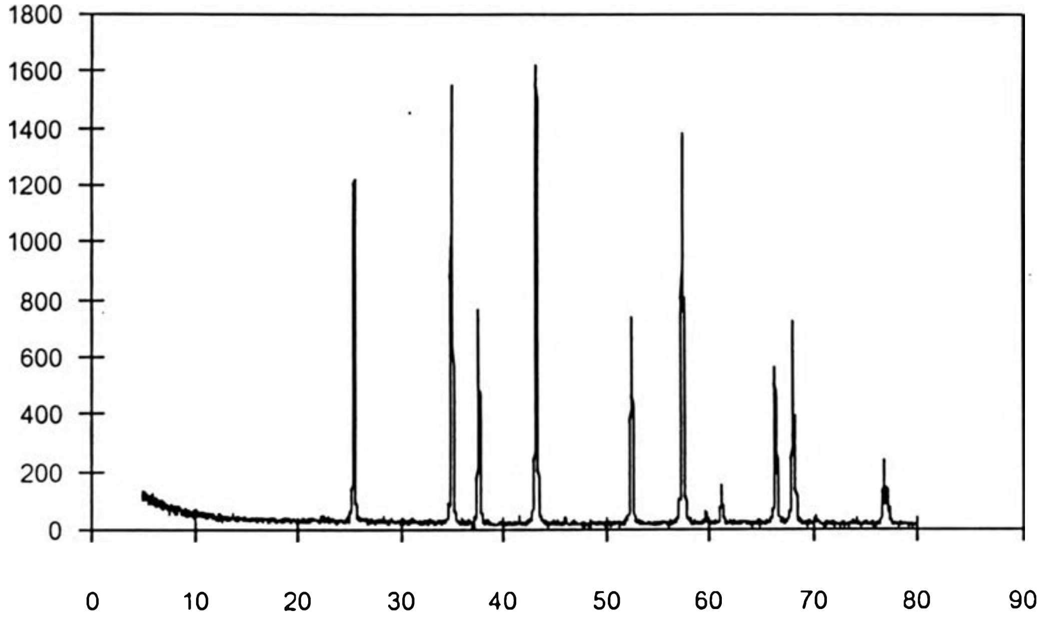


Figure 4.6 XRD result of Alumina ball with Ag .

4.1.3 Characterization of Alumina Powder

Physical properties of the alumina powder used in this study is shown in Table 4.2. This alumina powder has considerably high specific surface area of 213.8 m^2/g comparing to the low specific surface area of alumina balls.

Table 4.2 Physical properties of alumina powder prepared by sol-gel method

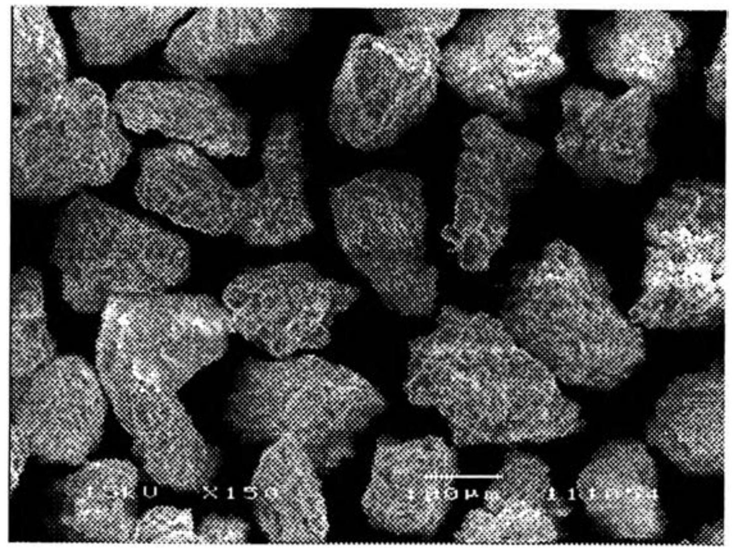
Property	Descriptions
Alumina structure[1]	α-Al_2O_3
Alumina shape	amorphous form
Average diameter, mm	0.173
BET surface area[2], m^2/g	213.8
Average pore diameter[3], °A	6.511
Total pore volume[4], cc/g	7.841×10^{-2}
Colour	White

1 from XRD characterization

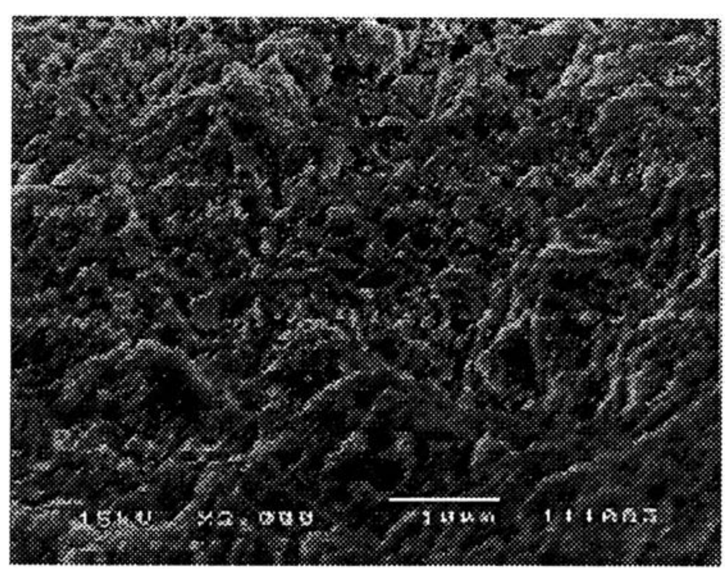
2, 3 from surface area analyzer

4 total pore volume for pore with Radius less than 8.1 at $P/P_0 = 0.1113$

Photographs taken by SEM which are shown in Figure 4.7 reveal that the particles of the alumina powder are irregular in shape and are porous. The porous structure is also confirmed by the measured value of the total surface area of 213.8 m^2/g which is much higher than the value of the alumina balls. From the XRD result, it shows that the alumina powder is in amorphous form (See Figure 4.8).



a) 150 magnification



b) 2000 magnification

Figure 4.7 Surface structure of alumina powder using SEM.

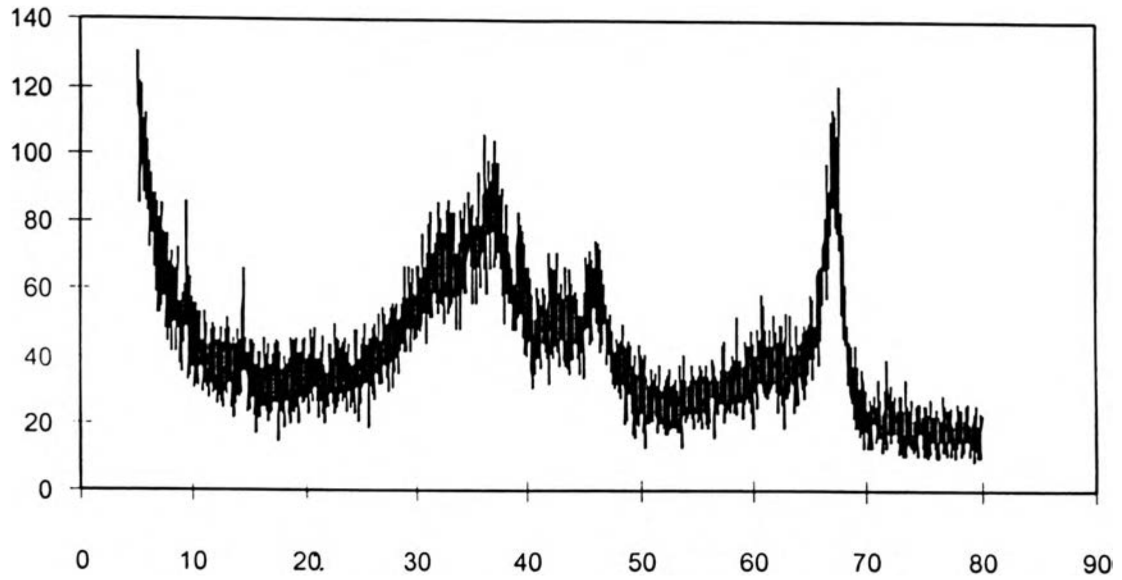


Figure 4.8 XRD result of alumina powder.

4.1.4 Silver Catalyst Supported on Alumina Powder

The preparation procedure of silver catalyst on alumina powder was similar to the method used for silver catalyst on alumina balls except the calcination temperatures which were 500 °C and 800 °C for alumina powder, and alumina balls, respectively. Three different silver loadings on alumina powder (5.97, 9.87 and 14.89%) were prepared in this study. As can be observed from Figure 4.9 for the silver supported on alumina powder with the silver loading of 9.87% in comparison to Figure 4.7 for alumina powder without silver, the size of silver are quite different from a few μm to 10 μm. As be described before, the catalyst was prepared at a low calcination temperature of 500 °C since the alumina powder had been produced by sol-gel method. Hence, a high temperature up to 800 °C could damage its high specific surface area. Consequently, the silver obtained on the surface of alumina powder was found in amorphous form as confirmed by XRD result (See Figure 4.10).

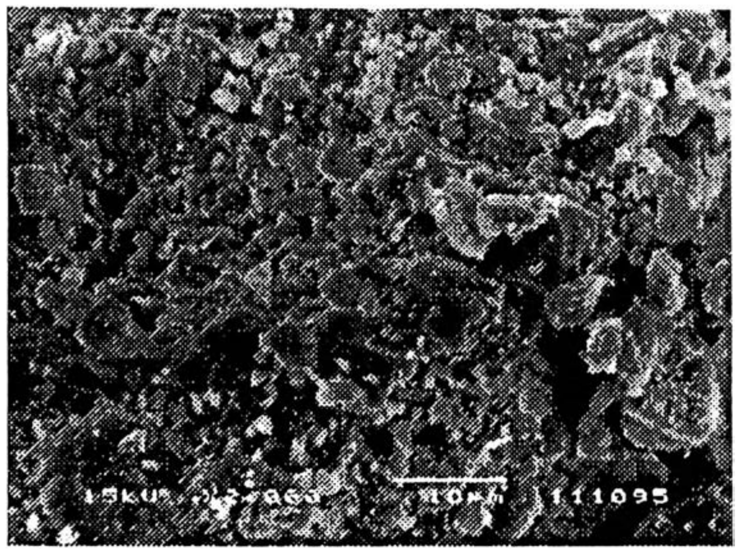


Figure 4.9 SEM picture of 9.87% Ag on alumina powder surface, X2000

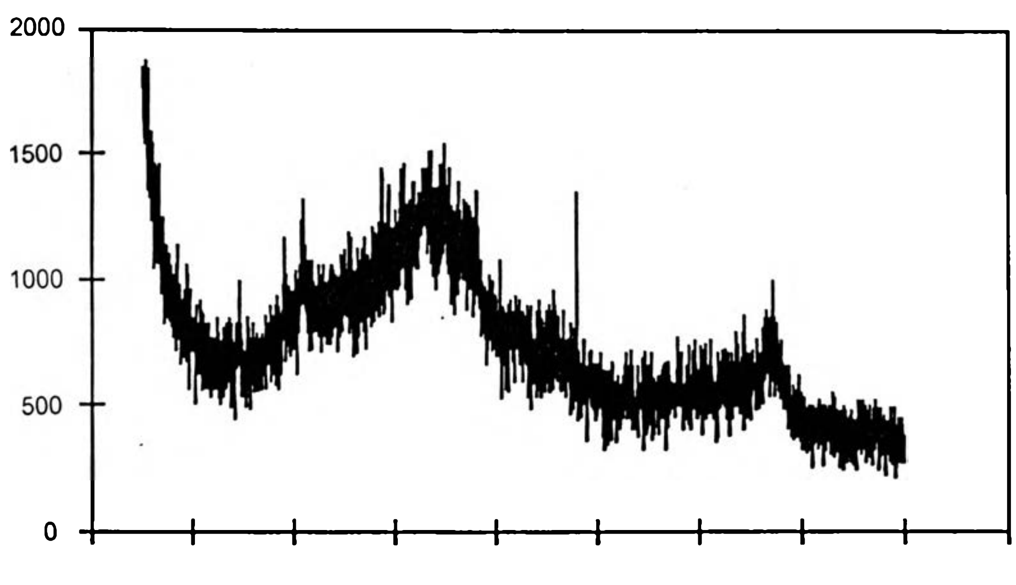


Figure 4.10 XRD result of alumina powder with Ag.

Table 4.3 shows all catalysts prepared on both supports of alumina balls and powder at different silver loadings using different calcination temperatures of 500°C and 800°C. The silver loading varied from 0.73% to 14.89%.

Table 4.3 Summary of catalysts prepared for single-killing study

Catalyst	**Support**	**Silver Loading***	**Reduction technique**	**Reduction Condition**
A	Alumina Balls	0.73%	Thermal	800°C/8 h
B	Alumina Balls	2.48%	Thermal	800°C /8 h
C	Alumina Balls	2.77%	Thermal	800°C /8 h
D	Alumina Balls	6.45%	Thermal	800°C /8 h
E	Alumina Powder	5.97%	Thermal	Ramped 500°C /8 h
F	Alumina Powder	9.87%	Thermal	Ramped 500°C /8 h
G	Alumina Powder	14.89%	Thermal	Ramped 500°C /8h

* % by weight

4.2 Disinfection Study of Silver Catalysts

All catalysts prepared on two supports (alumina balls or alumina powder) were tested their bacteriocidal activities by using *E. coli* as indicator organism. A simple experiment of single-pass killing study was conducted. All experimental data are given in Appendix B.

Before commencing the experimental work on E. coli killing efficiency, it was necessary to know how good the silver adhesion on the alumina surfaces was. A straightforward method of running distilled water through the single-pass killing apparatus was carried out. The silver content in the effluent samples was analyzed by using AAS. Table 4.4 shows that there is no significant loss of silver from the silver catalysts prepared on alumina balls. It can be concluded that this material is suitable for use as support for silver catalyst of disinfection application. This is very important to develop this appropriate technique to overcome any silver loss to the passing water in order ensure the safe of the disinfected water for drinking purpose.

Table 4.4 Silver content in the output samples flowing through alumina balls at different silver loadings

Silver loading (% wt)	**Silver content in the output sample (ppm)**
0.73	0
2.77	0
6.45	0

4.2.1 Alumina Balls Supporting Silver Catalysts

Table 4.5 summaries the experimental results of the single-pass killing study of catalysts, including blank alumina ball at different silver loadings and contact times. For the blank alumina ball, the result showed no any disinfection effect. It can be concluded that the blank alumina ball itself does not adsorb bacteria onto its surface in detectable amount. It is interesting to point out that either effects of multiplication and death can be ignored under the studied conditions. Therefore, all of there experimental runs were finished within 20 minutes is justified to ignore the effects of multiplication and death.

Figure 4.11 shows that the efficiency of *E.coli* killing clearly depends on the amount of silver loading and contact time. A significant increase of killing efficiency was observed when the silver loading was increased. This is because an increase in silver loading directly results in increasing superoxide free radicals which are responsible for reacting with *E. coli*. Figure 4.12 illustrates the effect of contact time on *E. coli* destruction efficiency at different silver loadings. For any given silver loading, an increase in the contact time also resulted in increasing the *E. coli* destruction efficiency. As can be seen from Figure 4.12, when the contact time is increased, the *E. coli* destruction efficiency increases almost linearely. This is because the amount of superoxide free radical can penetrate into the *E. coli* cells more if contact time is longer.

Table 4.5 Experimental results of the single-pass killing using silver catalysts supporting alumina balls at different silver loadings and contact times

Catalyst	**Ag loading (%wt)**	**Contact time (s)**	**% *E. coli* killed**
Blank	0	7	0
		10.5	0
		21	0
A	0.73	7	20.22
		10.5	26.04
		21	33.72
B	2.48	7	22.35
		10.5	26.97
		21	36.05
C	2.77	7	24.47
		10.5	27.59
		21	38.64
D	6.45	7	36.05
		10.5	43.02
		21	51.72

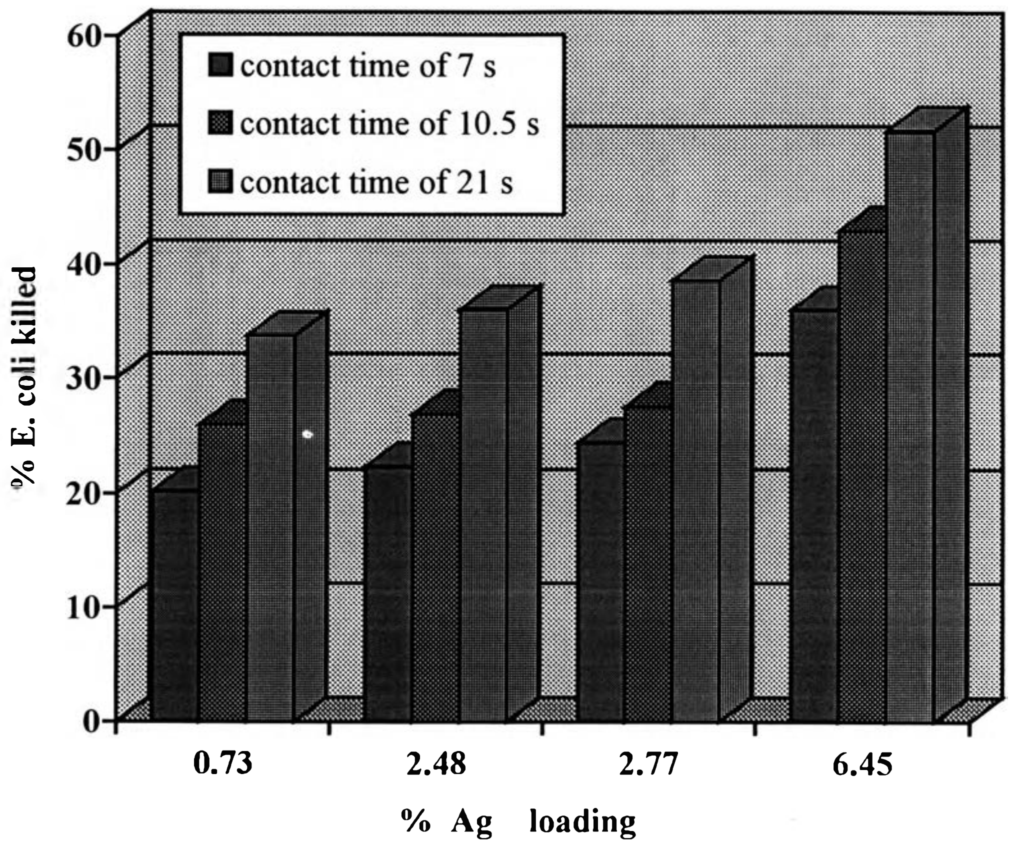


Figure 4.11 Effect of % Ag loading on *E. coli* destruction efficiency at different contact time using alumina balls as support.

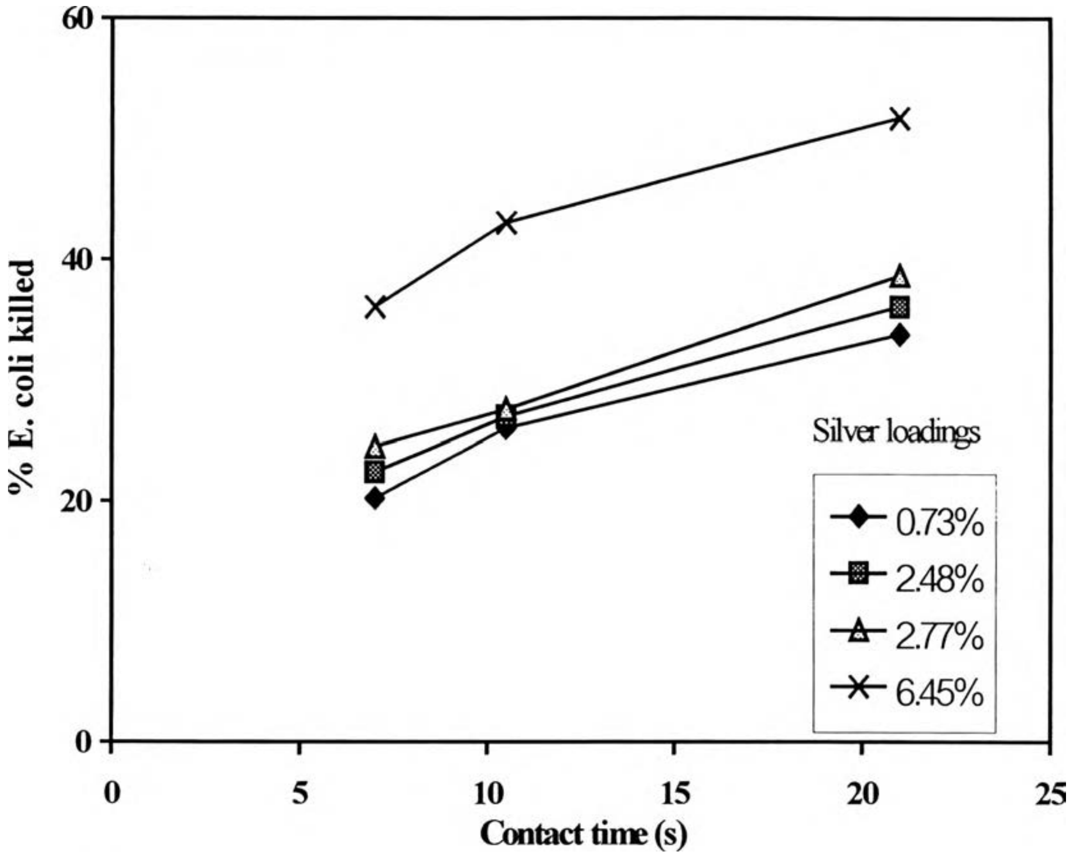


Figure 4.12 Effect of contact time on *E. coli* destruction efficiency at different silver loadings using alumina balls as support.

4.2.2 Alumina Powder Supporting Silver Catalysts

Table 4.6 shows the summary of the experimental results using alumina powder supporting silver catalysts at different conditions. As can be seen from Table 4.6 and Figure 4.13, it can be concluded that the blank alumina powder can slightly adsorb bacteria onto its surface because of its porous structure. Catalyst G containing the highest silver loading of 14.89% had the highest activity when it was compared with catalysts E, F and G. It was found that the *E. coli* destruction efficiency increased with increasing the amount of silver loading. At a given silver loading, the *E. coli* destruction efficiency increased significantly with increasing the contact time (See Figure 4.14). It should be pointed out that the effect of the contact time on the *E. coli* destruction was greater than that of the silver loading. For the case of alumina powder as a support, it has been found that a significant loss of silver appears obviously as shown in Table 4.6 and Figure 4.15. The significant loss of silver from the alumina powder resulted from the low temperature (500 °C) during the calcination step. It is not possible to employ a higher calcination temperature up to 800 °C as used for alumina balls since this high temperature will destroy its microporous structure.

Table 4.6 Summary of experimental results of single-pass killing study using alumina powder supporting silver catalysts

Catalyst	Silver loading (% wt)	Contact time (s)	Silver content in The output sample (ppm)	% *E. coli* killed
Blank	0	3.2	0	1.89
		4.8	0	5.88
		9.6	0	4.17
		24	0	8.70
E	5.97	3.2	0.01	18.42
		4.8	0.03	32.50
		9.6	0.12	54.55
		24	0.25	75.00
F	9.87	3.2	0.01	25.00
		4.8	0.05	38.78
		9.6	0.21	76.92
		24	0.32	90.74
G	14.89	3.2	0.04	40.00
		4.8	0.15	48.08
		9.6	0.38	86.27
		24	0.56	94.87

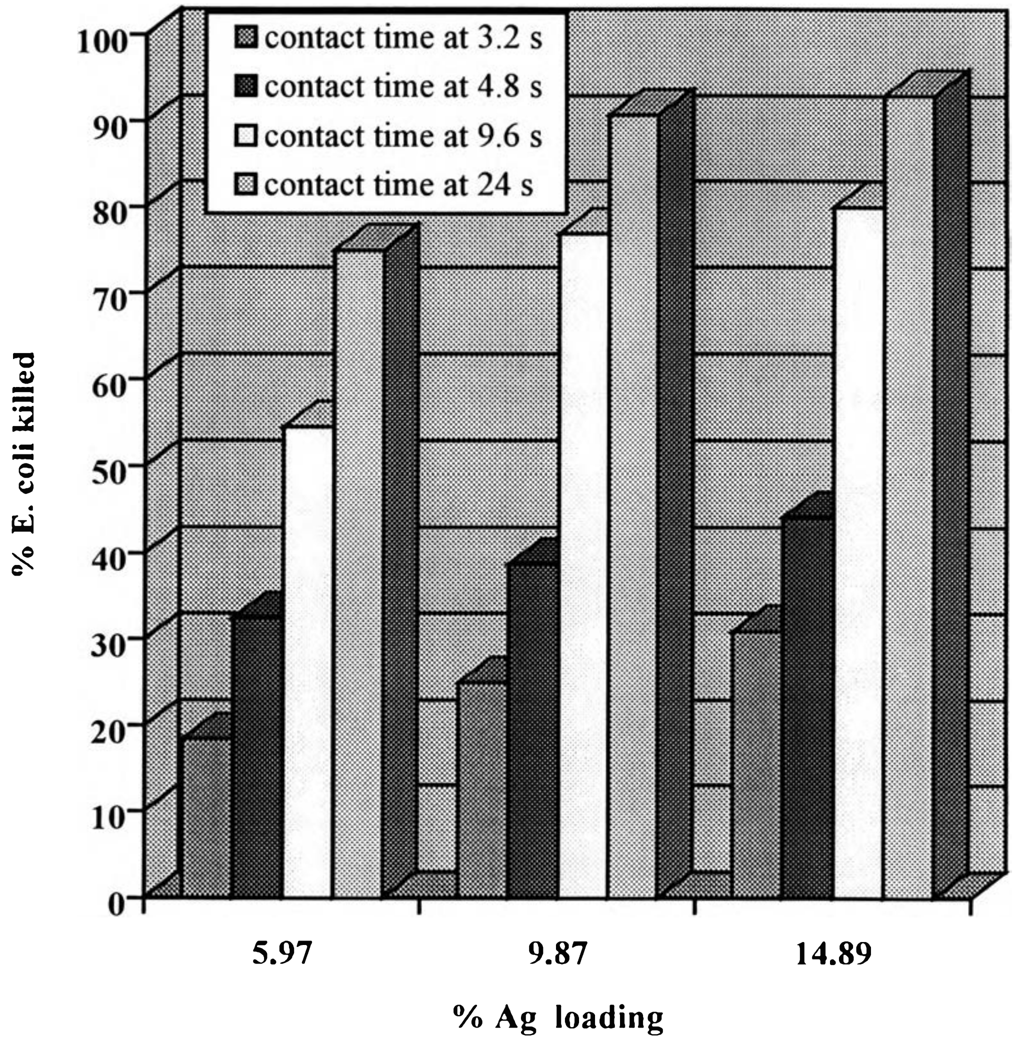


Figure 4.13 Effect of % Ag loading on *E. coli* destruction efficiency at different contact times using alumina powder as support.

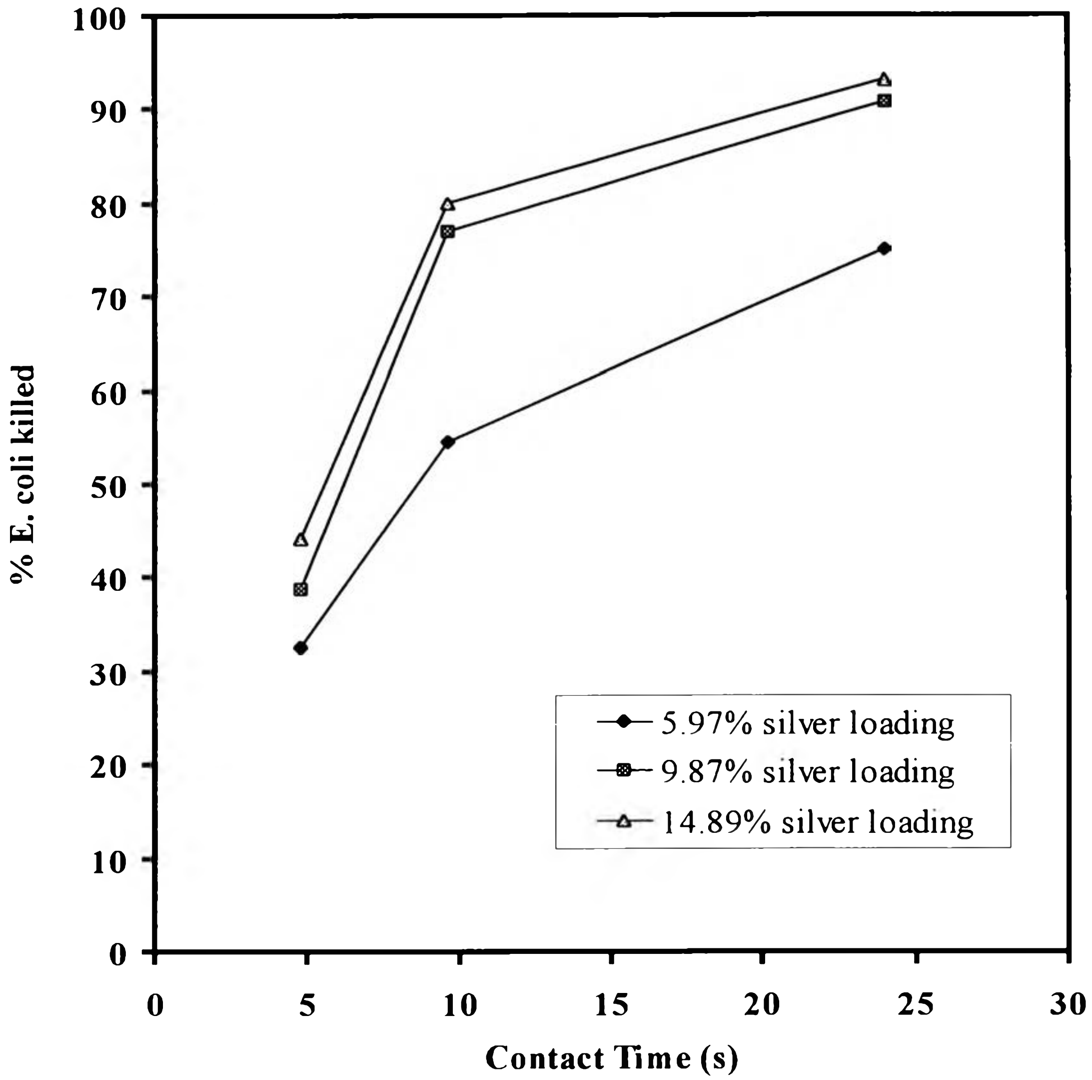


Figure 4.14 Effect of contact time on *E. coli* destruction efficiency at different silver loadings using alumina powder as a support.

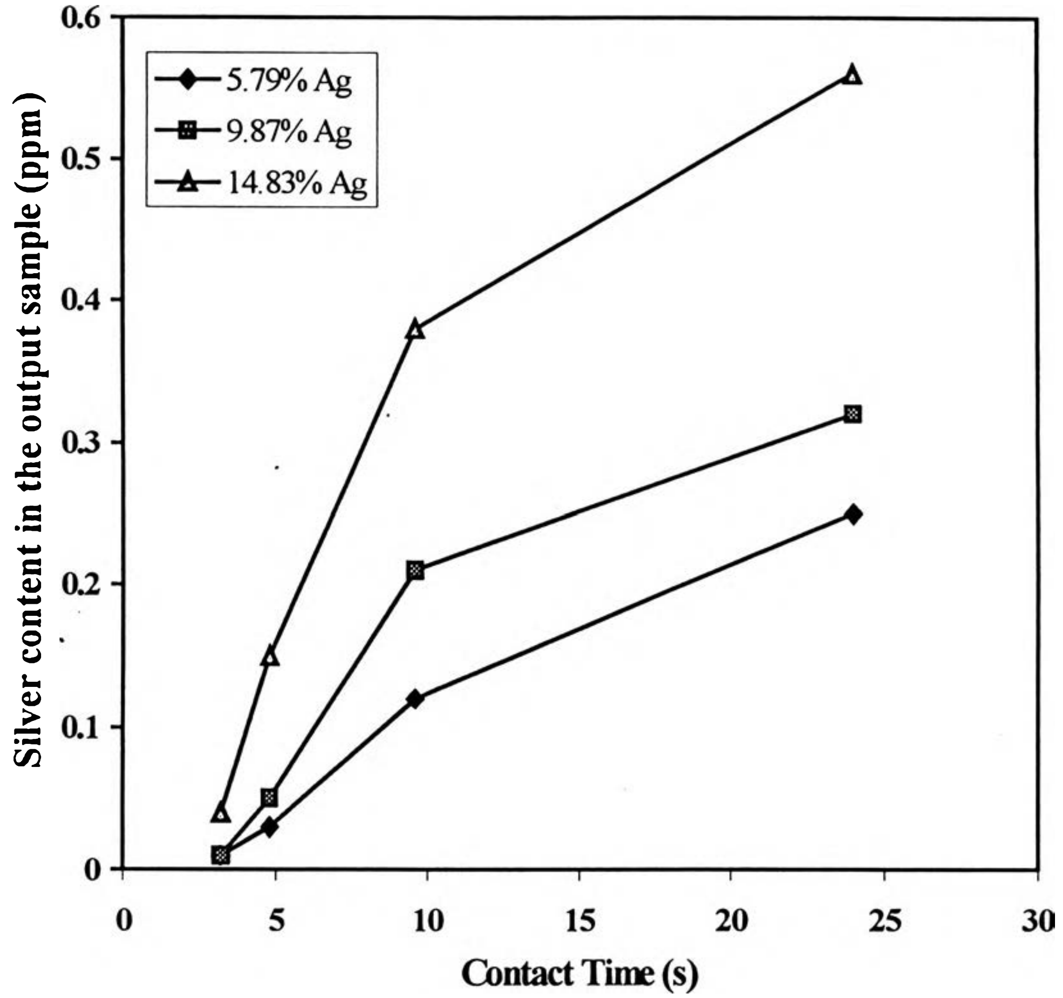


Figure 4.15 Silver content in output samples from the single-pass killing experiment at different contact times and silver loadings using alumina powder as a support.

4.3 Effect of Dissolved Oxygen Level on Bacterial Destruction

The impact of changes in dissolved oxygen level on the *E. coli* destruction efficiency is illustrated in Figure 4.16. Bubbling with pure nitrogen, air, and pure oxygen were applied to regulate the dissolved oxygen at low, medium and high levels, respectively. As can be seen from Figure 4.16, for alumina powder, a drastic increase in the *E. coli* destruction efficiency

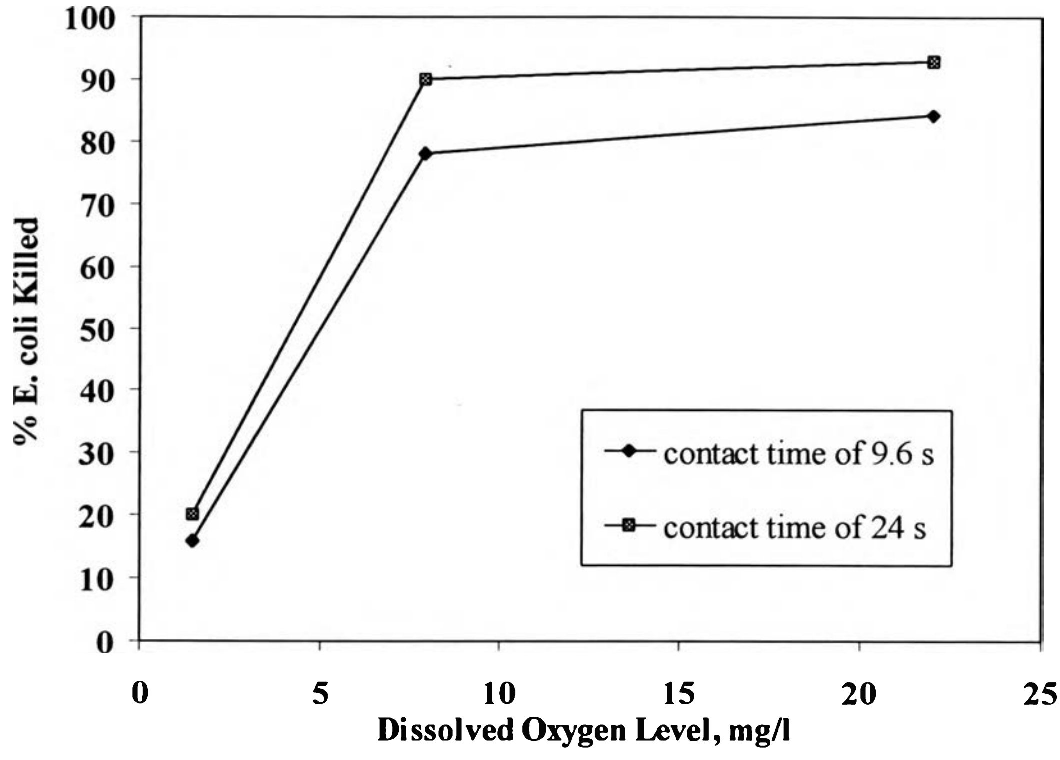


Figure 4.16 Effect of dissolved oxygen level on *E. coli* destruction efficiency at two different contact times using silver catalyst supporting alumina powder having silver loading of 9.87%.

occurs when the dissolved oxygen level is increased from 1.5 to 7.5 mg/l. Beyond D.O. level of 7.9 mg/l, an increase in dissolved oxygen level caused a small increase in the *E. coli* destruction efficiency. The results lead to a conclusion that the *E. coli* destruction efficiency depends on amount of superoxide free radical available in the system. The production of superoxide free radical depends on two factors of dissolved oxygen and amount of silver. At a high dissolved oxygen level, amount of superoxide free radical is limited by amount of silver. Moreover, the results can confirm that the *E. coli* destruction results from oxidation reaction pathway.

4.4 Comparison of Alumina Balls and Alumina Powder Supported for Silver Catalyst

Figure 4.17 shows comparison of *E. coli* destruction between two types of silver catalyst supports at different contact times. It was clearly seen that the alumina powder gave much higher *E. coli* destruction efficiency than the alumina balls because alumina powder has higher specific surface area than alumina balls.

A significant improvement in the *E. coli* destruction efficiency was achieved by increasing the contact time for the case of alumina powder. However, at a low contact time of 15.4 s, both alumina supports gave the same *E. coli* destruction efficiency. From the practical point of view, alumina balls should be considered to apply for disinfection purpose rather than alumina powder since alumina balls provide three important properties of no silver loss, low pressure drop and lower cost in comparison to alumina powder. However, attempts are needed to improve its bacteriocidal activity. Smaller size and better distribution of silver particles are needed to develop in order to improve the bacteriocidal activity.

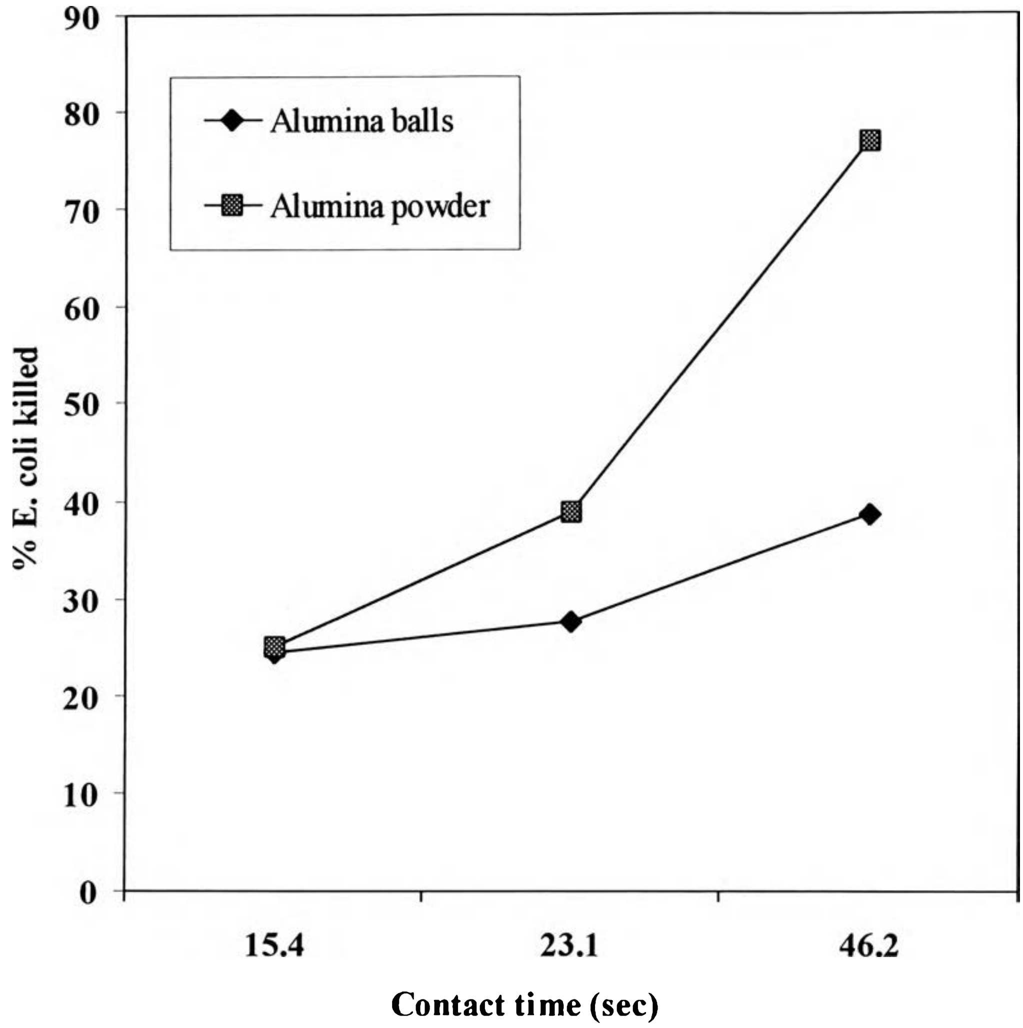


Figure 4.17 Comparison of two types of silver catalyst supports at 3.38 % Ag loading and 7.9 mg/l of D.O. for *E.coli* destruction at different contact times.