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COMPARISON OF PHOTOCATALYTIC SYSTEMS INCLUDING SILVER AND TITANIUM DIOXIDE NANOPARTICLES EFFICIENCIES FOR THE E. COLI REMOVAL FROM DRINKING WATER

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ABSTRACT

The removal and destruction of organic contaminants in groundwater can be addressed through the impregnation of adsorbents with photoactive catalysts. In this paper removal trend of E. coli from drinking water examined by nano silver and nano titanium dioxide. To perform this, four different concentration of silver nano particles and titanium dioxide under UV radiation (with 247 nm- wavelength) used. The results showed the nano particles of silver and titanium reach to 100% disinfection efficiency at the concentrations of 0.4 mg/l (with 20 minutes contact time) and 0.8 mg/l (with 40 minutes contact time), respectively.

For equal amounts of disinfectant and equal number of E. coli colonies in drinking water, disinfection potential for (nAg + V) is significantly higher than ($nTiO_2$ + UV). When the nano particles concentration increases, the disinfection rate rises, and it was higher and faster done by the nano silver particles comparing to nano-titanium particles ($P_{value} < 0.05$, $R^2 = 0.705$)

***Key words**: Disinfection, nano silver, UV, titanium dioxide.*

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Introduction

Pathogenic bacteria are one of the main reasons for worldwide water-borne disease causing a big threat to public health, hence there is an urgent need to develop cost-effective water treatment technologies. Nano-materials in point-of-use systems have recently attracted considerable research and commercial interests as they can overcome the drawbacks of traditional water treatment techniques. In addition to their high costs, the conventional water disinfection technologies, such as chlorination and ozonation, can lead to the formation of harmful disinfection by-products (DBPs), among the most dangerous of which are the Trihalomethanes (THMs), well-known for their high carcinogenic potential[(1)].

The challenge to achieve appropriate disinfection without forming harmful disinfection by products using conventional chemical disinfectants, as well as the growing demand for decentralized or point-of-use water treatment and recycling systems calls to new technologies for efficient disinfection and microbial control. Several natural and engineered nano materials have demonstrated strong antimicrobial properties through diverse mechanisms including photocatalytic production of reactive oxygen species that damage cell components and viruses (e.g. TiO_2 and ZnO), compromising the bacterial cell envelope (e.g. peptides, chitosan, ZnO and silver nanoparticles), interruption of energy transduction (e.g. nAg and aqueous fullerene nanoparticles). Although some nanomaterials have been used as antimicrobial agents in consumer products including home purification systems as antimicrobial agents, their potential for disinfection or microbial control in system level water treatment has not been carefully evaluated[(2)].

The photocatalytic process is now well known and recognized as an efficient method to remove organic pollutants present in aqueous phase such as pesticides, dyes or in gaseous phase such as volatile organic compounds (VOC). Several industrial reactors are now commercialized for this type of application. Main researches concerned water treatment or removal of pollutants, but disinfection was few studied[3,4]. Photocatalytic oxidation as a technique for microbial disinfection was first demonstrated by Matsunaga et al.

In recent years, semiconductor photocatalytic process has shown a great potential as a low-cost, environmental friendly and sustainable treatment technology to align with the "zero" waste scheme in the water/wastewater industry. The ability of this advanced oxidation technology has been widely demonstrated to remove persistent organic compounds and microorganisms in water. At present, the main technical barriers that impede its commercialisation remained on the post-recovery of the catalyst particles after water treatment[5,6].

Usually showing to be less active and require more irradiation time compared with TiO_2 slurries due to several problems such as mass transfer limitations and lower titania surface area[7]. A few studies performed tests to prove the efficiency of photocatalytic process to remove viruses. Since 2000, Rincon and Pulgarin studied thoroughly the effect of various parameters, such as natures of the support and of the photocatalyst and bacterial initial concentration on the photocatalytic efficiency. In 2004, Keller et al and developed and patented a photocatalytic reactor removing more than 99% of bacteria.Various solar reactors for photocatalytic water treatment mainly based on non-concentrating[8-10]. Photocatalytic water treatment using nanocrystalline titanium dioxide and nonosiver is a well-known advanced oxidation process (AOP) for environmental remediation .Manoj A. et al were explained the kinetics of the photocatalytic degradation of aqueous pollutants by NTO and Ag-n is still a subject of debate. Several recent reports claim that it follows the Langmuir-Hinshelwood model (L-H model) of kinetics. Herein, we report the studies on the efficiency of photocatalytic process to inactivate bacteria according to some parameters that influence to that removal rate.

Many catalysts exist that Capable to destroy chemical and biological water contaminants, among the more useful being ZnO, ZrO_2, CeO_2, Fe_2O_3, and WO_3[11]. The first step in photocatalysis reactions consists of the generation of the hole-electron pair through the irradiation of the TiO_2 particles with photonic energy equal to, or greater than, its band gap energy. The electron is then extracted from the valence band (VB) to the conduction band (CB). This process results in a positive region in theVB (Hole h^+) and a free electron (e) in the CB. The hole, at the catalyst surface, reacts with hydroxyl ions (OH) and adsorbs water to form free radicals (OH).

$TiO_2 + hy \rightarrow TiO_2 + -e\ (CB) + h+\ (VB)$: (Eq. 1)

$TiO_2\ (h^+) + OH- \rightarrow TiO_2 + OH^0$: (Eq. 2)

$TiO_2\ (h^+) + H_2O_{ads} \rightarrow TiO_2 + OH_0 + H+$: (Eq. 3)

Other secondary reactions can also occur, such as the formation of hydrogen peroxide, considering the reaction between superoxide radical and proton[12,13]. When TiO_2 absorbs the energy of impinging photons having equivalent or excess energy to the band gap, electron-hole pairs are generated. This means that an electron in the valance band earns sufficient energy to overcome the band gap and reach the conduction band, with the concomitant vacancy in the valance band (the hole). The band gap, is the void energy region which separates the valence band from the conduction band. For TiO_2, the band gap can be overcome by energy from UV-A photons (350-400 nm). The absorption of energy and the subsequent generation of the electron-hole pair is the initiating step[14,15].

Ag-modified TiO_2 photocatalysts have been synthesized using the hydrothermal method since this is a relatively simple route to load TiO2 nanoparticles with Ag[16]. In study of Camilo. A presented that photocatalyst's configuration was observed to be as anatase-brookite mixed phase particles with Ag partially oxidized aggregates on the TiO_2 surface, which increased visible light absorption of the material. Moreover, photoproduction of singlet oxygen was followed by EPR analysis under visible light irradiations following the formation of TEMPOL. Such photoproduction was totally decreased by using the singlet oxygen scavenger DABCO. Photocatalysts were tested towards the photocatalytic disinfection of water suing a solar light simulator and an interior-light irradiation setup.

Results evidenced an increase in the photooxidative effect of TiO_2, while dark processes evidenced that part of the inactivation process is due

to the Ag-TiO_2 surface bactericidal effect and possible lixiviated Ag+[17]. The main objective of this study is to investigate disinfection efficiencies of silver and titanium nanoparticles in drinking water and comparison of efficiencies of these tow nanoparticles.

Materials and methods

Characterization of Nano particles

Silver and titanium dioxide nano particles were purchased from Nano Sany Corporation. Physical characteristics of nano particles are shown in table-1.

characteristics	Nano silver	Nano titanium dioxide
Purity %	99.99	99 <
Size (nm)	20	25- 10
Specifi surface (m2/g)	18 -22	200 - 240
colore	black	White
Density (g/m3)	10.5	3.9
pH	-	6-6.5
Wight losing after drying%	-	4.17
Wight losing after burning %	-	8.24

Table 1: physical characteristics of nano particles.

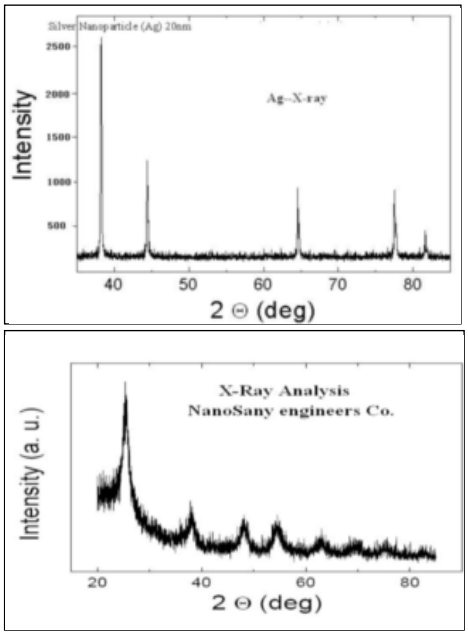

Figure 1: XRD pattern of silver nano particle(a) and titaniume dioxide nano particle(b).

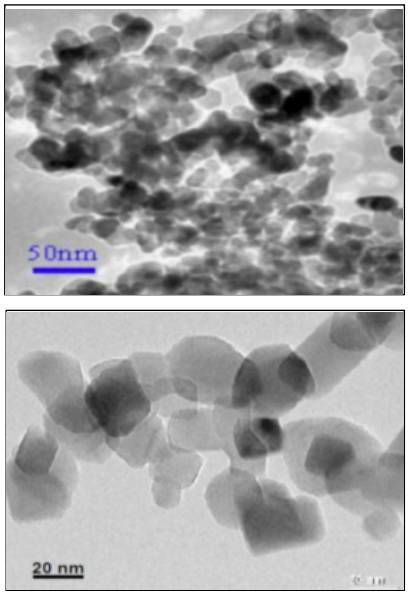

Figure 2: TEM images of silver nano particle(a) and titaniume dioxide nano particle(b).

According to the information given in table 1 and TEM image analysis, the mean size of nano silver and nano titaniume dioxide were 20 and 18 nm, indicating that both selected materials were nano-sized matters. The spesific surface area of nano silver and nano were 18-22 and 200-240 m2/g respectively, therefore specific surface of titaniume dioxide was greather than nano silver.

Figure 1 shows the XRD of nano particles to be used in this study and figure 2 shows the TEM images. It can be seen from figures that both selected materials were crystalline particles and the size of titanium oxide particle was smaller than silver particle. TEM image analysis confirms the information given in table 1 about particles size and surface area.

Disinfection experiments

E. coli bacteria were prepared as the lyophilized ampoules. Prepared suspensions which were made of E. coli ampoules were transferred into tubes containing tryptic soy broth (TSB) culture and were incubated at 37°C up to 24 hours. For final part, ampoules were transferred into EMB agar culture to obtain active bacteria through linear culture after 24 hours. Required bacteria concentrations were 100, 1000 and 10000 CFU which were prepared through sample dilution compared with 0.5 McFarland standard. Absorption ratio was read by spectrophotometer at 620 nm wavelength. To disinfect contaminated water, samples of Nano silver and titanium dioxide particles with a size of 25-10 nm and 20 nm, were used, respectively.

Samples were disinfected using different concentrations of nano silver particles (0.05, 0.1, 0.2, 0.4 mg/L) and nano titanium dioxide concentrations of (0.2, 0.4, 0.6, 0.8 mg/L). In these cases, each of these samples was exposed to UV- C at 247.3 nm wavelength with lamp intensity of 1.8 W/m^2. After 10, 20, 30, 40 and 60 minutes from the start time of disinfection, in order to evaluation fecal coliform elimination in the disinfection reactor, sampling from outlet water of system was done. In each part of test, sample was transferred into TSB culture and evenly distributed on culture surface and then was placed in incubator. After 24 hours the number of colonies was counted and result was reported as CFU unit. The pH range was set for all tests at neutral level (7.5± 0.5). The test procedure and counting methods was done according to standard method for water and wastewater examinations (21th edition), and disinfection efficiency was calculated according to following equation: $E = \frac{Ci - Cf}{Ci} \times 100$

To data analyzes, parametric tests including T-Test and ANOVA tests were applied after confirming normality by Kolmogorov-Smirnov test (P_{value} <0.05)

Results and discussion

The effect of nAg photo catalyst on disinfection efficiency

The effect of nAg Concentration

Table 2 simply shows the efficiency for application of nAg photocatalyst process at different times and concentrations. The minimum and maximum efficiency of bacteria removal at 0.05 mg/L concentration are 42 to 86 percent, but this percentage is not significant with UV without catalyst. (p_{value} > 0.05). The minimum, average and maximum removal efficiency is increased as nAg and time is increased, so that efficiency is 100% at 0.4 mg/L concentration and 20 minutes exposure time. ANOVA test shows that efficiency is not significant at 0.05 mg/L concentration only with UV application but it is significant at higher concentrations (P_{value}< 0.05) because as nAg concentration is increased, the ratio of light contact and production of radicals is increased. In addition, as nAg concentration is increased, the possibility for attachment of nano particles to bacteria surface and penetration and DNA damage is increased and bacteria become inactive. This part of our findings is consistent with Rabbani et. al[18] and Gu et.al findings[19].

Contact time (min)												nAg (mg/l)	Test number
60			40			20			10				
Max	Ave±SD	Min	Max	Ave±SD	Min	Max	Ave±SD	Min	Max	Ave±SD	Min		
86.2	11 ±76	64.8	60	2.4 ±57	55.2	56	1.8 ±54	52.4	42.4	43.2±1	42.4	o.o5	1
99.3	16 ±89	70.4	94.4	15 ±85	68	87.6	11 ±78	66	77.2	68±14	52	o.1	2
100	11 ±93	80	99.3	16.3±89	70.8	98.6	11 ±88	68	97.9	84.7±21	60.8	o.2	3
100	1.6 ±99	97.2	100	2.5 ±98	95.6	100	9.7 ±94	82.8	97.6	90.7±12	76.8	o.4	4

Table 2:The effect of nAg concentration on photo catalytic process for E. coli removal at different exposure times (×10^{5}CFU/ml)

The effect of bacteria colonies number

To determine the effect of E. coli colonies number (CFU/ml) on efficiency of process, three bacteria concentration (10^3, 10^4 and 10^5 CFU/ml) were exposed at 0.2 mg/l nAg. The figure 3 shows the effect of colonies number on E.coli removal efficiency ratio, so that photo catalytic process for 10^5 CFU/ml has 100% efficiency and it decreases as colony number increases. But LSD test shows that this effect is not significant for two respectively doses When colonies number is equal to 10^3 and 10^4 CFU/ml, removal efficiency before 20 minutes was 96.7%, while after this time was increased to 100%. When number of colonies is 10^3 and 10^5 CFU/ml, the difference for their effect is significant (P_{value}<0.05). Because as bacteria density is increased, contact between light and nano silver and photocatalytic products is reduced. Silver ions react with thiol groups of proteins and cause respiration enzymes to be inactive and produce ROS. Also silver ions become active due to presence of UV radiation and this strengthen the inactivation of viruses and bacteria[20].

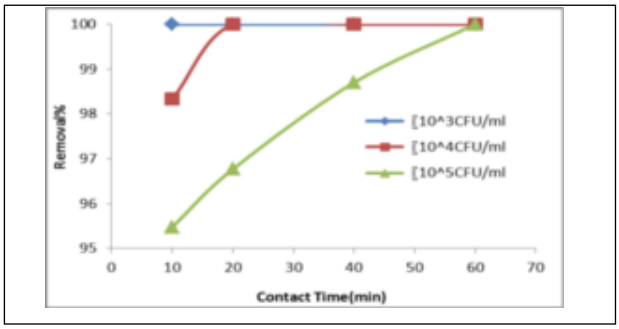

Figure 3: The effect of colonies number on nano-silver photocatalytic process (nAg concentration =0.2 mg/l).

The effect of contact time

Figure 4 shows the effect of different contact times i.e. 10, 20, 40 and 60 minutes contact times on disinfection efficiency (105 CFU/ml) for nano silver particles. As we expect, while contact time is increased, disinfection efficiency increases accord-

ingly. This finding is consistent with Rabbani et al. findings[18]. The ANOVA analyze related to comparison of contact times with concentration of nano silver equal 0.05 mg/l and disinfection efficiency, showed that removal efficiency and of at different contact times is significantly different and only this difference is not significant between 20 and 40 minutes contact times. Also this difference is not significant for higher concentration of nano silver ($P_{value} > 0.05$). Therefore, maximum activation of nano silver particles occur till 60 minutes contact time.

Contact time (min)												nAg (mg/l)	Test number
60			40			20			10				
Max	Ave±SD	Min	Max	Ave±SD	Min	Max	Ave±SD	Min	Max	Ave±SD	Min		
82.9	11 ±74	65.2	77.8	9.8 ±69	59.3	64.5	9.9 ±56	49.5	44.8	7.6±51	37.2	o.o5	1
90.3	4 ±85.9	82.9	83.5	6.8 ±77	70	72.4	8.6 ±65	55.9	58.6	11±68.5	45.3	o.1	2
93.1	3.1 ±89	87.1	85.5	4.1 ±81	77.3	80	8 ±87.3	64.5	76.6	84.7±21	55.9	o.2	3
100	11 ±90	78.9	100	12 ±88	75.1	94.2	11 ±84	71.9	86.5	90.7±12	37.2	o.4	4

Table 3: The effect of $nTiO_2$ dose on photocatalytic E. coli removal at different time (CFU/ml).

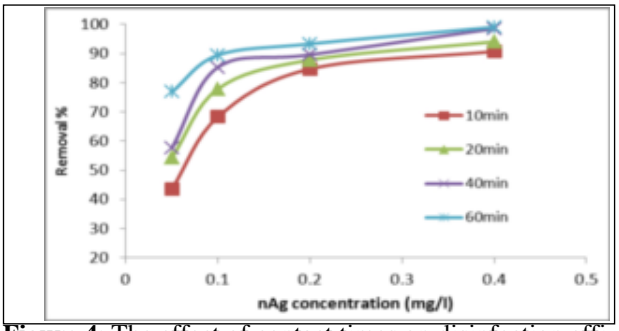

Figure 4: The effect of contact times on disinfection efficiency of nAg photo catalytic (×10^{5}CFU/ml).

The effect of $nTiO_2$ photo catalyst on removal efficiency

The effect $nTiO_2$ concentration

According to earlier studies which indicate that TiO_2 catalyst plays an effective role on disinfection process[21], four dose of TiO_2 were applied (0.2, 0.4, 0.6 and 0.8 mg/l) and bacteria density for water sample was set for 105 CFU/ml. The results in table 2 and 3 show that removal ratio of E. coli colonies was increased as TiO_2 catalyst increases.

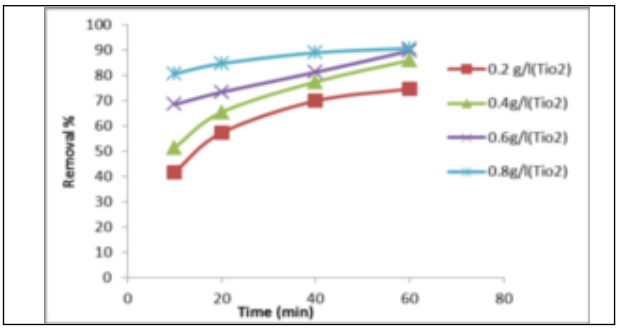

Figure 5: The effect of $nTiO_2$ application time on photocatalytic process for E.coli removal at different time (×10^{5}CFU/ml).

Simantris et al. for photocatalytic disinfection process used TiO_2 nano particles with concentration of 0.5-1 g / L for total removal of coli forms and enterococci, and found that increasing TiO_2 catalyst load intensify bacteria destruction and also the inter cellular damage and eventually bacteria mortality rate is increased[21, 22].

Pratap redi et al. in their research which was done about the effect of TiO_2 in water with E. coli concentration of CFU/m found that as catalyst concentration rises, the efficiency for removal increases, so that for 0.75 gram per liter concentration for 40 minutes, removal efficiency was 99%. Kalman et al. research showed that at high concentration of n TiO_2, the effect of turbidity and shadow has been dominated and the amount of light which reaches to nano particle would be diminished[23] .

The effect of contact time

Figure 6 shows the ANOVA analyze related to effect of contact time on disinfection efficiency using UV/n TiO_2 photocatalytic process with E. coli concentration of 105 CFU/ml.

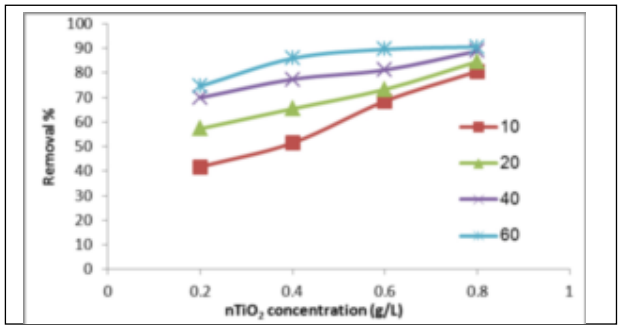

Figure 6: TThe effect of $nTiO_2$ contact time on photocatalytic E. coli removal (×10^{5}CFU/ml).

It is seen that difference between disinfection efficiency for 10 minutes contact time (with nTiO2 concentration of 0.2 and 0.4 g/l) and other contact times i.e. 20,40 and 60 minutes is significant. Mean while, this difference at higher concen-

tration i.e. 0.6 and 0.8 g/l, even though has increasing trend, but is not significant ($p_{value} > 0.05$).

Liu et al. investigated the photocatalytic decomposition of E coli in water using UV and a new kind of nano particle i.e. ($nTiO_2$ N-Dope) and they found that sun light with contact time of 20 minutes reduces E coli colonies number from 105 to 10^9 CFU/ml and the inactivation process follows the first order reaction[21]. Pratap redy et al. used only TiO_2 and fixed TiO_2 on Hβ Zeolite for e coli disinfection with a bacteria concentration of 10^7 CFU/ml and found that removal efficiency improves as contact time increases so that in the case of TiO_2 application, bacteria was removed after 280 minutes[23]. Kumar and Raza studied photo catalytic disinfection of water using Ag-TiO_2 composite nano crystalline and found that by increasing contact time to 60 minutes, bacteria number was reduced dramatically[24].

Conclusion

Efficiency of nano silver particles for E. coli removal is significantly higher than the single catalyst application including nAg and $nTiO_2$, it means that UV light has intensifying effect on the performance of nano particles. The minimum, average and maximum efficiency removal for E. coli improves as concentrations of silver nano particles and contact time increases, so that in the concentration of 0.4 mg/L and contact time equal to 20 minutes, they obtained as to 82.8%, 94.1 ±9.7% and 100%, respectively. The efficiency for photo catalytic performance using silver nano particles at concentrations higher than 0.05 mg/L is significantly difference with single UV application.

The minimum, average and maximum efficiency removal for E. coli for $nTiO_2$ + UV at concentration of 0.8 mg/L and contact time equal to 40 minutes were obtained as to 75.1% , 88.9 ± 12.7% and 100%, respectively. The efficiency for bacteria removal using titanium dioxide at 0.8 g/l and 0.2 g/L concentrations are significantly difference, but it is not significant at other concentrations. The efficiency for bacteria removal using titanium dioxide at 0.8 g/l and 0.2 g/L concentrations are significantly difference, but it is not significant at other concentrations. Even though increasing nano particles dose result in an increase trend for bacteria destruction but this increase is slowly and is related to diffraction effect of light (due to increasing nano particles).

For equal amounts of disinfectant and equal number of E.coli colonies in drinking water , disinfection potential for nAg photo catalyst is significantly higher than $nTiO_2$ photo catalyst. Also disinfection rate increases as nano particles concentration raises and it was higher for nano silver particles ($R^2 = 0.943$) comparing nano-titanium particles ($R^2 = 0.705$). For all statistica analyses, $p_{value} < 0.05$ was considered.

References

1) C.E. Lawrance, P.R. Taylor, B.J. Trock, A.A. Reilly, Nat. Cancer Inst. 72 (1984), 563.
2) Li Q, Mahendra S. Antimicrobial nanomaterials for water disinfection and microbial control: potential applications and implications. Water Researches Journal. 2008 Nov; 42(18): 4591-602.
3) M. Kaneko, I. Okura (Eds.), Photocatalysis Science and Technology, Biological and Medical Physics Series, Springer, 2002
4) www.residusolution.com, www.agroenvironnement.com, www.purifics.com/products, Actual. Chim.,
5) T. Matsunaga, R. Tamoda, T. Nakajima, H. Wake, Microbiol. Lett. 29 (1985) 211.
6) S. Parra, S.E. Stanca, I. Guanaquillo, K.R. Thampi, Appl. Catal. B: Environ. 51 (2004) 107-116.
7) D. Gumy, C. Morais, P. Bowen, C. Pulgarin, S. Giraldo, R. Hadju, J. Kiwi, Appl. Catal. B Environmental 63 (2006) 76.
8) A.-G. Rincon, C. Pulgarin, Appl. Catal. B Environmental 49 (2004) 99.
9) D. Gumy, C. Morais, P. Bowen, C. Pulgarin, S. Giraldo, R. Hadju, J. Kiwi, Appl. Catal. B Environmental 63 (2006) 76
10) V. Keller, N. Keller, M.J. Ledoux, M.C. Lett, Chem. Commun. (2005) 2918.
11) O. Seven, B. Dindar, S. Aydemir, D. Metin, M.A. Ozinel, , J. Photochem. Photobiol., A 165 (2004) 103
12) http://france.elsevier.com/direct/CRAS2C. (2007), . Chim., in press
13) Lee S-K and Mills A. Detoxification of water by semiconductor photocatalysis. J.Ind.Eng.Chem. 2004; 10(2): 173-187.
14) Dalrymple, K. , design and optimization of photocatalytic air disinfection systems. PhD proposal, 2009
15) Sunada K, Watanabe T, Hashimoto K. Studies on photokilling of bacteria on TiO2 thin film. Journal of Photochemistry and Photobiology A: Chemistry. 2003 3/20/;156(1–3):227-33.
16) Y. Lai, Y. Chen, H. Zhuang, and C. Lin, "A facile method for synthesis of Ag/TiO2 nanostructures," Materials Letters, vol. 62, no. 21-22, pp. 3688-3690, 2008. View at Publisher · View at Google Scholar · View at Scopus.
17) Camilo.A, Csstro.A.J, Performance of Ag-TiO2 Photocatalysts towards the Photocatalytic Disinfection of Water under Interior-Lighting and Solar-Simulated Light Irradiations, 201 (2012): 261045, 10.

18) Rabbani D, Miranzadeh MB, Ghadami F, Zarjam R. Effect of Nanosilver Solution on Coliforms Removal in Synthetic Polluted Water. Journal of Applied Technology in Environmental Sanitation. 2013; 3(1): 15-20.
19) Gao J, Youn S, Hovsepyan A, Llaneza VL, Wang Y, Bitton G, et al. Dispersion and toxicity of selected manufactured nanomaterials in natural river water samples: effects of water chemical composition. Environmental science & technology. 2009 May 1; 43(9): 3322-8. PubMed PMID: 19534153. Epub 2009/06/19.
20) Nair RG, Roy JK, Samdarshi SK, Mukherjee AK. Enhanced visible light photocatalytic disinfection of gram negative, pathogenic Escherichia coli bacteria with Ag/TiV oxide nanoparticles. Colloids and surfaces B, Biointerfaces. 2011 Aug 1; 86(1): 7-13. PubMed PMID: 21489760. Epub 2011/04/15. eng.
21) Liu Y, Li J, Qiu X, Burda C. Novel tiO2 nanocatalysts for wastewater purification: tapping energy from the sun. Water science and technology : a journal of the International Association on Water Pollution Research. 2006;54(8):47-54. PubMed PMID: 17163012. Epub 2006/12/14. eng.
22) Li H, Zhu X, Ni J. Comparison of electrochemical method with ozonation, chlorination and monochloramination in drinking water disinfection. Electrochimica Acta. 2011 11/30/; 56(27): 9789-96
23) Pratap Reddy M, Phil H, Subrahmanyam M. Photocatalytic Disinfection of Escherichia coli over Titanium (IV) Oxide Supported on Hβ Zeolite. Catal Lett. 2008 2008/06/01; 123(1-2): 56-64. English
24) Kumar RV, Raza G. Photocatalytic disinfection of water with Ag–TiO2 nanocrystalline composite. Ionics. 2009 2009/10/01; 15(5): 579-87. English

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