Journal of Clean Energy Technologies, Vol. 1, No. 2, April 2013

Disinfection By-Products Removal by Nanoparticles Sintered in Zeolite

Kubra Ulucan, Cansu Noberi, Tamer Coskun, Cem Bulent Ustundag, Eyup Debik, and Cengiz Kaya

Abstract—Disinfection process by chlorine has been applying effectively in drinking water treatment processes; nevertheless it causes the formation of THMs which are thought to be carcinogen. Restrictions of THMs had been imposed by organizations in most of the countries. In Istanbul, these limit values were not exceeded in present time, but organic content of drinking water supplies is accreted by the increment pollution on occasion of population growth. This will lead to investigate and apply an extra treatment unit for THM removals. In this study, application of nanoparticle was researched in THM removal from tap water. Nanoparticle used in the process was sintered into zeolite in coin form. The results were promising. It was observed that unsintered form was more effective on removal of THMs than sintered form of α-Fe_2O_3. Furthermore, nanoparticles in zeolite form advanced the adsorption capacity of zeolite.

***Index Terms*—Adsorption, α-Fe_2O_3 nanoparticle, Disinfection by-product, Trihalomethane**

I. INTRODUCTION

Population growth in the world increased the drinking water demand; subsequently increased the amount of water used and the pollution in drinking-water supplies. This, in turn, leads to the requirement of drinking water purification. The most important step in conventional drinking water treatment systems is disinfection process used to remove microbial contamination that can cause infection of epidemic illness. Chlorine used in the disinfection of water causes to formation of by-products (DBPs) such as aldehydes, chloramines, haloasetic acids (HAAs) and trihalomethanes (THMs) which are formed by the complex reactions between organic matters (humic acid, aminoacids, carbonhydrates etc.) and chlorine and/or bromine [1].

HAAs and THMs are the most frequently occurred compounds in high concentrations among disinfection by-products and are great concern cause of the potential impact on public health. Presence of four major THMs (chloroform, bromoform, bromodichloromethane, dibromochloromethane) in drinking water is known to be carcinogen on animals [1]. Because of these publich health effects, World Health Organization (WHO), the U.S. Environmental Protection Agency (EPA) and the European Union standards have proceeded to control their formation in drinking water and restricted by the limit values of disinfection by-products (DBPs), which are reduced over time [2]-[3].

In order to reduce DBPs formation, there are few processes used which are most applicable, but mostly not effective methods such as the usage of filters (activated carbon etc.[4]-[5]); but they used to remove the materials that lead to formation of DBPs before disinfection processes (THM precursors) . Nevertheless the organic matter is attempted to remove, most of it can stay; and after disinfection process by chlorine DBPs are formed.

The increasing use of nanoparticles in every field of life increased the potential usage in environmental pollution. Even though the investigations about usage of nanoparticles in order to control environmental pollution are generally on soil remediation, in recent years the slow growth in numbers of investigations on water pollution shows that the applications of nanoparticles will gain importance globally in the future. The most applied ones within these mentioned nanoparticles are carbon nanotubes, titanium oxide, ferrous oxides and nano zero-valent iron. Limited numbers of articles about removal of metallic pollutants [6]-[8] and also halogenated hydrocarbons [9]-[13] and inorganic compounds [15] from aquatic environment by nanoparticles indicate that nanoparticles are used effectively [14]-[16].

Currently, due to the unique surface reactivity of nano scale materials, the application of these materials in environmental field is advanced and enables to remove pollutants effectively in a few time [17]. These low-cost materials are more effective than conventional adsorbents because of having high surface area for adsorption; in other words, they have surface area that has more atoms and molecules to adsorb pollutants [16]-[18]. Because of their nanopore, even in low concentration of contamination can be adsorbed and thus, an advantage of less produced waste is come into forefront [18]. Moreover, nanoparticles are not toxic and harmful to environment [16].

Applications of variety of nanoparticles in polluted water treatment are exist. These nanoparticles can be considered as carbon based nanoparticles, metal oxide based nanoparticles, titanium oxide based nanoparticles and nano zero valent iron [14]-[16]. Carbon based materials, widely known as carbon nanotube (CNT), have gained considerable interests for aquatic remediation processes. Due to the large surface area and thermal stability, recently CNT has been used in mostly heavy metal adsorption, organic matter removal and drinking water processes. Another adsorbent except CNTs, metal oxide based nanomaterials are commonly applied in drinking water facilities [16]. The most favorable advantage of magnetic activity of magnetic nanoparticles is that they can be separated easily from water using magnetic field. On the

Manuscript received November 23, 2012; revised January 17, 2013.

K. Ulucan, T. Coskun and E. Debik are with Department of Environmental Engineering, Yildiz Technical University, Istanbul, Turkey (e-mail: kulucan@ yildiz.edu.tr).

C. Noberi, C. B. Ustundag and C. Kaya are with the Department of Metallurgy and Material Engineering, Yildiz Technical University.

DOI: 10.7763/JOCET.2013.V1.28

occasion of chemical stability, magnetite (Fe_3O_4) and maghemite (α-Fe_2O_3) are prevalently applied in water treatment facilities. In addition to these magnetic nanomaterials, metal nanoparticles such as $MgFe_2O_4$, $ZnFe_2O_4$, $CuFe_2O_4$, $NiFe_2O_4$, ZrO_2 and NiO are applied in the removal of phenol, phosphate [14]. Unlikely as in metal oxide based nanomaterials, magnetic field separation is not effective in TiO_2 based nanomaterials. With the photocatalytic activity in UV light, TiO_2 based nanoparticles are come in forefront in degradation of toxic pollutants with less harmless end-products [16]. In addition to iron oxide nanoparticles, in the literature zero valent iron nanoparticle (nZVI) is emphasized as the most effective in degradation of pollutants. Recently, the studies on nanoscale metallic materials in water treatment process showed that the application of nanoscale iron particles are effective in transformation and detoxification of various environmental contaminants such as chlorinated pollutants, chlorinated organic solvents, organochlorine pesticides, herbicides, polycyclic aromatic hydrocarbons, radionucleoids, organic compounds and almost all halogenated hydrocarbons [14], [16]-[20].

nZVI is a promotive nanoparticle for water treatment facilities due to the capability to remove inorganic pollutants in high removal rates. Besides the high adsorption capacity in its high surface area, it generates OH• radicals that subsequently degrade target pollutants [22]. The layer that can oxide organic matter is a promising characteristic of nZVI.

Magnetic nanomaterials are mostly investigated in the removal of heavy metals which it is reported in some studies that total removal of Cr(VI) can be acquired [16]. This indicates that usage in water treatment facilities can provide to reach limit requirements in a few time of applications.

THM concentration in drinking water of Istanbul does not exceed the limit of 100μg/L according to WHO standards [3]. Nevertheless increment in population will lead to contamination of drinking water supplies, subsequently increment of THM formation will be observed. For this purpose, preliminary study is practiced in order to establish a filter bed containing nanoparticles to remove THMs.

In this study, removal of THMs from drinking water was investigated using α-Fe_2O_3. It was thought that the application of nanoparticles in powder form is not appropriate and difficult to separe from water, therefore the powder form and sintered form in zeolite were applied and impact on removal rate was investigated.

II. Material and Method

Nanoparticle (α-Fe_2O_3) was synthesized in the laboratory of Material Engineering Department at Yildiz Technical University. In order to prepare α-Fe_2O_3 nanoparticles, 3,332 g of $FeCl_3$ and 2,97 g of urea are diluted in 166,6 ml of distilled water. After stirring with a magnetic stirrer for awhile, 24,9 ml of surfactant was added and pH was detected as 2. After addition of 166,6 ml of butanol, pH did not changed. This mid-product was kept in autoclave for 12 hours in 150°C. Centrifugation was performed to the sample removed from autoclave which had a pH of 8.5. The solid phase obtained after centrifugation was kept in drying oven for 48 hours in 85°C and later on particles was placed on a watch-glass for calcination which was performed in 350°C in calcination furnace. SEM and TEM analysis belong to synthesized α-Fe_2O_3 can be seen in Fig. 1 and Fig. 2.

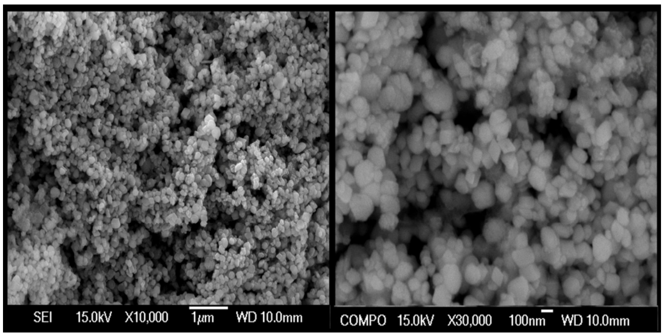

Fig. 1. SEM image of α-Fe_2O_3

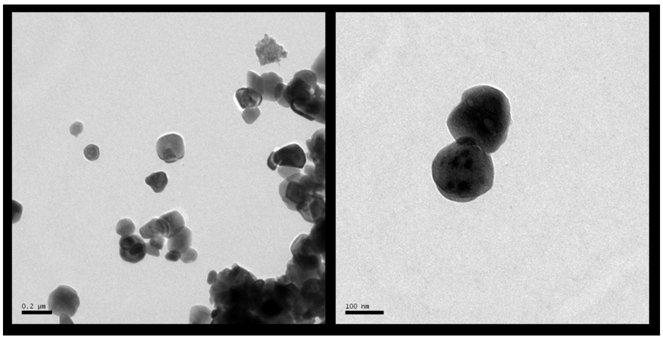

Fig. 2. TEM image of α-Fe_2O_3

Synthesized α-Fe2O3 was mixed homogenously in the rates of 2, 5, 10 and 30% with zeolite. They were compressed in high pressure into the form of a coin (Fig. 3), later on they were sintered in furnace in high temperature. In order to investigate the nanoparticle's activity in adsorption process, an experimental set is conducted with the sintered coin containing zeolite.

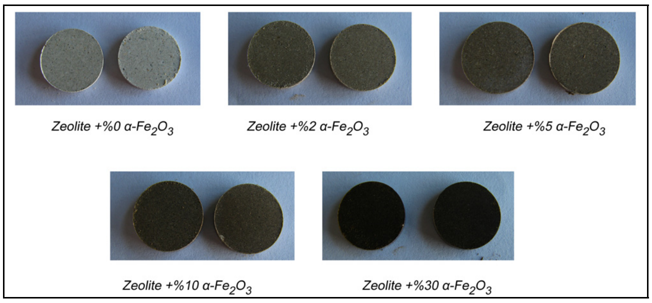

Fig. 3. Photographs of sintered nanoparticles

TABLE I: CONCENTRATIONS OF THMS

Parameter	Concentration, μg/L
Chloroform	15,5
Dichlorobromomethane	16,3
Dibromochloromethane	13,2
Bromoform	4,3
Total THMs	49,3

To determine the effects of different time and nanoparticle concentrations on removal mechanism, experimental sets were practiced using an orbital shaker in 250 rpm, in 18^{o}C and for 100 ml of sample volume. Sample was obtained from tab water in Davutpasa Campus of Yildiz Technical University. Temperature of sample was adjusted at 18C for all experimental sets. The concentrations of four major THMs were analyzed in GC-ECD in accordance with EPA Method 551 and given in Table I.

III. RESULTS AND DISCUSSION

In order to determine the effect of nanoparticle concentration for the process, experimental sets were conducted using 10, 25, 50, 150 mg α-Fe_2O_3 in 100 ml of samples. Sintered coins containing the mentioned amounts in zeolite were weighted totally in 0, 4 gr.

Effulent concentrations and removal rates of Chloroform, Dichlorobromomethane, dibromochloromethane, bromoform and total THMs can be seen in Fig. 4- Fig. 8, respectively. Removal efficiencies were low numerically due to the low influent concentration, however the effluent concentrations of both THMs was considerably minor.

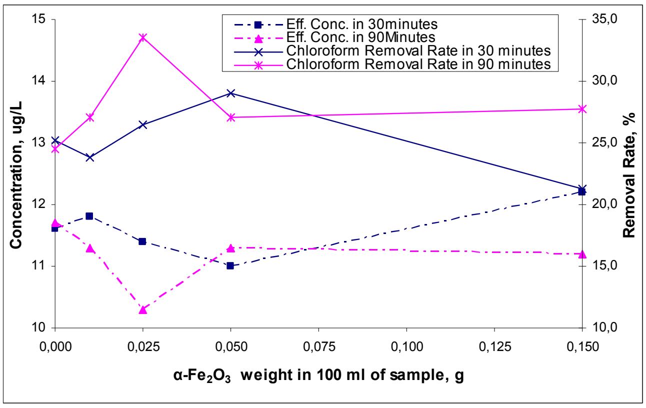

Fig. 4. Effluent conc. and removal rates of chloroform

In Fig 4, changes of chloroform concentration according to time and the amount of nanoparticles can be seen. Whereas optimum removal was attained in the research with 50mg α-Fe_2O_3 for 30 minutes, best removal was with 25 mg α-Fe_2O_3 for 90 minutes. This was similar in other THM compounds (Fig. 5-Fig. 7).

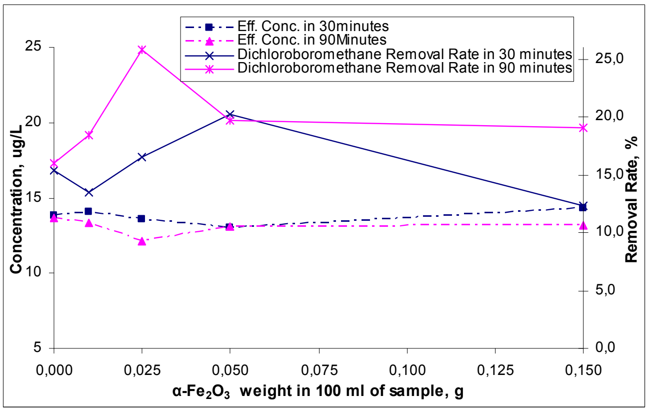

Fig. 5. Effluent conc. and removal rates of dichlorobromomethane

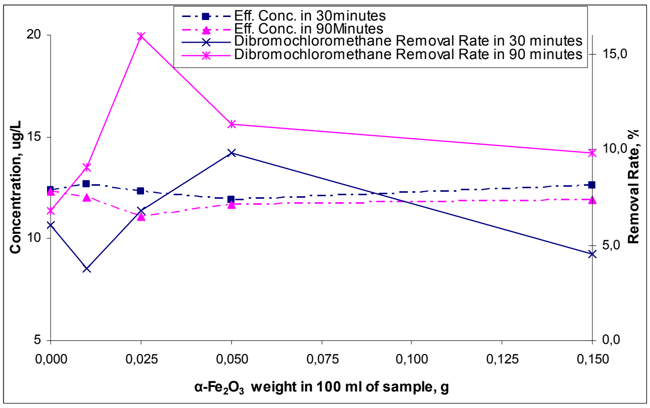

Fig. 6. Effluent conc. and removal rates of dibromochloromethane

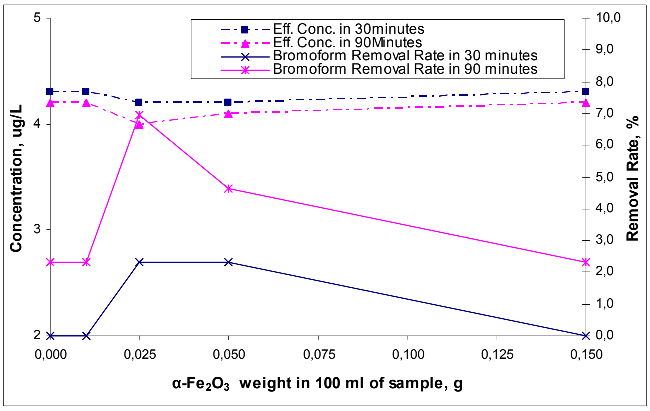

Fig. 7. Effluent conc. and removal rates of bromoform

In all samples, after optimum α-Fe_2O_3 concentration, removal rates decreased. In sintering process, when the nanoparticles amount in zeolite was increased, nanoparticles could be changed into microscale. This could be a reason for decrement of removal rates.

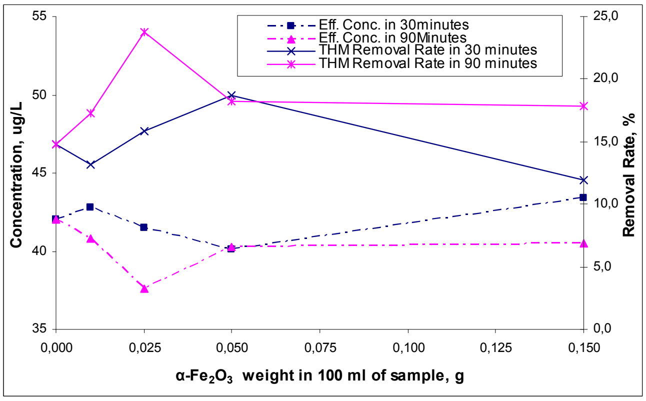

Fig. 8. Effluent conc. and removal rates of total THMs

Total THMs were decreased into the concentration of 37,6 μg/L in the experiment by zeolite coin containing 5% nanoparticle (25 mg/100 ml sample) in 90 minutes. Considering the removal rates of compounds; chloroform had the highest removal rate within THM compounds; and dichlorobromomethane, dibromochloromethane and bromoform were followed it respectively. The lowest removed compound was bromoform. Bromoform had in the lowest concentration in total THMs (4,3μg/L) therefore, the reason was thought to be in low influent concentration.

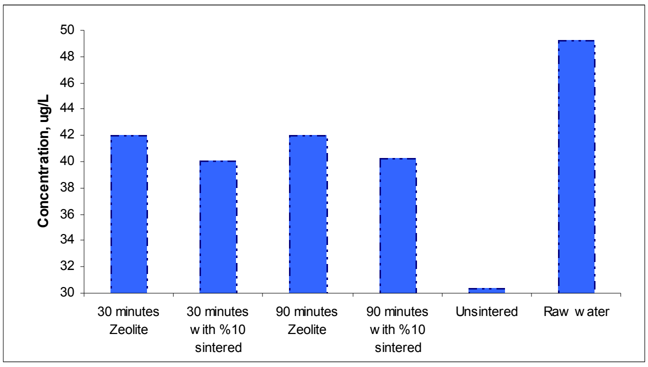

Fig. 9.Comparison of sintered and unsintered form of α-Fe_2O_3 in effluent total THM concentration

Difference within the sintered and unsintered form, and also zeolite and nanoparticle can be seen in Fig. 9. In order to observe this difference, all experiments were conducted with 50 mg α-Fe_2O_3 in 100 ml of sample. When the removal by zeolite and nanoparticles were compared, it can be said that nanoparticles in zeolite could increase removal. Low difference within the time comparison of short and long contact time can also be seen in Fig. 9. This difference was thought due to the analytical analysis precision. More nanopores of unsintered α-Fe_2O_3 were the effective reason for higher removal rate than sintered forms in zeolite. However suitable sintering processes can be investigated to obtain the same results as in the unsintered form.

IV. CONCLUSION

Study results of THMs removal from drinking water by α-Fe_2O_3 sintered in zeolite form showed that chloroform had the highest removal rate within THM compounds and dichlorobromomethane, dibromochloromethane and bromoform were ordered. Furthermore, nanoparticles in zeolite form increased the adsorption capacity of zeolite. Low decrement on removal rates had been observed when time is altered.

It was also noticed that unsintered form of α-Fe_2O_3 was more effective in removal of THMs. More nanopores of unsintered α-Fe_2O_3 were the effective reason of well removal rate than sintered forms in zeolite. However suitable sintering processes should be investigated to obtain the same results as in the unsintered form and also synthesizing method should be improved in order to enhance surface area and particle size of nanoparticles.

REFERENCES

[1] Yi-Li Lin, Pen-Chi Chiang, and E. Changb, “Removal of small trihalomethane precursors from aqueous solution by nanofiltration,” *Journal of Hazardous Materials*, vol. 146, pp. 20 – 29, 2007.

[2] US EPA, 2004 “Edition of the drinking water standards and health advisories”, EPA 822-R-04-005, Office of Water, U.S. Environmental Protection Agency, Washington, DC, 2004.

[3] *Guidelines for Drinking-Water Quality*, WHO, 3rd ed., 2003.

[4] G. Capar and Ü. Yetis, “Removal of THM precursors by GAC: Ankara case study,” *Water Research*, vol. 36, pp. 1379-1384, 2002.

[5] H. Humbert, H. Gallarda, H. Suty, and J. P. Croue, “Natural Organic Matter (NOM) and pesticides removal using a combination of ion exchange resin and Powdered Activated Carbon (PAC),” *Water Research*, vol. 42, pp. 1635 – 1643, 2008.

[6] G. Jegadeesan, K. Mondal, and S. B. Lalvani, “Arsenate remediation using nanosized modified zerovalent iron particles,” Environ. Prog, vol. 24, pp. 289–296, 2005

[7] H. Zhu, Y. Jia, X. Wu, and H. Wang, “Removal of arsenic from water by supported nano zero-valent iron on activated carbon”, J. Hazard. Mater, vol. 172, pp. 1591–1596, 2009

[8] Hardiljeet K. Boparai, Meera Joseph, and Denis M. O’Carroll, “Kinetics and thermodynamics of cadmium ion removal by adsorption onto nano zerovalent iron particles”, *Journal of Hazardous Materials* vol. 186, pp. 458–465, 2011

[9] C. Chang, F. Lian, and L. Y. Zhu, “Simultaneous adsorption and degradation of g-HCH by nZVI/Cu bimetallic nanoparticles with activated carbon support”, *Environmental Pollution*, vol. 159, pp. 2507-2514, 2011

[10] S. C. Yang, M. Lei, T. B. Chen, X. Y. Li, Q. Liang, and C. Ma, “Application of zerovalent iron (Fe(0)) to enhance degradation of HCHs and DDX in soil from a former organochlorine pesticides manufacturing plant”, *Chemosphere*, vol.79, no.7, pp. 727-732,2010.

[11] X. Qui and Z. Fang, “Degradation of Halogenated Organic Compounds by Modified Nano Zero-Valent Iron,” *Progress In Chemistry* , vol. 22, pp. 291-297, 2010.

[12] N. M. Zhu, Y. Li, and F. S. Zhang, “Catalytic dechlorination of polychlorinated biphenyls in subcritical water by Ni/Fe nanoparticles”, *Chemical Engineering Journal*, vol. 171, no. 3, pp. 919-925, 2011.

[13] R. J. Barnes, O. Riba, M. N. Gardner, T. Scott, S. A. Jackman, S. I. Thompson, “Optimization of nano-scale nickel/iron particles for the reduction of high concentration chlorinated aliphatic hydrocarbon solutions,” *Chemosphere*, vol. 79, pp. 448–454, 2010.

[14] Y. C. Sharma, V. Srivastava, V. K. Singh, S. H. Kaul, and C. H. Weng, “Nanoadsorbents for the removal of metallic pollutants from water and wastewater,” *Environmental Technology*, pp. 583-609, 2009.

[15] X. Q. Li, D. W. Eliot, and W. X. Zhang, “Zero valent iron nanoparticles for abatement of environmental pollutants:materials and engineering aspects,” *Critical Reviews in Solid State and Materials Sciences*, vol. 31, pp. 111-112, 2006.

[16] T. A. Kurniawana, M. E. Sillanpääa, and M. Sillanpää, “Nano–adsorbents for remediation of aquatic environment: local and practical solutions for global water pollution problems,” *Critical Reviews in Environmental Science and Technology*, in press.

[17] R. D. Ambashtaa, M. Sillanpää, “Water purification using magnetic assistance: a review,” *Journal of Hazardous Materials*, vol. 180, pp. 38–49, 2010.

[18] P. T. Anshup, “Nobel metal nanoparticles for water purification: a critical review”, *Thin Solid Films*, vol. 517, pp. 6441 – 6478, 2009.

[19] S. K. Brar, M. Verma, R. D. Tyagi, and R. Y. Surampalli, “Engineered nanoparticles in wastewater and wastewater sludge – evidence and impacts”, *Waste Management*, vol. 30, no. 3, pp. 504-520, 2010.

[20] W. X. Zhang, C. B. Wang, and H. L. Lien, “Treatment of chlorinated organic contaminants with nanoscale bimetallic particles,” *Catalysis Today*, vol. 40, pp. 387 - 395, 1998.

[21] J. T. Nurmi, P. G. Tratnyek, V. Sarathy, D. R. Baer, J. E. Amonette, K. Pecher, C. M. Wang, J. C. Linehan, D. W. Matson, R. L. Penn, M. D. Driessen, “Characterization and properties of metallic iron nanoparticles: spectroscopy, electrochemistry, and kinetics”. *Environmental Science & Technology*, vol. 39, pp. 1221- 1230, 2005.

[22] A. J. Feitz, S. H. Joo, J. Guan, Q. Sun, D. L. Sedlak, and T. D. Waite, “Oxidative transformation of contaminants using colloidal zero-valent iron; colloids and surfaces a: physicochem,” *Eng. Aspects*, vol. 265 , pp. 88– 94, 2005.

Kübra Ulucan works as a research assistant at Yıldız Technical University in Environmental Engineering Department.

Ulucan received her BSc in Environmental Engineeri in 2007 from Yildiz Technical University, Istanbul, Turkey. After one and half year of work experience in private sector she turned back to her MSc degree and worked as ra esearch assistant. In 2010 she worked for her thesis in the laboratory of Chemical and Material Engineering Department in the University of Cagliari, Italy. In 2011 she received her MSc degree in Environmental Engineering Program at Yildiz Technical University, Istanbul, Turkey. She is still research assistant and a doctorate student at Yildiz Technical University.

She studied bilge water treatment using electrochemical treatment processes in her MSc thesis. Now she is working on nanotechnology applications on drinking water treatment systems.