Advanced Materials and Nanotechnology for Sustainable Energy Development

Guest Editors: Ziyang Huo, Cheng Hao Wu, Zhongwei Zhu, and Yuxin Zhao
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Contents

Advanced Materials and Nanotechnology for Sustainable Energy Development, Ziyang Huo, Cheng Hao Wu, Zhongwei Zhu, and Yuxin Zhao
Volume 2015, Article ID 302149, 1 page

Harmful Effects of Nanoparticles on Animals, Jean-Marie Exbrayat, Elara N. Moudilou, and Emmanuel Lapied
Volume 2015, Article ID 861092, 10 pages

Analysis of Thermal Properties on Backward Feed Multieffect Distillation Dealing with High-Salinity Wastewater, Jianliang Xue, Qin Qin Cui, Jie Ming, Yu Bai, and Lin Li
Volume 2015, Article ID 518015, 7 pages

Iron Contamination Mechanism and Reaction Performance Research on FCC Catalyst, Zhaoyong Liu, Zhongdong Zhang, Pusheng Liu, Jianing Zhai, and Chaohe Yang
Volume 2015, Article ID 273859, 6 pages

Experimental Assessment of Water Sprays Utilization for Controlling Hydrogen Sulfide Releases in Confined Space, Dongfeng Zhao, Chao Li, Jun Liu, Guoying Zhou, Qingdong Zhang, and Chunshuang Liu
Volume 2015, Article ID 958252, 9 pages

Influence of OH⁻ Ion Concentration on the Surface Morphology of ZnO-SiO₂ Nanostructure, Jessica Ven G. Tinio, Key T. Simfroso, Amber Dea Marie V. Peguit, and Rolando T. Candidato Jr.
Volume 2015, Article ID 686021, 7 pages
Editorial

Advanced Materials and Nanotechnology for Sustainable Energy Development

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Received 8 October 2015; Accepted 16 November 2015

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Energy is the material foundation of human activities and also the single most valuable resource for the production activities of human society. Materials play a pivotal role in advancing technologies that can offer efficient renewable energy solutions for the future. This special issue has been established as an international foremost interdisciplinary forum that aims to publish high quality and original full research articles on all aspects of the study of materials for the deployment of renewable and sustainable energy technologies. The special issue covers experimental and theoretical aspects of materials and prototype devices for sustainable energy conversion, storage, and saving, together with materials needed for renewable energy production. It brings together stakeholders from universities, industries, government agents, and businesses that are involved in the invention, design, development, and implementation of sustainable technologies.

The research work has already been published in this special issue which discusses comprehensive technologies for wastewater treatment, strategies for controlling gaseous pollutant releases within chemical plant, evaluation of FCC catalysis poisoning mechanism, clean technologies for fossil fuel use, new-type photocatalysis material design with controllable morphology for solar energy conversion, and so forth. These studies describe important, intriguing, and systematic investigations on advanced materials and technologies for dealing with the key technologies and important issues that continue to haunt the global energy industry. They also tie together many aspects of current energy transportation science and technology, exhibiting outstanding industrial insights that have the potential to encourage and stimulate fresh perspectives on challenges, opportunities, and solutions to energy and environmental sustainability.

Ziyang Huo
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Review Article

Harmful Effects of Nanoparticles on Animals

Jean-Marie Exbrayat, Elara N. Moudilou, and Emmanuel Lapied

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Received 7 July 2015; Revised 29 September 2015; Accepted 30 September 2015

Academic Editor: Zhongwei Zhu

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Since several years nanoparticles (NPs) are produced by industries and used in several fields of activities. They are finally found in aquatic and terrestrial environments, where they are ingested by living organisms in which they accumulate, before being eliminated. In organisms, NPs represent foreign elements with their own physicochemical properties due to their small size. So NPs may interfere with the normal physiological mechanisms of the embryos, growing animals, and adults, and it is indispensable to understand their potentially direct or indirect harmful effects on living organisms. It has been already shown that NPs could be toxic to bacteria, algae, invertebrates, and vertebrates. In this review, several examples of recent studies are given. We will examine successively the effects of NPs on terrestrial and semiaquatic and aquatic vertebrate and invertebrate animals.

1. Introduction

Nanoparticles (NPs) are substances the diameter of which does not exceed 100 nm. This size provides them with physical and chemical properties different from materials usually found in environment [1, 2]. Several types of NPs can be distinguished. Natural ones are found in soils, natural waters, or volcanic dust. They are generated by both geological and biological processes. Even when toxic, numerous organisms can adapt and evolve in environments rich in natural NPs [3]. Since several years NPs are produced by industries and used in agriculture, electronics, medicine, pharmacy, cosmetology, and so forth [4]. Studies carried out in USA and Europe showed that Ag-NPs, TiO₂-NPs, and ZnO-NPs from sewage treatment may be toxic for aquatic organisms [5].

NPs are finally found in aquatic and terrestrial environments, where they are ingested by living organisms in which they accumulate, before being eliminated by the immune system or other pathways. In organisms, NPs represent foreign elements with their own physicochemical properties, so they may interfere with the normal physiological mechanisms of the embryos, growing animals, and adults. In embryos, NPs sometimes disrupt the development, bringing on malformations which can be lethal. Not only do the chemicals constituting NPs react according to well-known mechanisms, but the size of NPs itself confers some particular properties which certainly interfere with physical, chemical, and biological activities of the organism [3]. Consequently, due to their small size, NPs can easily penetrate across the cell membrane, avoiding defense mechanisms. So, NPs then migrate into the cell and reach organelles such as mitochondria, modifying the cell metabolism and provoking cell death. If NPs are not enough small to penetrate into the cell, they can interfere with the cell membrane, disrupting the membrane functions such as ion transport or signal transduction. The chemical composition and physical properties of NPs can be cytotoxic. Positive electric charges of NPs can destroy membrane lipid bilayers. Surface coating of NPs can also interfere with cell structure [6]. In addition, NPs effects could be influenced by other substances such as pollutants. NPs can also adsorb materials having harmful effects on the organisms [3].
Since several years, some works were devoted to discover and understand these effects, but most of them still remain to be discovered. So, in front of the omnipresence of NPs today, it became indispensable to understand their potentially direct or indirect harmful effects on living organisms. It has been already shown that NPs could be toxic to bacteria, algae, invertebrates, and fish species, as well as mammals [3]. Today, several living models are used in order to measure the impacts of NPs on the organisms. Studies concerning mammals, such as mouse, or bony fishes, such as the zebrafish, showed that nanoparticles exerted harmful effects on the reproduction and embryonic development [7, 8]. Some experiments using in vivo and in vitro cultured animal tissues showed that Ag-NPs caused an oxidative stress characterized with well reactive molecules containing free oxygen radicals (reactive oxygen species or ROS), genotoxicity with DNA break, or cell apoptosis [9]. Studies regarding the environmental impact of engineered nanoparticles (ENPs) are hampered by the lack of tools to localize and quantify them in water, sediments, soils, and organisms. Neutron activation has been also used so as to study the effects of Co-NPs in the earthworm Eisenia fetida. Using scintillation counting and autoradiography, 4 nm Co-NPs constituting a nanopowder (59 m²/g) were detected in spermatogenic cells, cocoons, and blood [10].

Nanoparticles such as Ag-, ZnO-, or CuO-NPs are frequently used as bactericides. But after releasing into wastes and environment, toxic effects can also affect nontarget organisms. A review of literature pointed out that such effects were observed in protozoa, nematodes, crustaceans, fish, or cell cultures [11]. Effects were different from that obtained after inhalation [12, 13]. But, presently, the knowledge about the harmful effects of NPs remains such as a patchwork. Consequently, Kahru and Dubourguier proposed several ways to systematize this study field: (1) identify the most harmful effects of NPs on the most sensitive biological groups and (2) gather ecotoxicological information in order to evaluate the risks considering the NP type, such as NiO2-NPs, ZnO-NPs, CuO-NPs, Ag-NPs, single wall nanotubes (SWNTs) or single walled carbon nanotubes (SWCNT-NTs), multiwall nanotubes (MWCNTs), and C60 fullerene, and experiment in significant organisms such as bacteria, algae, yeast, protozoa, nematodes, earthworms, crustaceans, fish, amphibians, and mammals [14]. Kong et al. also expressed the question of experimental conditions to understand the cytotoxic effects of NPs, considering the choice of target-cell types, the preparation of NP samples, and the type of cytotoxic effects [15].

It is possible to consider the toxicity affecting the organisms living in all the environments (air with inhalation, fresh or marine water, and terrestrial environment). In order to search for toxic effects of NPs, experiments and analysis have been performed in several types of organisms: in protozoa, in numerous invertebrates, in vertebrates, and in adults as well as in embryos.

In this review, several examples of recent studies are given. Some animal models such as rodents, fish, or amphibians were often used. But other animals sometimes less conventional such as sea urchin, earthworms, or still mussels or oysters were also used in well interesting and useful studies. We will examine successively the study of the effects of NPs on terrestrial, semiaquatic, and aquatic vertebrate and invertebrate animals. In the text logic, the animal model and its natural environment were the starting point, but NP types also may be this starting point.

2. Effects of NPs on Terrestrial Animals Species

2.1. In Mammals. Mammals and especially humans are exposed to NPs which can penetrate in the body with inhalation, and a lot of works concerning medical effects have been published [16]. NPs can also penetrate the body in a transcutaneous manner. In all the cases, NPs size permits endocytosis to penetrate a cell and transcytosis to penetrate several cells, one after the other. So, when they are inhaled, NPs are able to reach nervous ends of the olfactory epithelium and then upstream the axons going to the olfactory bulbs in the brain where they affected neurons. In another way, NPs attempted the lungs, then reached blood, and attempted the blood-brain barrier. They also can reach other organs such as bone marrow, lymph nodes, spleen, or heart. It has been shown that NPs can provoke inflammation and both prooxidant and antioxidant activities, oxidative stress, and modification of mitochondrial distribution. These effects were dose-dependent and exerted according to the NP type [16].

Some experiments performed with rats and mice showed true harmful effects of NPs on brain. In the rat, an exposition to Cu-NPs (40 and 60 nm diameter) provoked the proliferation of endothelial cells of brain capillaries when they were administered to low concentrations (about 1.5 µg/mL). Higher concentrations (about 50 µg/mL) induced an increase of prostaglandine E2. Extracellular levels of TNFα and ILβ were significantly high, and the toxicity finally affected the blood-brain barrier [17]. Another study also performed on rat showed that a 24-hour exposition to Ag-NPs measuring 25, 40, or 80 nm affected the blood-brain barrier, inducing a proinflammatory reaction which could develop a brain inflammation accompanied with neurotoxic effects [18]. Cytotoxic effects were induced by the smallest NPs (25 and 40 nm) compared to largest ones (80 nm) [18]. Ag-NPs measuring 7.5 nm originated the emaciation of adult rat, with a decreasing of its locomotor activity [19]. Other works, performed on rat or mouse brain, confirmed the harmful effects of NPs, sometimes at a strong level, on the permeability of blood-brain barrier, thus affecting brain blood fluxes, with consequently the formation of cerebral edema. Morphological effects could provoke neurons injuries, modification of the activity of some glial cells, and the loss of myelin fiber due to the activation of HSP (hotshock proteins). The effects of Cu-NPs and Ag-NPs measuring 50 to 60 nm were more important than Al-NPs measuring also 50 to 60 nm [20]. It was also noticed that the effects were more important in rat than in mouse [20]. Comparable works, performed on the pig, showed pathogenic effects of 25, 40, and 80 nm Ag-NPs, 40 and 60 Cu-NPs, and 3 and 5 nm Au-NPs on
the blood-brain barrier, with an attenuated effect of Au-NPs [21]. In the rat, 45 nm Ag-NPs affected the action of acetylcholine with a production of NO (nitric oxide) inducing hyperactivity of the tracheal smooth muscle [22]. In mouse, injection of 25 nm Ag-NPs (100 or 500 mg/kg) originated an oxidative stress. NP aggregates were observed in spleen red pulp, lungs, and kidneys and in the nasal airway, without any significant morphological variations except in the nasal cavity [23]. The effects of Au-NPs (5 and 15 nm diameter) have been examined on a culture of mouse fibroblasts. NPs penetrated into the fibroblasts where they remained stocked. Only the smallest NPs (5 nm) presented some toxic effects on the shape of cells which became narrow and contracted, disrupting the cytoskeleton actin. Cells exposed to Au-NPs during 72 hours presented a degradation of the heavy chain of clathrin, a cytoskeleton protein [24].

Conversely, 80 to 200 nm Se-NPs used usually to protect the endotracheal tube in some medical conditions against bacterial infection did not present any cytotoxic effect on the fibroblast of rat dermis [25].

2.2. In Earthworms. Engineering nanomaterials (ENMs) frequently used are able to salt out NPs in the environment and more especially within the soil, where they may affect the burrowing organisms. NPs may also be accidently recycled into the soil or carried with the wind. In parallel to their potential toxicity, penetration of NPs into the soil associated with incorporation to the soil solution modifies their bioavailability conditions [26].

Earthworms are essential for the incorporation and fragmentation of organic debris, mineralization of organic matter, and recycling of mineral nutrients. Their burrowing activity is also crucial for water filtration and stabilization of erosion effects. In addition, earthworms constitute a large part of the soil biomass (from 60 to 80%) and their biology is widely admitted indicator of the soil health. Thus, some experiments were programmed in order to detect the effects of NPs on their biology. Several methods were used to consider these effects, one of them targeting the apoptotic process. Nevertheless, different earthworm species cannot be considered as equivalent models in these types of experiments. *Lumbricus terrestris* is an anecic worm, living deeply in the ground but eating at the soil surface; *Eisenia fetida* is an epigeic species spending its entire life cycle within the litter of the soil surface, or within compost. Thus, these animals are not submitted to the same toxic influence [26].

2.2.1. Tests in Eisenia Genus. A lot of tests have been performed using *Eisenia fetida*. Some experiments using 20 nm Ag-NPs in suspension in water (1 to 100 mg/mL) showed that the number of apoptotic cells increased with the concentration of Ag-NPs which never aggregated. In *Eisenia fetida*, these NPs were eliminated in 24 hours. The effects of NPs were weaker in the soil than in water. Apoptotic cells were observed in cuticle and intestinal epithelium, which are the parts of body directly exposed to NPs. In consequence, it might be concluded that NPs affected the extended barrier constituted with mucus and antibacterial molecules; they also affected the absorption of nutrients and the immune protection offered by the chloragogenous tissue [26]. *Eisenia fetida* exposed during seven days to 4 nm Co-NPs retained the NPs during eight weeks during which only about 20% of ingested NPs were excreted. These NPs were found in blood and cocoons and spermatogenic cells [10].

TiO$_2$ enters in the composition of several soil layers and is considered to be inert. This molecule is widely used in many industrial products, such as sunscreens. Toxic effects of TiO$_2$-NPs may be related to the formation of free radicals with water in the presence of sun light. Their toxic effects were measured on human cells and on vertebrate and invertebrate animals. TiO$_2$-NPs provoked DNA damage with or without light; it is known that they originated apoptosis in hamster fibroblasts with stretched micronuclei [27, 28]. Independently, the effects of TiO$_2$-NPs have been also investigated in earthworms. In *Eisenia fetida*, 10 to 20 nm TiO$_2$-NPs at concentrations higher than 1 g/kg of soil affected enzymatic activities, damaged mitochondria, and induced apoptosis [28]. *Eisenia andreii* and *Eisenia fetida* were exposed to 5, 10, and 20 nm TiO$_2$-NPs. Several tests concerning mortality, reproduction, avoidance of substances, and growth of juveniles were performed on natural and artificial soils. These soils received TiO$_2$-NPs in water solution or powder or were amended with TiO$_2$-NPs. When soil contained 20 to 10,000 mg NPs/kg, no significant effect was observed. Nevertheless, the worms avoided amended soils containing 1000 to 5000 TiO$_2$-NPs/kg showing that earthworms were able to differentiate soils with 10,000 mg TiO$_2$-NPs/kg from soils with particles (1 μm or several μm in size). These results showed that earthworms were able to differentiate particles and nanoparticles through a mode of detection which remains still unknown [29].

A study focused on the uptake, excretion, and biodistribution of 4 nm Co-NPs and 20 nm Ag-NPs, soluble Co, and Ag salts in *Eisenia fetida* showed that Co ions and Co-NPs were accumulated and that both Ag ions and Ag-NPs were quickly excreted. Only 32% of accumulated Co ions and Co NPs were excreted. High accumulation of cobalt was observed in blood and digestive tract. Co NPs showed a release of ions while Ag ions and NPs appeared more inert [30]. Some individuals belonging also to the species *Eisenia fetida* were exposed during several weeks to 30–50 nm Ag-NPs coated with polyvinylpyrrolidone (PVP), a hydrophilic substance, or with oleic acid, a hydrophobic substance. Some of them were exposed to AgNO$_3$ (salt). Whatever the source of Ag, worms accumulated Ag with variations according to the concentration. Accumulation was higher with ions (Ag$^+$) than with NPs. No difference of toxicity was observed between 30 and 50 nm NPs coated with PVP or oleic acid [31]. In *Eisenia fetida* also exposed to Ag-HPs coated with PVP or to Ag NO$_3$ salt, the expression of several genes of oxidative stress, catalase activity, glutathione reductase inhibitors, phosphatase, and Na$^+$/K$^+$ ATPase varied again according to the concentration and the duration of exposure to AgNO$_3$ or 30 to 50 nm Ag-NPs [31]. Whatever the form in which Ag was administered, mechanisms of toxicity were comparable [32]. The toxic effects of ZnO-NPs and TiO$_2$-NPs were also investigated in *Eisenia fetida*. In natural soil, ZnO-NPs were quite toxic in opposition to TiO$_2$-NPs.
But when earthworms were exposed in a sandy soil, no toxicity was observed whatever the type of NP. After four months of exposure to artificial soils, earthworm reproduction was affected by both types of NPs. However, toxic effects of ZnO-NPs were more important than TiO$_2$-NPs ones [33, 34]. Measures of bioaccumulation of both labeled C-nanotubes and pyrene in *Eisenia fetida*, considered as a starting point of terrestrial trophic chain, showed bioaccumulation factors with nanotubes two times smaller than those measured with pyrene [35].

Several works concerned the effects of NPs on immune system of the earthworm *Eisenia fetida*. In this species, Ag-NPs were phagocyted and accumulated by coelomocytes. Consequently, an oxidative stress and an important alteration of the immune system were observed. Practically, no Ag$^+$ ion was salted out from Ag-NPs, these NPs being thus excreted as intact particles. In the same earthworm exposed to Co-NPs, a strong accumulation of Co was observed in both blood and digestive tract. [36].

### 2.2.2. Tests in Lumbricus Genus. *Lumbricus*, another earthworm genus, was also used to control some biological effects of NPs. In *Lumbricus terrestris* exposed to Ag-NPs, the measure of apoptosis constituted a tool to evaluate the toxicity of Ag-NPs often used in multiple uses such as antimicrobial substance for work clothes [37]. Several experiments showed apoptosis to affect the intestinal epithelium when directly in contact with NPs, especially in typhlosole in which apoptosis affected chloragogenous cells having a function comparable to that of liver in vertebrates or hepatopancreas in mollusks and arthropoda [38].

Again in *Lumbricus terrestris*, when $10 \times 50$ nm TiO$_2$-NPs coated with Al(OH)$_3$ and polydimethyl siloxane (PDMS) were added to food, no increasing of apoptotic cells was observed. If the same NPs were dispersed in the soil, the number of apoptotic cells increased in cuticle, like in animals exposed to NPs in water. Finally, the effects of TiO$_2$-NPs were not significantly different between water and soil. TiO$_2$-NPs induced effects weaker than Ag-NPs, and the same tissues were affected in both cases. In animals bred in water, TiO$_2$-NPs accumulated in gut lumen but never in tissues [27]. In *Lumbricus terrestris*, harmful effects of TiO$_2$-NPs were observed for lower concentrations ($100$ mg/Kg) than those in *Eisenia fetida* ($1000$ mg/kg) [27, 28].

In *Lumbricus rubellus*, a shortness of development and reduction of growth were observed after exposure to C60 fullerene-NPs [36, 39, 40]. Sublethal concentrations of fullerene-NPs decreased the gene expression of HSP. The worms exposed to these nanoparticles presented cuticle damage and pathological sign on epidermis, muscles, and intestinal barrier [36, 39].

Coelomocytes showed immunodepression after exposure to in vitro C60 fullerene-NPs [36, 39, 41]. By contrast with *Lumbricus rubellus*, no effects on the antioxidant enzyme both expression and activity and on any other toxic activity were observed in *Eisenia fetida* exposed to C60 fullerene-NPs [36, 39, 41].

### 3. Effects of NPs on Semiaquatic Animals (Amphibia)

Amphibians are divided into anurans, urodelans, and caecilians. As semiaquatic animals, their larval life is aquatic with adapted anatomy and physiology. They breath with gills, the gut is particularly elongated with loops for an herbivorous diet, the excretory system is adapted to a water life with a strong elimination of water, and they possess tail and caudal fin in order to move by swimming. When they become terrestrial, these animals are submitted to a metamorphosis which is a dramatic period of life. This phase is characterized with important modifications of respiratory system including disappearance of gills and development of lungs. Consequently the circulatory system is obviously modified. Gills disappearing, aortic arches become devoted to both small and large circulations. Kidneys become terrestrial organs of excretion with the possibility to economize water. The tail regresses in anurans but persists in urodelans and sometimes in caecilians. Anterior and posterior legs develop in anurans and urodelans. The animal is submitted to a destruction-reconstruction phase and is then very fragile. A lot of apoptotic cells are observed in tadpoles [42]. Metamorphosis is under thyroid and pituitary control. Thus, amphibians constitute excellent models to appreciate the toxic effects of several substances such as NPs on pituitary and thyroid.

In several works, the effects of NPs on stress and thyroid hormones have been investigated using in vitro cultures of caudal fins in *Lithobates catesbeianus* (*Rana catesbeiana*) tadpoles [43, 44]. In this species, the effects of Ag-NPs, Ag-NPs aggregates, and ZnO-NPs on the expression of several genes with or without 3,3′,5′-triiodothyronine (T3) were recorded using qPCR. Results were compared to that obtained for tissues exposed to AgNO$_3$, Ag particles measuring several $\mu$m, and Cd telluride particles also measuring several $\mu$m. Ag-NPs and small aggregates affected the expression of transcripts linked to T3, with several stress molecules. ZnO-NPs did not perform any effect. Small concentrations of Ag-NPs disrupted T3 signal without inducing any stress [43].

Other experiments concerning the effects of TiO$_2$-NPs were also performed on in vitro cultures of *Lithobates catesbeianus* tadpole fins. The effects were measured through transcription of genes encoding for thyroid hormones receptors (*thra* and *thrb*) implicated in metamorphosis, for larval keratine type 1 (*rkl*), stress proteins (*hsp30*), superoxide dismutase (*sod*), and catalase (*cat*). The levels of transcription were not affected whatever the TiO$_2$ form. Significant effects have been observed after exposure to 20 nm NPs [44]. A study with epithelial strains from *Xenopus laevis* showed a toxicity of Cu under three different forms: Cu$^{+}$, 6 nm CuO-NPs, and 100 nm aggregates of CuO-NPs. Cytotoxic effects were different according to the kind of compound, with effects depending on the stage of cell cycle. Mitotic cells treated with all the three kinds of substances stopped their division with a significant increasing of the number of apoptotic cells, after a time depending on the kind of Cu substance. After 48 h as well as 6 and 7 days, treatment with 6 nm CuO-NPs or Cu$^{+}$, respectively, provoked a significant decreasing of cell
proliferation and an increase of apoptosis. Some treatments were identical on differentiated cells, but after a shorter time of exposure [45].

A study about embryonic development of amphibians showed a weak lethal effect on the embryos but early at the highest concentrations. CuO-NPs, TiO$_2$-NPs, and ZnO-NPs did not provoke embryo death but performed teratogenic effects particularly on intestine when concentrations were higher than 50 mg/L. ZnO-NPs triggered the most severe effects on the intestinal barrier, thus allowing NPs to reach connective tissue. TiO$_2$-NPs were weakly teratogenic with perhaps hidden physiological effects. Dissolved ions coming from CuO-NPs could be responsible for some effects but not ZnO [46]. The evaluation of toxic effects of TiSiO$_2$-NPs, measuring lesser than 50 nm, showed a mortality lesser than 11% in tadpoles of Pelophylax perezi (Rana perezi). Inversely, important effects were observed on lactate and melanin, with consequently an increasing of oxidative stress. TiSiO$_2$-NPs certainly performed long-time effects on these animals [47].

Contrary to general harmful effects of NPs, some experiments showed that ZnO-NPs (more than 40 nm) can improve several visual functions. Electroretinograms (ERG) highlighted that these NPs significantly increased the wavelength amplitude in toads adapted to obscurity, when they were exposed to light. In addition, ZnO-NPs improved the visual sensitivity and shortened the time of rhodopsin regeneration, a pigment implicated in the sensitivity to the light [48].

An interesting study was devoted to the trophic transfer of NPs along the trophic chains [49]. Indeed, the authors exposed earthworms Eisenia fetida to 10–20 nm Au-NPs. Worms were then eaten by bullfrogs Lithobates catesbeianus. Results were compared to bullfrogs directly eaten with the same NPs. Presence of Au-NPs was found in several frog organs: liver, kidney, spleen, muscle stomach, and intestine. They represented about 0.09% when NPs were directly ingested and 0.12% when bullfrogs were fed with earthworms. These results clearly demonstrated the possibility of a trophic transfer of Au-NPs.

4. Effects of NPs on Aquatic Animals

Large quantities of NPs are found in both marine and freshwater aquatic environments. Several works performed on aquatic organisms allowed knowing the effects of these NPs. However, these effects are variable. Recent studies considered NPs as a new nature of pollutant, the effects of which depending on their size, which are still not well-known. Several laboratory studies suggested harmful effects on fishes and invertebrates after exposure. Conventional or lesser conventional animal models were used to assess the nature of these potential effects [4]. Thus, some works focused on bony fishes, more especially the zebrafish Danio rerio, or the trout Oncorhynchus mykiss. Other studies targeted Daphnia and other crustaceans, sea urchin, mollusks, or still plankton.

4.1. In Fish. Young salmons were exposed to Ag-NPs commercial suspensions and prepared ones with AgNO$_3$ reduced with NaBH$_4$. The size of both commercial and prepared colloidal Ag-NPs was set between 3 and 220 nm. Gilts of fish accumulated Ag-NPs in all the experiments except when concentration of NPs was the lowest (1 μg/L). Responses were concentration dependent and triggered an increase of stress molecules in gills such as plasmatic glucose or presence of HSP 70. An inhibition of Na$^+$/K$^+$ ATPase depending on concentration indicated a default of osmoregulation. At the highest concentrations (100 μg/L), Ag-NPs induced a necrosis of gill lamellae, and 73% of individuals died. These experiments highlighted the impact of NP mode of preparation on toxic effects [50].

On the other hand, NPs may be constituted in a single metal or a single metallic oxide or in several metals. Thus, chemical characteristics and behavior of metallic-NPs are linked with both the dynamics of aggregates and the equilibrium of metal ions, and the acute toxicity of metal-NPs could be linked to the presence of these free metal ions. Biological effects of NPs may be linked to the presence of ion carriers and to the capacity of endocytosis. Some works showed that NPs could induce lethal effects on fishes when concentrations varied from the order of μg/L to mg/L in the environment. In several fish species, metallic-NPs can be more toxic than dissolved forms. In young zebrafish, LC-50 was reached at 0.71 mg/L for Cu-NPs and 1.78 mg/L for dissolved Cu. Unknown mechanisms are certainly implicated. It is obvious that these NPs cause sublethal effects such as breath toxicity, disruption of tissue elements, inhibition of Na$^+$/K$^+$ ATPase, and an oxidative stress [51].

Pathologies affecting a lot of organs, such as gills, liver, intestine, and brain, suggested that the response to NPs and metal salts presented some common points. Several effects on development were also observed. Ag-NPs went across the chorion, the envelope surrounding the egg or the developing embryo. Cu-NPs and ZnO-NPs would be more toxic for embryos and juveniles than the corresponding salt. It remains possible that metal-NPs interfered with corresponding stress responses, maybe by stimulation [51]. Mechanical effects of NPs and other nanomaterials on fish began to be studied since the end of 2000s. These studies focused on the mechanisms of absorption, distribution, metabolisation, and excretion of substances in fishes by comparison with other chemical substances. These aspects have been examined for TiO$_2$-NPs and C60 fullerene in several organs: gills, digestive tract, liver, and adrenals. NPs penetrated the tissues by endocytosis more intensively than with ionic carriers, like for the corresponding metal ion, or by diffusion. In fishes, NPs were rarely excreted by kidneys but could be eliminated with bile. However, data remain still incomplete to date [52].

The effects of ZnO-NPs were investigated on in vitro cultures of hepatocyte strains coming from human and fish. These NPs aggregated, which strongly contributed to the toxicity on fish cells. For human cells, the toxicity would be caused by the dissolved salts released by NPs [53]. A comparative study performed on in vivo zebrafish and in vitro culture of tumoral human hepatocytes Huh7 showed that the Ag-NPs (120 nm in diameter) penetrated into the hepatocytes inducing an oxidative stress characterized with the presence of ROS, INF$\gamma$ expression, and endoplasmic reticulum (ER) disruption. Transcription alterations of p53
and Bax genes implicated in apoptosis were also observed. Yet, some differences were noted between fish and human hepatocytes, suggesting that there were several mechanisms of stress linked to the modification of ER. Development of zebrafish embryos submitted to Ag-NPs was also affected, inducing malformations [54].

In vitro studies on zebrafish showed that Ag-NPs induced neurotoxic effects different from Ag+ ones. The effects of Ag-NPs with different sizes (12 and 28 nm), Ag-NPs coated with PVP (45, 63, 65, and 324 nm), and Ag ions were also different on the embryonic development. Ag+ slowed the development of swim bladder, implicating also several malformations; Ag-NPs effects were lower. Fish behavior was also modified in front of light stimuli: the smallest PVP-coated NPs originated hyperactivity and the largest PVP-coated ones originated a hypoactivity [55]. A deep analysis highlighted that the effects of 1–20 nm Ag-NPs introduced in zebrafish embryos were found in adult nervous system. Ag ions released by Ag-NPs could provide increasing mortality and malformations. Ag-NPs could act on cell differentiation with the intermediary of cell inhibition with acetylcholine [56]. Also in zebrafish embryos Ni-NPs were responsible for mortality and induced malformations. The intestine became very thin on the contact with Ni-NPs, contrarily to the solution of Ni with which no effect was found. Skeletal muscles were affected by 30, 60, and 100 nm Ni-NPs and also by soluble Ni. So, toxicity of 30, 60, or 100 nm Ni-NPs was very little different from soluble nickel one. Inversely, large particle clusters of aggregated 60 nm Ni-NPs with a dendritic structure were particularly toxic on both intestine and skeletal muscles. Thus, the configuration of Ni (NP, aggregates, or ion) was more important than its size [57]. 10 nm Au-NPs moved in all the parts of body in zebrafish embryos. These particles accumulated in aggregates the sizes of which being function of the concentration, but the effects on the development were not proportional to concentrations. Malformations obtained could be due to the random distribution of Au-NPs within cells during development. With the toxicity depending on chemical properties, Au-NPs were lesser toxic than Ag-NPs. Thus, zebrafish embryos can be used as in vitro models, especially concerning biocompatibility of materials [58].

Zebrafish is certainly a good model for NPs studies, but other fish species such as trout are also largely used. The effects of TiO2-NPs and C-NPs were researched in trout hepatocytes. For that, the effects investigated concerned nanomaterials currently used such as C60 fullerene, MWNTs, SWNTs, with or without a define function, and TiO2-NPs measuring 5 to 200 nm. Experiments showed that these substances were found showing ecotoxicological effects. But several analyses revealed a presence of Co residues, which did not enter in NPs constitution but found their origin in the manufacture proceeding. Trace elements were perhaps responsible for toxic effects. Indeed, mechanisms, such as a facilitated transport linked to the presence of NPs, could increase the toxic response comparatively to only an exposure to the same molecules in aqueous solution [59]. In Ochorynchus mykiss, the effects of 87 nm Cu-NPs and CuSO4 were compared. Juvenile trouts were exposed to several concentrations of CuSO4 and Cu-NPs. An accumulation of NPs and CuSO4 was observed in gills, but with different proportions. No accumulation of both products was observed in spleen, brain, or muscle, but an increasing of Cu was noted with both NPs and salts. Whatever the kind of Cu, Cu-NPs were not toxic for hydromineral regulation, but a decrease of Na+/K+ ATPase was observed in brain and intestine. Finally, the toxic effects of Cu-NPs seem to be similar to that of CuSO4, but at lower concentrations [60]. Exposition of Ochorynchus mykiss to about 20 nm TiO2-NPs provoked several gills pathologies characterized by edema and thickness of gill lamellae. No perturbation of blood and blood cells was observed. Metal content in tissue was not affected except for Cu and Zn according to the NPs concentration and more especially in the brain. A decrease of Na+/K+ ATPase was observed in gills and intestine. Substances such as thiobarbituric acid (TBA) depending on concentration increased in gills and brain. Minor variations of lipids were observed in the liver in which several hepatocytes became apoptotic [61]. Other metabolism variations were also observed [61]. In in vitro culture of hepatocytes belonging to several species, Ag-NPs provoked a dose-dependent decrease of the membrane integrity and cell metabolism. Au-NPs increased ROS without any cytotoxic effect. With an addition of carbonic acid, no alteration of the cytotoxic potentiality of NPs and of the capacity to induce ROS was observed. Indeed, on culture of trout hepatocytes, effects of Ag- and Au-NPs were sometimes in opposition [62].

A work appreciated the effect of lesser than 25 nm TiO2-NPs eaten by Danio rerio embryos and larvae on development. In a first experiment, these NPs were ingested when they were added to commercial food, and, in another experiment, fishes were fed with algae previously exposed to TiO2-NPs. At low concentrations, hatching was premature, and the impact on juvenile animals was not strong. But, after exposure to contaminated food, the digestive physiology was altered after 14 days of exposure [63].

4.2. In Crustaceans. Crustaceans are usually used to appre-ciate the effects of toxic in polluted environments. So crustaceans such as Daphnia magna or Thamnocephalus platyurus have been also used to test the potential harmful effects of NPs, sometimes with comparison with corresponding metal toxic.

In Daphnia magna, AgNO3 mainly affected the reproduction, and 20 nm Ag-NPs affected growth [64]. Several types of TiO2-NPs used in industry presented photocatalytic effects on Daphnia and algae; that is, the effects of these substances were different according to the lighting and their nature [65]. Toxic effects of Ag-NPs when Ag is linked to PVP or collargol (Ag-NPs linked to proteins) were very strong for Daphnia magna and Thamnocephalus platyurus, compared to that of AgNO3. Ag-NPs were 10 times more toxic than AgNO3 in terms of EC50 [66]. Toxic effects of AgNO3, colloidal solutions of 15 nm Ag-NPs, and Ag-NPs suspensions forming 25 to 100 nm aggregates were investigated in Daphnia magna. Teratogenic effects and repercussions on swimming were observed according to the concentration and the Ag form. Aggregates of Ag-NPs suspensions were the most toxic; NPs were fixed under the crustacean carapace, affecting directly
the animal swimming [67]. *Daphnia magna* exposed to algae contaminated with TiO$_2$-NPs showed an accumulation of Ti within the digestive tract. When the exposition was chronic, growth and reproduction decreased, and the toxicological impact of these nanomaterials could be modulated with the age of the NPs [68].

4.3. Other Aquatic Organisms. Since a long time, echinoderms and bivalve mollusks represent good animal models to appreciate the effects of toxins in salt water. So, after having been tested in presence of chemical pollutant, they are also used to understand the effects of NPs.

The effects of metallic oxide-NPs (SnO$_2$-NPs, CeO$_2$-NPs, and Fe$_3$O$_4$-NPs) were tested on immune cells in the sea urchin *Paracentrotus lividus*. NPs were found in coelomocytes, which constitute the immune cells of sea urchins. These cells presented a well reduced cholinesterasic activity, an underregulation of stress proteins, and variable morphological alterations of ER lysosomes [69].

In bivalve mollusks, immune function is targeted by NPs. The first essay showing immunomodulation induced by NPs in bivalves was performed in *Elliptio complanata* in 2008 [70]. Since this time, various works focusing on the effects of NPs on the immune system were performed with the mussel *Mytilus galloprovincialis*. Several NPs types were absorbed by the hemocytes, affecting several of their parameters, such as lysosomal activity, phagocytosis capacity, production of free radicals, or an increase of the apoptotic activity. A lot of NPs exerted an effect on immune system. In the oyster *Crassostrea gigas*, the exposition to several kinds of NPs also provoked effects on oxidative stress and lysosomal activity and apoptosis, more especially into the gills and digestive gland, and on the embryonic development. Accumulation of NPs was also observed in several tissues depending on the nature of NPs. In *Mytilus edulis*, TiO$_2$-NPs presented some in vivo immunomodulator effects. TiO$_2$-NPs were aggregated in water and then could paste on the gills, join directly the digestive gland, and penetrate cells with consequent lysosomal perturbation and modification of the expression of genes implicated in the antioxidant stress and in the immune response, especially lysozymes and antimicrobial peptides. NPs may be carried out of the digestive tract via the hemolymph and through hemocytes in which they induce functional modifications, in particular lysosomal function, phagocytosis, production of NO and ROS implicated in oxidative stress, with the apoptosis initiation, as well as in membrane and mitochondria. Significant variations of expression of antioxidant and immunity genes were also observed. Yet, TiO$_2$-NPs originated an underregulation of immune genes in the digestive gland and hyperregulation of these same gens in hemocytes [36].

Using metatranscriptomic analysis, that is, the analysis of RNA quantities extracted from a planktonic sample, consisting of a community of aquatic small organisms, some toxic effects of Ag$^+$ ions and free 6 nm Ag-NPs affecting the composition of planktonic sample and the metabolism of its members were searched. For that, authors used a metatranscrinomic analysis, that is, the analysis of RNA quantities extracted from the planktonic sample. Compared to controls, significant results were obtained after treatment with Ag-NO$_3$ (5 µg/L) but not with Ag-NPs. These results showed that ionic Ag was more toxic than Ag-NPs [71].

5. Conclusions

NPs are more and more used and they enter in the composition of different substances such as SIM cards of cell phones or sunscreens. After having consumed these products, free NPs can be released in the environment and in the air as well as in water or soils. Thus, NPs are new potentially toxic substances. They can induce effects directly linked to their chemical composition like a lot of other industrial products including pesticides, but, in addition, their own nature with generally a size smaller than 100 nm, intermediary between particles (several µm and more), and molecules and ions confer them particular properties which remain to be discovered. The effects of NPs begin to be known, but a great effort of investigation remains to be done, in particular on organisms used as bioindicator, and a characterization of highly toxic NPs remains to be established. To date, numerous works concerning NPs focus on the understanding of the effects of NPs on organisms living in soil, such as mammals or earthworms, semiaquatic organisms, such as amphibians, or freshwater or marine organisms, such as fishes, invertebrates, algae, and plankton.

A new research domain is now developing in order to measure the potential harmful effects of this useful NPs and to allow an efficient protection of the environment. Interdisciplinary investigations are, more than in other domains, certainly essential [72]. In addition, these studies will allow one to find new biological mechanisms, still unsuspected, which will give new knowledge about cell life.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgment

The authors are grateful to Philomène Cuzin who helped them in bibliographic search.

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Research Article

Analysis of Thermal Properties on Backward Feed Multieffect Distillation Dealing with High-Salinity Wastewater

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Received 7 May 2015; Accepted 25 June 2015

Academic Editor: Zhongwei Zhu

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Theoretical investigations on thermal properties of multieffect distillation (MED) are presented to approach lower capital costs and more distilled products. A mathematical model, based on the energy and mass balance, is developed to (i) evaluate the influences of variations in key parameters (effect numbers, evaporation temperature in last effect, and feed salinity) on steam consumption, gained output ratio (GOR), and total heat transfer areas of MED and (ii) compare two operation modes (backward feed (BF) and forward feed (FF) systems). The result in the first part indicated that GOR and total heat transfer areas increased with the effect numbers. Also, higher effect numbers result in the fact that the evaporation temperature in last effect has slight influence on GOR, while it influences the total heat transfer areas remarkably. In addition, an increase of feed salinity promotes the total heat transfer areas but reduces GOR. The analyses in the second part indicate that GOR and total heat transfer areas of BF system are higher than those in FF system. One thing to be aware of is that the changes of steam consumption can be omitted, considering that it shows an opposite trend to GOR.

1. Introduction

Wastewater is the by-product of petrochemical enterprises, including oily wastewater, sulfur-containing wastewater, saline wastewater, and high-concentration ammonia-nitrogen wastewater [1, 2]. The wastewater will be greatly harmful to the environment if they are untreated and discharged directly. Petrochemical enterprises have been plagued by saline wastewater treatment owing to its high salt and biotoxicity. The MED is one of the most successful traditional desalination technologies [3], which presents a number of advantages: low scale formation, easy operation, high performance ratio (PR), and operating with any available source of heat energy (e.g., waste heat from petrochemical enterprises and power plants) [4–6]. In each effect of MED system, pure water is produced at slightly lower pressure than the previous effect. The water evaporates at lower temperatures with the pressure decreasing; therefore, the produced vapor of the first effect evaporator serves as the heating steam for the second effect and so on [7]. An increase of effect numbers can lead to a higher PR. On the basis of energy consumption and heat transfer obtained, MED has been found to be more efficient than MSF [8].

Jernqvist et al. [9] and Etourney [10] developed a simulation code for the MED system with shell and tube evaporators; subsequently the influences of different design parameters on PR were studied. Shakib et al. [11] developed a thermodynamic model for MED desalination with thermal vapor compression (METVC) and its main objective was optimization of METVC from economical and thermodynamic point of view. Although the general computer code and optimal model for thermoeconomic optimizations of MED desalination systems [4, 11–13] had been studied by many reports, few studies have been reported on the thermal properties of MED so far. The purpose of this work was to...
analyze the thermal properties of BF system concentrating high-salinity wastewater. Therefore, a mathematical model was developed based on mass and energy balance. In this paper, the work consisted of two parts: at first, the influences of effect numbers, evaporation temperature in last effect, and feed salinity were studied. These specifications include steam consumption, GOR, and total heat transfer areas. Furthermore, the performance comparisons between FF system and BF system were conducted in the second part.

2. Mathematical Model

The MED system usually consists of some evaporators, several flashing chambers, and a condenser. The mathematical model is developed for MED concentrating saline wastewater based on mass and energy balance. In the mathematical model, at first mass and energy balance equations have been developed for the system and then evaporator heat transfer areas balance equations are designed [14–16].

2.1. Mass Balance. In the evaporator, the mass balance can be considered as follows:

\[
M_{b,\text{in}} \times X_{b,\text{in}} = M_{b,\text{out}} \times X_{b,\text{out}}.
\]  

In the flashing chamber, the mass balance can be considered as follows:

\[
M_v = M_{f,\text{w}} \times X_{f,\text{w}},
\]

where \(M_{b,\text{in}}\) and \(M_{b,\text{out}}\) are the mass flow rate of feed brine water and mass flow rate of condensed brine water, respectively, \(t/h\).

\(X_{b,\text{in}}\) and \(X_{b,\text{out}}\) are the salinity concentration of feed brine water and mass flow rate of condensed brine water, respectively, %.

2.2. Energy Balance. In the evaporator, the energy balance can be considered as follows:

\[
(M_{v,\text{in}} \times r_{\text{in}} + M_{b,\text{in}} \times C_{p,\text{in}} \times t_{b,\text{in}} - M_{b,\text{out}} \times C_{p,\text{out}} \times t_{b,\text{out}}) \times \eta = M_p \times h,
\]

where \(C_p\): specific heat capacity, J/(kg\(^\circ\)C),

\(\eta\): heat utilization efficiency

\(h\): enthalpy;

\(t_{v,\text{out}} = t_b - \text{BPE} - \Delta t.
\]

The BPE is the boiling point elevation and is estimated as follows:

\[
\text{BPE} = X(b + CX) \times 10^{-3}
\]

\[
b = (6.71 + 6.34 \times 10^{-2}t + 9.24 \times 10^{-5}t^2) \times 10^{-3}
\]

\[
C = (22.238 + 9.59 \times 10^{-3}t + 9.24 \times 10^{-5}t^2)
\]

\[
\times 10^{-8}.
\]

The heat transfer equation is as follows:

\[
M_{v,\text{in}} \times r_{\text{in}} + M_{v,\text{out}} \times r_{\text{out}} = AK(t_c - t_b)
\]

\[
K = \frac{1}{(1/\alpha_c + (1/\alpha_b) + R_w + R_f)}.
\]

\(\alpha_c\): heat transfer coefficient in condensing surface, W/m\(^2\)\(^\circ\)C;

\(\alpha_b\): thermal resistance of tube, W/m\(^2\)\(^\circ\)C;

\(R_w\): thermal resistance of furring, W/m\(^2\)\(^\circ\)C;

\(R_f\): falling film evaporation heat transfer coefficient, W/m\(^2\)\(^\circ\)C.

In the condenser, the calculation of energy balance is as follows:

\[
M_v \times r = M_{f,\text{w}} \times \left(\epsilon_{p,\text{out}} \times t_{\text{out}} - \epsilon_{p,\text{in}} \times t_{b,\text{in}}\right).
\]

The heat transfer equation is as follows:

\[
M_v \times r = K_c \times A_c \times \Delta t_{\text{LMTD}}.
\]

In the flashing chamber, the mass balance can be considered as follows:

\[
M_v \times r = M_{f,\text{w}} \times \epsilon_{p,\text{in}} \times t_{\text{c,\text{in}} - M_{f,\text{w,\text{out}}} \times \epsilon_{p,\text{out}}}
\]

\[
\times t_{\text{c,\text{out}}}
\]

\(t_{\text{out}} = t_v + \Delta t
\]

\[
\Delta t = 0.33 \times \frac{t_{\text{c,\text{in}} - t_v}}{t_v}.
\]

2.3. Total Heat Transfer Areas Balance. In the first evaporator, the heat transfer area is calculated as follows:

\[
A_1 = \frac{M_{b,\text{in}} \times \epsilon \times (t_1 - t_0) + M_{b,\text{out}} \times r}{\eta \times (t_1 - t_{\text{v,\text{1}} - BPE})}
\]

In the other evaporator, the heat transfer area is calculated as follows:

\[
A_n = \frac{M_{b,\text{out,\text{n-1}}} \times r}{\eta \times (\Delta t - \text{BPE})}.
\]

So the total heat transfer area is equal to

\[
A = A_1 + A_2 + \cdots + A_n.
\]

2.4. Calculation Parameters. Traditionally, salinity wastewater from petrochemical enterprises often contained a large percentage of organic matter (including oil type matter) and suspended matter [16]. The stability of MED process would be influenced if they were not removed. So it was firstly pretreated by biological treatment facilities, RO, and ultrafiltration (UF) to remove the organic matter and suspended matter and then entered the MED to desalinate. Therefore, the saline wastewater in this study was obtained from a typical refinery in China. In order to investigate the influences of key parameters on performance of MED, the calculation parameters of MED were shown in Table 1.
3. Results and Discussion

3.1. Influences of Effect Numbers on Thermal Properties of MED. Figure 1(a) presented each effect evaporation capacity of different effect numbers of MED. As seen, the amount of steam generated by evaporation in each effect was less than the amount generated in the previous effect. This was due to the specific latent heat of vaporization increased with the decrease in the effect temperature. Consequently, the amount of vapor generated in an evaporator by boiling was less than the amount of condensing steam used for heating in the following evaporator. Furthermore, under the same distilled products, the higher effect numbers of MED system were, the smaller amount of each effect was. Figure 1(b) presented each effect heat transfer areas of different effect numbers of MED. Obviously, heat transfer areas of MED decreased with the increase of effect numbers in the same effect numbers of MED system, and heat transfer areas of the first effect evaporator were the largest. This was because secondary steam generated each effect which reduced with effect numbers under the same distilled products, and temperature differences between each effect gradually increased, which resulted in reducing the heat transfer areas of each effect evaporator.

Table 2 showed the variation of steam consumption, GOR, and total heat transfer areas with the effect numbers at the same distilled products, respectively. It can be observed that steam consumption decreased and GOR rose with the increase of effect numbers. This was because, in the first effect, the latent heat of the feed steam was used to heat the feed water towards the saturation temperature and a smaller amount of vapor was formed. This process was repeated in subsequent effects, where the feed water was heated and an additional amount of vapor was formed. In addition, although the increment of heat transfer areas was smaller in each effect evaporator, total heat transfer areas of
the evaporator obviously increased with the increase of effect numbers.

### 3.2. Influences of Evaporation Temperature in Last Effect on Thermal Properties of MED

Figure 2 showed the changes in steam consumption with the increase of effect numbers under the constant distillated products. As seen, the increase in evaporation temperature in last effect reduced steam consumption due to the increase in the temperature drop per stage, which enlarged the driving force for heat transfer and reduced the steam consumption. Figure 3 presented GOR raised with the evaporation temperature in last effect. This was mainly due to the fact that the latent heat of water vapor at high temperature was smaller [17]. Meanwhile, total evaporation capacity consisted of flashing production from brine water and fresh water besides evaporation from the transferring heat tube [18]. Thus, the amount of vapor generated in previous evaporator was more than the amount of the following evaporator. When the evaporation temperature in last effect increased, the evaporation capacity difference between adjacent effects was smaller. The amount of vapor generated from first effect increased and brine temperature from the first effect was raised, so the brine could obtain more heat. Therefore, GOR was positive correlated with evaporation temperature in last effect.

Figure 4 showed that total heat transfer areas rose with the evaporation temperature in last effect. The higher effect numbers were, the greater influence of evaporation temperature in last effect on total heat transfer areas was. The growth rate of total heat transfer areas accelerated with the increase of evaporation temperature in last effect when effect numbers were higher. For instance, when evaporation temperature in last effect increased from 41°C to 51°C, total heat transfer areas increment was 26.34% and GOR increment was just 9.36% in six effects of MED. To sum up, increasing in evaporation temperature in last effect heightened slightly GOR, but bigger increment of total heat transfer areas was needed.

### 3.3. Influences of Feed Salinity on Thermal Properties of MED

Figures 5 and 6 presented the influences of feed water salinity on steam consumption and GOR, respectively. As shown, steam consumption rose and GOR gradually decreased with the increase of the feed salinity, which meant that the treatment effect was reduced. There might be a few reasonable explanations for this phenomenon as follows. Firstly, the viscosity increased with the feed salinity, and then the diffusion coefficient and the thermal conductivity
In the feed solution were also reduced. At the same time, the distilled product and the secondary steam formed from each effect were reduced. In addition, the influence of the boiling point elevation (BPE) was raised with the salinity. As a result, effective heat transfer temperature difference was raised with the effect numbers and heat transfer efficiency decreased. Thereby, the thermal efficiency of the system reduced, which resulted in the increased steam consumption and the decreased GOR.

Figure 7 illustrated the influences of feed salinity on the total heat transfer areas. As seen, there was a positive correlation between evaporator total heat transfer areas and feed salinity. This was due to concentration of each effect increased with the feed salinity, so the loss of heat transfer temperature difference caused by BPE increased. Subsequently, a reduction of temperature difference adjacent effect and evaporation capacity of each effect resulted in an increase of total heat transfer areas.

3.4. Comparison of Performance of BF and FF. Figure 8 presented the comparison of steam consumption and GOR between FF system and BF system. As shown, these two systems had similar variations in steam consumption and GOR. With the increase of effect numbers, steam consumption decreased and GOR increased. Furthermore, BF system had lower steam consumption and higher GOR. The major cause was that BF system had a significant advantage compared with FF system. In BF system, the brine of first effect came from second effect and the brine temperature was often higher than the condenser outlet temperature. Hence, less
feed steam heated the feed water towards the saturation temperature and more was left to heat the brine to enlarge the vapor which was generated by boiling. In invariant feed salinity and evaporation temperature in last effect, all the feed water of FF system had to be heated to the boiling temperature in the first effect before boiling commences. In other words, some of heating steam condensed did not accomplish any evaporation in the first effect. Therefore, feed steam flow rate had to be increased to maintain the constant distilled products, so BF steam had higher consumption and lower GOR.

As shown in Figure 9, total heat transfer areas of BF system were higher than FF system, and the total heat transfer areas differences between two systems increased with the effect numbers. This was because the feed water from the condenser entered the last effect; in the of BF system, the temperature of feed water was below the saturation temperature, so more evaporation areas were needed to heat the brine to the saturation temperature. However, in FF system, the feed water was supplied to the first effect of the highest temperature, and the heating brine temperature was higher than saturation temperature, so the heating brine flashed in evaporation. This was why the total heat transfer areas of FF system were lower than BF system.

### 4. Conclusions

To analyze the influences of key parameters on thermal properties of BF system concentrating high-salinity wastewater system, a mathematical model was developed based on the energy and mass balance. The results indicated that the effect numbers were very important to keep the balance between lower costs and more distilled products in the MED system. More distilled products could be produced with high effect numbers than those with low effect numbers. Also, higher effect numbers led to higher capital costs and distilled product costs. GOR increased slightly with the evaporation temperature in last effect, but the total heat transfer areas rose greatly. The heat transfer temperature difference caused by boiling point increased with the feed salinity, which increased steam consumption and total heat transfer areas. Thereby, GOR decreased with an increase of feed salinity. Furthermore, it was observed that GOR and total heat transfer areas of BF system were higher FF system.

### Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

### Acknowledgments

The authors are very grateful to the National Nature Science Foundation (Grant nos. 51408347, 51178463, 21307149, and 51474140) and Scientific Research Foundation of Shandong University of Science and Technology for Recruited Talents (Grant no. 2014RCJ018) for financial support of this study. The authors’ deepest gratitude goes to the anonymous reviewers for their careful work and thoughtful suggestions that have helped improve this paper substantially.

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Research Article

Iron Contamination Mechanism and Reaction Performance Research on FCC Catalyst

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Received 7 May 2015; Accepted 25 June 2015

Academic Editor: Zhongwei Zhu

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FCC (Fluid Catalytic Cracking) catalyst iron poisoning would not only influence units’ product slate; when the poisoning is serious, it could also jeopardize FCC catalysts’ fluidization in reaction-regeneration system and further cause bad influences on units’ stable operation. Under catalytic cracking reaction conditions, large amount of iron nanonodules is formed on the seriously iron contaminated catalyst due to exothermic reaction. These nodules intensify the attrition between catalyst particles and generate plenty of fines which severely influence units’ smooth running. A dense layer could be formed on the catalysts’ surface after iron contamination and the dense layer stops reactants to diffuse into inner structures of catalyst. This causes extremely negative effects on catalyst’s heavy oil conversion ability and could greatly cut down gasoline yield while increasing yields of dry gas, coke, and slurry largely. Research shows that catalyst’s reaction performance would be severely deteriorated when iron content in E-cat (equilibrium catalyst) exceeds 8000 μg/g.

1. Introduction

Resid oil, especially Vacuum Resid oil, is an intermediate product with the least value in refineries. Refineries’ economic profits are largely dependent on VR’s (Vacuum Resid oil) conversion scheme and deepness. RFCC (Resid Fluid Catalytic Cracking) process has advantages of high processing capacity, good application ability, and high economic benefits which are very suitable for our country’s current secondary processing situation in petroleum industry. Therefore, RFCC is an important way of VR conversion in order to improve refineries’ economic profits and the research and development of RFCC catalyst are one of the key technologies.

There are large amounts of heavy metal such as vanadium [1], nickel [2], and iron [3] and these elements have strong poisoning effects on catalyst. When nanovanadium is deposited on catalyst surface, the vanadic acid which is similar to phosphoric acid that is formed by redox reaction would destroy zeolite’s crystal structure and lead to low catalyst conversion and bad product distribution. Different from vanadium poisoning, when nickel is deposited on catalyst surface with a large quantity, nanonickel’s dehydrogenation activity would lead to increasing yields of dry gas and coke [2]. As to iron poisoning, except for iron in feedstock, the carried iron during crude oil’s transportation could also lead to catalyst’s iron poisoning. In recent years, there are sometimes iron poisoning phenomena that occurred in domestic refineries [3–12]. But, unfortunately, our researchers have not had profound understanding on catalyst iron poisoning. Iron poisoning at low concentration has mild poisoning effect on catalyst, but, with more and more iron deposits on catalyst significantly, catalysts’ reaction performance would be deteriorated greatly, especially for heavy oil conversion activity.

This paper discusses iron’s poisoning effect on catalysts from the angle of practical industrial production and comes up with simple classification on catalyst iron ions poisoning level.
2. Experiment

2.1. Equivalent-Volume Impregnation on Catalyst. First, a certain amount of sample is weighed and placed in beaker, and then deionized water is added dropwise while stirring with glass stick. The amount of water added is recorded when thixotropy of catalyst is observed. The nickel ion contamination sample’s preparation is the same with vanadium ion contamination sample’s preparation and the nickel ion used is nickel nitrate with 9H$_2$O.

2.2. Preparation of Model Catalyst. The preparation process of model catalyst is as follows. First Kaolin-clay (Suzhou Kaolin company) is mixed with water. When the system is thoroughly dispersed, alumina binder (Shandong Alumina company) and relevant zeolite (Lanzhou Petrochemical company) are added into system in order. After stirring for an hour, the mixture is spray dried and shaped into semifinished catalyst. After calcinations and filtration wash, the finished catalyst sample is prepared.

2.3. Characterization. Particle size and crystal morphology of the samples were examined with a scanning electron microscopy (SEM) and energy dispersive spectrometer (EDS), which was carried on S4800. X-ray fluorescence spectroscopy (Axios) was used to analyze the iron content in all the samples.

2.4. Advanced Cracking Evaluation (ACE). Advanced Cracking Evaluation (ACE) is developed by KTI Technology company, USA. The device is equipped with a single reactor and both reaction and regeneration process take place in the same reactor. The device has a small size, low consumption of raw material, and a high automatic level and it is very suitable for labs to do research on catalyst’s performance and selectivity on catalyst formula. In this experiment, the weighed, unevaluated catalyst is injected into ACE unit’s fluidization catalytic cracking reactor through ACE unit’s experimental injection system; feedstock is also injected into reactor through oil pump system with a certain quantity. The catalyst and feedstock perform catalytic cracking reaction under setting evaluation parameter. The reacted oil gas is stripped with nitrogen and gasoline, diesel, heavy oil, and other liquid products are collected in condensing collector while dry gas, LPG, and other gas products are collected in gas collector. The composition analysis is done according to SH/T0558 method with simulated distillation gas chromatography and UOP Method 539 with refinery gas analysis gas chromatography, respectively. After stripping, the catalyst in reactor is regenerated with air, the CO in the regenerating flue gas is converted to CO$_2$ with reforming furnace, and eventually the coke value is tested by in situ FTIR CO$_2$ analyzer. After the regeneration, the reactor is cooled and the catalyst in reactor is automatically unloaded to wasted catalyst can. According to the weight of each component, the product slates can be calculated and FCC catalyst’s selectivity and its reacting rules can be obtained and then FCC catalyst’s cracking performance is evaluated.

![Figure 1: SEM images of E-cat iron poisoning ((a) low iron; (b) moderate iron; (c) high iron).](image)

3. Conclusion and Discussion

3.1. Iron Poisoning’s Influence on E-Cat’s Morphology. Lab research shows that catalyst iron poisoning would cause severe damage to catalyst particle and its spherical shape. Figure 1 shows SEM (scanning electron microscope) pictures of equilibrium catalysts with different iron poisoning levels. In Figure 1, when E-cat iron content is relatively low (around 4000 µg/g), the catalyst’s surface is smooth; with the increase of iron concentration (around 6000 µg/g), the E-cat’s surface becomes apparently less smooth; after the iron concentration further increases to around 8000 µg/g, many fissures and nodules are formed on the surface of E-cats. These E-cats
with rough surface rub with each other and generate large quantity of fines in catalysts’ reaction-regeneration system. The lab research further analyzed iron distribution on the surface of E-cats with high iron poisoning level. The research found out that the nodules on catalysts’ surface have higher iron content and the tested E-cat sample has the iron content as high as 13200 \( \mu \text{g/g} \). The area that has no nodules has lower iron content of 7300 \( \mu \text{g/g} \). The result is shown in Figure 2. According to iron content of E-cat, we denote them as E-cat1 (4000 \( \mu \text{g/g} \)), E-cat2 (6000 \( \mu \text{g/g} \)), and E-cat3 (8000 \( \mu \text{g/g} \)).

3.2. Criterion of FCC Catalysts' Poisoning Level. The lab made comparison evaluations on reaction performances of catalysts with different iron poisoning levels with ACE units. Figure 3 is the alteration curve of catalyst’s conversion rate and heavy oil yield correlated with catalyst iron poisoning level. Figure 4 shows that when catalysts’ iron poisoning is low, both bottom yield and conversion rate are, respectively, increasing and decreasing at a moderate speed; when E-cat has higher level of iron poisoning (around 8000 \( \mu \text{g/g} \)), both bottom yield and conversion rate are, respectively, increasing and decreasing quickly.

In catalytic cracking reaction process, LCO is not only the heavy oil molecules’ cracking product, but also the catalysts’ cracking raw material. Figure 4 shows alteration trend of LPG and gasoline’s yield along with LCO and bottom yield correlated to catalysts’ iron poisoning. In Figure 5, we could see that, with the catalysts’ iron poisoning level increasing, LPG and gasoline’s yields decreased significantly and LCO and bottom’s yields increased obviously. Similar to the trend of conversion rate and bottom yield’s change correlated to catalyst iron content, when catalyst has higher iron content (around 8000 \( \mu \text{g/g} \)), LCO and bottom’s yields increase rapidly while LPG and gasoline’s yields decrease quickly.

Figure 5 shows that, with the increase in catalyst iron content, the dry gas and coke’s yields are also increased significantly. Due to iron ions’ severe damage to catalysts’
surface, thermal cracking takes place largely and leads to increasing in dry gas and coke's yields. Besides, similar to nickel ions, iron also has high dehydrogenation activity. Therefore, when E-cat has high iron poisoning level, iron ions' dehydrogenation activity will also lead to increasing in dry gas and coke's yields.

Research also found that when catalyst has high iron content (around 8000 μg/g), catalysts' color will turn red, which has great difference with regular catalysts. Figure 6 shows the appearances of the same catalyst that applied in different refineries. From catalysts' appearances we could see that the HB E-cat shows obvious red color due to its high iron content which is more than 8000 μg/g.

3.3. Reaction Performances of E-Cats with Different Iron Poisoning Levels. Table 1 lists ACE unit evaluation results of three E-cats with different iron poisoning levels. The E-cats E-cat1, E-cat2, and E-cat3 have gradually increasing iron poisoning levels. From Table 1, we could see that E-cat3 has the highest dry gas and coke yields and lowest conversion rate and light oil yield due to its highest iron poisoning level. It is consistent with the evaluation results of tests on E-cats with different iron poisoning levels; when catalyst has high iron content, its reaction performance degenerates quickly and target product's yield significantly decreases.

E-cats’ iron poisoning happens occasionally in refinery. When iron ions deposit on catalysts’ surface at a large quantity, the low melting point eutectic formed by iron and catalyst particles would cover catalysts’ surface and block feedstock molecules' diffusion to catalysts' inner pores, which leads to lower feedstock cracking ability and target products yield. Besides, catalyst iron poisoning would lead to rough catalyst surface. Rough catalysts collide with each other and generate large quantities of fines that reduce catalysts' utilization efficiency, increase processing costs, and even cause E-cats' fluidization problems in the reactor-regeneration system.

3.4. Iron Poisoning Mechanism. Iron is a transition metal that can have a devastating effect on catalyst performance [7–10, 13]. Like vanadium, iron can form a eutectic. However, while vanadium can be found throughout the whole catalyst particle, iron typically sticks to the external surface. The appearance of the FCC catalyst changes from smooth spherical particles into particles with a bumpy nodularized surface (Figures 1 and 2). Iron deposited on the catalyst agglomerates into small crystals of magnetite at the catalyst surface. The nodules at the surface are formed by matrix capped with magnetite. The magnetite crystallites readily react with H₂S in the riser forming iron sulfide. In the regenerator, iron sulfide is reoxidized to magnetite (liberating the S as SO₂). Oxidation of iron sulfide not only is strongly exothermic
but also proceeds at lightning speed as it is catalyzed by its own product, iron oxide. The huge amount of heat unleashed in a very brief time melts the surrounding matrix. Where vanadium “only” forms a eutectic, iron forms a eutectic and infuses sufficient heat to melt a layer of the silica-alumina matrix at the particle surface up to several microns deep. The result is the formation of a dense layer (iron oxide), typically a few microns in depth (Figure 8). The zeolite and matrix at the core of the catalyst particle are unaffected by iron, but they are no longer available for cracking due to the diffusion barrier formed at the surface. The iron poisoning process is shown in Figure 7.

4. Conclusion

Catalyst iron poisoning will not only affect FCC unit’s product slate, but also cause catalyst fluidization problem in the reactor-regenerator system when situation is serious and further jeopardize unit’s stable operation. Therefore, iron poisoning should be paid high attention.

(a) Under catalytic cracking condition, catalyst with high iron poisoning level has large quantities of nodules on the surface due to exothermic reaction. E-cats with rough surface collide with each other and generate large quantity of fines that jeopardize FCC unit’s stable operation.

(b) After catalyst iron poisoning, a layer of dense material is formed on the surface of catalyst. This layer blocks feedstock molecules’ diffusion to catalysts’ inner pores, which leads to significant decrease on gasoline yield and great increase on dry gas and coke’s yields. Research shows that when E-cat’s iron poisoning level is above 8000 μg/g, catalysts’ reacting performance would dramatically degenerate.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgment

The authors thank the Ministry of Science and Technology Management of PetroChina for providing financial support.

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Experimental Assessment of Water Sprays Utilization for Controlling Hydrogen Sulfide Releases in Confined Space

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Received 13 March 2015; Accepted 26 May 2015

Academic Editor: Ziyang Huo

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This paper reported the utilization of water spray for controlling H$_2$S release in a confined space, which is especially important in industry. A typical spray tower was modified to simulate the confined space for people's enterable routine operation (e.g., pump room), in which the dilution capacity of water sprays can also be evaluated. This work consists of two parts: the first part focuses on the influences of different operating conditions on chemical dilution capacities of water sprays in mechanisms; the second one is comparison between two nozzle configurations for evaluating their feasibilities of practical application. Water sprays express eligible performance for H$_2$S release control even though their dilution capacity was weakened at high gaseous concentrations and rates of releases. The presence of Na$_2$CO$_3$ can significantly improve absorption effectiveness of H$_2$S in water and the optimal Na$_2$CO$_3$ additive was found to be 1.0 g L$^{-1}$ in this test. Compared with Na$_2$CO$_3$, adjusting water flow rate may be an effective strategy in enhancing dilution capacity of water sprays due to the fact that larger flow rate led to both less dilution time ($T_D$) and dilution concentration ($C_D$). Furthermore, multinozzle configuration is more efficient than single-nozzle configuration under the same water consumption.

1. Introduction

A variety of factory employees are killed or seriously injured each year in confined space due to accidental releases of hydrogen sulfide (H$_2$S). A small limited space which receives minimal ventilation is conducive to the accumulation of hazardous gases and can constitute serious detriments to laborers once the accident occurred. An example is the pump room of wastewater treatment plant (WWTP), in which the emissions of H$_2$S commonly occur because of pipelines corrosion and irregular operation. The consequences will be disastrous especially when a high concentration gaseous release of H$_2$S takes place. It is known that inhalation of H$_2$S higher than 1000 ppm can cause an instantaneous death after a few breaths. Although worker security in process areas has been extensively improved with installation of toxic gas monitors (e.g., E-nose system) [1, 2], further studies in the development of reliable mitigation devices are still necessary. So far, however, the effective resolutions for controlling accidental release of H$_2$S in confined space remain deficient.

Although the dispersion of hazardous clouds can be controlled by a lot of techniques such as thermal inactivation, fans, and specific foams, they are technically and economically unviable for utilization in the confined space [3, 4]. Water spray, by contrast, is suitable for both of the confined and unconfined spaces.

The dilution/dispersion capacity of water sprays has been studied for many years [5–9]. It can improve the dilution/dispersion rate of these hazardous components in air, by means of the subsequent mechanisms (containment action, diluting action, and physical and chemical absorption) [5, 10]. In general, two kinds of technical solutions can be selected for dealing with different nature of gases. One is the use of fresh water sprays for water-soluble gases, such as ammonia (NH$_3$) and hydrogen fluoride (HF); the other one is the use of doped water sprays with alkaline additives for less-soluble gases, such as H$_2$S and chlorine (Cl$_2$). The second solution has not always been studied with regard to the water and soil contamination involved [11]. Nevertheless, the use of the first solution on mitigation of Cl$_2$ has been...
proved to be inefficient without chemical additives [12]. As for H\textsubscript{2}S, it is more difficult to dissolve in water than Cl\textsubscript{2}. Hence, the use of alkaline additives is imperative to promote the mass transfer from the gaseous phase to the liquid one [13]. Various alkalis (e.g., sodium hydroxide (NaOH), sodium hypochlorite (NaOCl), sodium carbonate (Na\textsubscript{2}CO\textsubscript{3}), and sodium bicarbonate (NaHCO\textsubscript{3})) are able to remove H\textsubscript{2}S after having been added in the liquid phase. The most frequently used is Na\textsubscript{2}CO\textsubscript{3} due to low cost, ecofriendliness, efficiency, weak corrosion, and irritation to the skin.

Herein, systematic tests were carried out to assess the dilution capacity of water sprays utilization for mitigating H\textsubscript{2}S releases occurring in a confined space. Both dilution time ($T_D$) and dilution concentration ($C_D$) were proposed as the measurement of water spray effectiveness. The first part of this paper is to investigate the influences of different experimental parameters on the dilution capacity. The second part illustrates the improving dilution capacity of water sprays by using multinozzle configurations.

2. Experimental Sections

2.1 Modified Spray Tower. A classic spray tower was modified to evaluate the applicability of water sprays for controlling H\textsubscript{2}S releases in a confined space. This device was comprised of a column cavity equipped with water supply and water spray nozzles, as well as the H\textsubscript{2}S source and gas detectors, as illustrated in Figure 1(a).

2.1.1. Column. The forced dispersion of H\textsubscript{2}S was carried out in the Plexiglas column with internal diameter of 0.6 m, height of 1.5 m, and wall thickness of 15 mm against H\textsubscript{2}S corrosion. Besides the gas-liquid space, the column also afforded the locations for H\textsubscript{2}S release, spray nozzles, and gas detection.

2.1.2. H\textsubscript{2}S Source. The integration of cylinder of H\textsubscript{2}S (0.49%, 10 bars) and cylinder of compressed air (10 bars) can achieve a steady gaseous release and was employed as H\textsubscript{2}S source. The mixed H\textsubscript{2}S gas was eventually released into the column through the stainless steel tube located at the height of 10 cm above the bottom. In addition, a cover was used to prevent droplets from falling into the intake tube (Figure 1(b)). The steady releases were inspected by means of the dynamic multiple gases distributing system (DMGDS, MF-5B, China), which endowed a good repeatability of gas flow rate ($\geq$95.5%) and a small relative error of gas concentration ($\leq$1.5%).

2.1.3. Water Supply and Water Spray Nozzles. The downward spray nozzles were fixed at the top of the column. As shown in Figure 1(c), four nozzles were situated symmetrically around the central one. Na\textsubscript{2}CO\textsubscript{3} solution was stored in the tank and transported into the spray nozzles through the magnetic pump (CQB15-10-85F, China). Water flow rates were measured by a turbine flow meter (LWGYS-C, China).

During the tests, a number of full cones (QDBB, China) were used to create two nozzle configurations. One involves the simultaneous use of a set of four same surrounding nozzles and the other one contains a single central nozzle. All these special spray nozzles were mainly characterized by flow rates and angles (Table 1). The water flow rate represented

![Figure 1: Schematic diagram showing the experimental setup: (a) overall layout; (b) gas inlet; (c) top layout.](image-url)
the water consumption of spray nozzles, and the nozzle angle determined the coverage area of droplets.

2.1.4. Gas Detection. A circular measurement network with the H$_2$S leaking point (a stainless steel pipe) at the center of the circle was used throughout the tests. Four gas sampling points were symmetrically distributed on the wall of column at a height of 0.4 m above the bottom to establish the dilution capacity on four transects running different directions from the leaking point. Instead of the respiration, diluted H$_2$S was pumped at $2.5 \times 10^{-5}$ m$^{-3}$s$^{-1}$ into the flexible pipe connected with a H$_2$S analyzer (MultiCheck 2000, America). This analyzer can meet the requirements of evaluation with a measurement accuracy of ±0.1 ppm reading in the range of 0 to 500 ppm.

2.1.5. Exhaust System. The column needed to be cleaned up at the end of each test, with the exhaust system including an air compressor and gas absorber. With the help of air compressor (Dynair, DA7001, China), retained H$_2$S was blown into an alkali liquor-filled absorber through the gas outlet on the top of column (Figure 1(c)).

2.2. Procedure. The principal of the lab-scale tests conducted was to release H$_2$S into a confined space and to measure the reduction of concentration with water spray operating. More details were shown below. Firstly, a natural release without water sprays operation was passed into the column. Secondly, the water supply system was started once the H$_2$S concentration in sampling points exceeded 10 ppm (the National Institute for Occupational Safety and Health (NIOSH) recommended a permissible exposure limit of H$_2$S of 10 ppm at the workplace). During the processes of spraying, the H$_2$S concentration was recorded at intervals of 10 seconds. Thirdly, when H$_2$S concentrations decreased to a steady level, the gas inlet and water supply system should be turned off sequentially. It was also worth noting that each test consisted of a natural release and a forced dispersion with water sprays needed to last for approximately 2 minutes. Finally, remains of H$_2$S in column should be removed with the exhaust system at the end of each test so as to continue the next one.

### Table 1: Spray nozzles main characteristics.

| Spray nozzle configurations | Spray pattern | Water flow rate per nozzle ($\times 10^{-5}$ m$^{-3}$s$^{-1}$) | Spray angle (°) |
|----------------------------|--------------|----------------------------------------------------------|----------------|
| One-nozzle set             |              | 0.83                                                     | 30             |
|                            |              | 1.6                                                      | 30             |
|                            |              | 3.3                                                      | 30             |
|                            |              | 5.0                                                      | 30             |
|                            |              | 6.7                                                      | 30             |
| Four-nozzle set            |              | 1.6                                                      | 15             |
|                            |              | 3.3                                                      | 15             |
|                            |              | 6.7                                                      | 15             |

2.3. Results and Discussion

3.1. The Assessment of Dilution Capacity of Water Sprays. Many previous assessment methods include dilution ratio (DR), forced dispersion coefficient (FD), and mitigation factor (DF), which were almost defined as the ratio of the free dispersion gas concentration to the concentration in presence of spraying [3, 5, 7]. These approaches, nevertheless, were limited to the open field instead of enclosed spaces considering an expansive spatial scale for detection. Given this, dilution time ($T_D$) and dilution concentration ($C_D$) were used to assess the effectiveness of downward water sprays in a confined space, as interpreted in Figure 2.

According to concentration variations, the forced dispersion of H$_2$S release with water spray can be divided into two stages. The initial unsteady stage, fast dilution stage (DS), was symbolized by the violent fluctuation of H$_2$S concentration after first contact with droplets. Then the H$_2$S concentration was constant down to a transitional point. We defined it as critical concentration ($C_C$), where there were no more obvious changes on the variation of H$_2$S concentration ($\Delta C \leq 0.1$ ppm). In the second stage, constant DS, the relatively stable H$_2$S concentration occurred until the absorption balance was ultimately achieved. Therefore, dilution time ($T_D$) can be considered as the duration of the first stage, for the evaluation of dilution rate of water sprays. Since the concentrations variations in constant DS were minimal, it is fine to choose the concentration at 120 seconds as the dilution concentration ($C_D$), which can well demonstrate the absorption effectiveness of water spray. Moreover, Figure 2 also depicts the evolution of H$_2$S concentration in four orthogonal directions of the same horizontal level. The result reveals the homogeneous dispersion of gas without disturbance (e.g., wind), so measurement of H$_2$S concentration in any sampling points was of conformity.
3.2. The Influences of Different Parameters on the Dilution Capacity of Water Sprays. Basically, the dilution capacity of water spray depends on its own characteristics (water flow rates, the alkali concentration, etc.); extrinsic parameters include gas nature (concentration) and gas release rates. To analyze the influences of these parameters on the dilution effectiveness of water spray, a series of tests with one-nozzle configuration were performed. The experimental conditions were listed in Table 2.

| Inlet H₂S concentrations $C_{H₂S}$ (ppm) | Operation conditions | Na₂CO₃ concentrations $C_{Na₂CO₃}$ (g L⁻¹) | Water flow rates $Q_L$ (m³·s⁻¹) |
|----------------------------------------|----------------------|-----------------------------------------------|-------------------------------|
| Test (a) 1000–5000                   | $5 \times 10^{-5}$   | 1.2                                           | $5 \times 10^{-5}$             |
| Test (b) 3000                        | $5 \times 10^{-5}$–$1.7 \times 10^{-5}$ | 1.2                                           | $6.7 \times 10^{-5}$           |
| Test (c) 3000                        | $8.3 \times 10^{-5}$ | 0–1.2                                         | $6.7 \times 10^{-5}$           |
| Test (d) 3000                        | $6.7 \times 10^{-5}$ | 1.0                                           | $0.8 \times 10^{-7}$–$6.7 \times 10^{-5}$ |

3.2.1. Dilution Time of Water Spray Tested. Figure 3 presents the variation of dilution time ($T_D$) of water spray for different experimental conditions. Remarkably, $T_D$ increased with the inlet H₂S configuration ($C_{H₂S}$) and gas release rate ($Q_G$) (Figures 3(a) and 3(b)), while it decreased with the increase of water flow rate ($Q_L$) and did not seem to rely on the Na₂CO₃ concentration ($C_{Na₂CO₃}$) (Figures 3(c) and 3(d)). The most reasonable explanation for these differences of $T_D$ was that the falling droplets induced a violent air flow by acting on their dispersion [5]. In the processes of spraying, the horizontal movement of gas molecule was weakened but vertical movement was strengthened at the same time. Thus this effect could effectively prevent the H₂S diffusion to the outside of the “capture zone,” as well as enhancing the opportunities of gas-liquid mass transfer. Virtually, the measurement of air flow commonly used was the Reynolds number (Re), which was defined as the ratio of inertial forces ($f$) to viscous forces ($τ$) [14]. In the current work, the true value of Re was difficult to determine with interference of the fast droplets, but the trends of Re still could be deduced by the following equations:

$$f = udρ,$$  \hspace{1cm} (1)

$$τ = μd,$$ \hspace{1cm} (2)

$$Re = \frac{f}{τ} = \frac{dud}{μ},$$  \hspace{1cm} (3)

where $f$ is the inertial forces of gas flow, $τ$ is the viscous forces of gas flow, $u$ is the gas velocity, $ρ$ is the density of H₂S gas, $μ$ is the viscosity of H₂S gas, and $d$ is the diameter of column.

When $C_{H₂S}$ increased, according to (3), Re increased with the combined action of an increase of the gas density since $ρ_{H₂S}$ (1.385 Kg·m⁻³) > $ρ_{Air}$ (1.169 Kg·m⁻³) and a decrease of the gas viscosity since $μ_{H₂S}$ (1.239 Pa-s) < $μ_{Air}$ (1.845 Pa-s). And also, Re increased with $Q_G$ ( $u$ on account of (3)). Severe turbulence could reasonably result in decreasing of $T_D$; however, $T_D$ extended as we can see in Figures 3(a) and 3(b). It was ascribed to significant enhancement of gas diffusion caused by increasing H₂S within confined space, and often this enhancement in field test was easy to be counteracted by unstable atmosphere (e.g., wind). Consequently, the indoor toxic gas releases are more jeopardous for workers than those occurring outdoors. When $C_{Na₂CO₃}$ increased, a decrease of $T_D$ can be observed in Figure 3(c). The effect of Re can be ruled out since it was $C_{Na₂CO₃}$ independent based on (3). Thereby the result arose from the enhancement of absorption in water with the increase of $C_{Na₂CO₃}$. It seemed that the action was very slight to the reduction of $T_D$ (about 10 seconds), but the mitigation was inefficient without the presence of Na₂CO₃. It could be confirmed by the fact of water curve in Figure 3(c) that the H₂S concentration decreased rapidly in the first 60 seconds and then increased again. When $Q_L$ increased, $T_D$ decreased distinctly (Figure 3(d)). The reason was that strengthening gas-liquid collision acted by falling droplets improved the interference of the air flow resulting in the increase of Re.

3.2.2. Absorption Effectiveness. In addition to the dilution time ($T_D$), Figure 3 indicates the variation of absorption effectiveness of water sprays for different experimental conditions as well. Although the change of dilution concentration ($C_D$) was analogous to the variation of $T_D$, the driving force was very different. The gas-liquid mass transfer accompanied with neutralization led to the persistent and efficacious absorption in water. In this study, the volume mass transfer coefficient ($k_{g,a}$ or $k_{d,a}$) was used to characterize the gas-liquid mass transfer and to interpret the change of $C_D$. To date, most of the previous works put their emphasis on dealing with mass transfer coefficient in spray towers. Turpin et al. [15, 16], Javed et al. [17], Codolo et al. [18, 19], Yeh and Rochelle [20], Dimiccoli et al. [21], Tanda et al. [22], Ma et al. [23], and Zeng et al. [24] had experimentally determined mass transfer coefficients and founded empirical correlations. According to these literatures, the mass transfer coefficient in our work can be calculated by the following relation:

$$\frac{1}{K_g} = \frac{1}{k_g} + \frac{1}{EHk_i},$$  \hspace{1cm} (4)
Figure 3: The influences of different parameters on the dilution capacity of water sprays: (a) \( \text{H}_2\text{S} \) concentration; (b) gas release rates; (c) \( \text{Na}_2\text{CO}_3 \) concentrations; (d) water flow rates.

In the experiment, the neutralization between \( \text{H}_2\text{S} \) and \( \text{Na}_2\text{CO}_3 \) was rapid and it was considered to be pseudo-first-order. Thus the overall mass transfer coefficient can be described in terms of individual mass transfer coefficients. Based on the two-film theory, considering that there is an excess of \( \text{Na}_2\text{CO}_3 \) concentration, the reactant in the liquid film does not decrease throughout the spraying process. Although \( \text{H}_2\text{S} \) is sparingly soluble, a fast chemical reaction consisted of an enhancement factor \( (E) \) promoting the solubility coefficient \( (H) \) of \( \text{H}_2\text{S} \) in water [15]. In this case, the mass transfer rate is controlled by the gas phase resistance, and the liquid phase resistance can be ignored, so

\[
K_g \approx k_g. \tag{5}
\]

According to Codolo et al. [19], the gas phase volumetric mass transfer coefficient \( (k_ga) \) can be calculated by equation:

\[
k_ga = \frac{Q_G}{A h R T} \ln \left( \frac{C_{\text{H}_2\text{S},I}}{C_{\text{H}_2\text{S},D}} \right), \tag{6}
\]

where \( a \) is the volumetric interfacial area, \( Q_G \) is the gas flow rate, \( A \) is the area of the column, \( h \) is the distance between sampling ports and the bottom of column, \( R \) is the universal gas constant, \( T \) is the temperature (25°C), \( C_{\text{H}_2\text{S},I} \) is the inlet concentration of \( \text{H}_2\text{S} \), and \( C_{\text{H}_2\text{S},D} \) is the dilution concentration of \( \text{H}_2\text{S} \) measured in 120 seconds.

Figure 4 illustrates the variations of \( k_ga \) for \( \text{H}_2\text{S} \) absorption under different experimental conditions. As seen, \( k_ga \)
increased in all of the four tests. It is well known that an increase of $k_g \alpha$ was conducive to the H$_2$S absorption and the reduction of $C_D$, but it was reversed with the results in Figures 4(a) and 4(b). This was because an improvement of $k_g \alpha$ was implemented by increasing the numbers of H$_2$S molecules, and the interpretation could be demonstrated with the formula of H$_2$S removal efficiency proposed by Turpin et al. [15]. It revealed that H$_2$S absorption effectiveness was inversely proportional to $C_{H_2S}$ and $Q_G$ although $k_g \alpha$ increased with gaseous concentrations and gas release rates.

On the other side, the results of $k_g \alpha$ in Figures 4(c) and 4(d) show a good coincidence with absorption effectiveness. Indeed, when $C_{Na_2CO_3}$ increased, more Na$_2$CO$_3$ molecules diffused into the gas-liquid interface, liquid phase mass transfer resistance ($1/EHk_l$) decreased, and so $k_g \alpha$ was improved. When $Q_L$ increased, the larger numbers of droplets available for the transfer led to the increase of $k_g \alpha$. Evidently, these two actions both promoted H$_2$S absorption while keeping H$_2$S releases constant.

Combined with Sections 3.2.1 and 3.2.2, it is easily observed that water sprays express eligible performance for H$_2$S release control even though their dilution capacity was weakened at high gaseous concentrations and rates of releases. The presence of Na$_2$CO$_3$ can significantly improve the absorption of H$_2$S in water with only decreasing $C_D$ and the optimal Na$_2$CO$_3$ additive was found to be 1.0 g L$^{-1}$ in this test. Compared with Na$_2$CO$_3$, adjusting water flow rate may be an effective strategy in enhancing dilution capacity of water sprays due to the fact that larger flow rate led to both less $T_D$ and $C_D$. Perceptibly, unlike a small scope of $C_D$ between 1.4 and 4.5 ppm, $T_D$ varied at a broad range of 50 to 90 seconds. This illustrates that internal and extrinsic parameters had more profound impact on the dilution rate than the absorption effectiveness of water sprays, suggesting that the movement of air flow played a significant role in the dispersion of gas releases. As a result, a promising future can be expected with intensive studies on the reduction of dilution rate.

3.3 The Improvement of Using Multinozzle Configuration for the Dilution Capacity of Water Sprays. As mentioned

![Figure 4: The influences of different parameters on $k_g \alpha$: (a) H$_2$S concentration; (b) gas release rates; (c) Na$_2$CO$_3$ concentrations; (d) water flow rates.](image-url)
above, increasing the water flow rate was the most effective migration pathway for the accidental releases of H$_2$S gas. Unfortunately, as more water is reserved and consumed, the cost-per-use of water spray would rise during use. To reduce the water consumption without undermining the dilution capacity, some tests with comparisons between one-nozzle set and four-nozzle set were performed in case of the same total water consumption. Simultaneously, different opening angles were produced to keep the similar coverage area of the volume in the column by droplets, as illustrated in Figure 5; the advantage of this design was able to eliminate the wall effects in gas detection.

Figure 6 compares the dilution capacity of water sprays using two spray nozzle configurations. It can be observed that, in light of $T_D$ and $C_D$, the effectiveness of using four-nozzle set was better in the water flow rate range of $1.6-6.7 \times 10^{-5}$ m$^3$ s$^{-1}$. This can be explained by the different droplet sizes dependent on the nozzles. In the processes of spraying, the droplets provided affluent interfacial area through which the gas-liquid mass transfer took place [15]. Because of breakup and coalescence mechanisms, the droplets generated by a given nozzle do not have the same size after their formation but at best belong to the same range of sizes. Previous studies [16, 21] have demonstrated the distribution of droplet size was Gaussian, and it was narrower with nozzles which had a smaller orifice diameter. As for spray nozzles, their orifice diameters are always special and must be matched with $Q_L$ [18]. For a fixed liquid flow rate, when four small nozzles were used together, the size of droplet became smaller with the increasing number of droplets, and so the exchange area available for the gas-liquid transfer got bigger. The increasing number of droplets did not only enhance the air flow, but also improve the gas-liquid mass transfer. In fact, the use of multinozzle set did very well both in water consumption and in performance improvement. Moreover, this means could also significantly reduce the impact of using alkaline additive on the earth’s surface.

4. Conclusions

This study demonstrated that accidental releases of hazardous H$_2$S gas can be well controlled by utilizing water sprays with the presence of alkaline additives. Water sprays express eligible performance for H$_2$S release control even though their dilution capacity was weakened at high gaseous concentrations and rates of releases. The presence of Na$_2$CO$_3$ can significantly improve the absorption of H$_2$S in water and the optimal Na$_2$CO$_3$ additive was found to be 1.0 g L$^{-1}$. Adjusting water flow rates is preferable to enhance dilution capacity of water sprays because of the fact that larger flow rate led to both less $T_D$ and $C_D$. Furthermore, the dilution rate or $T_D$ is more greatly impacted by internal and extrinsic condition, implying that strengthening the interference of air flow was a preferable strategy in the dispersion of gas releases. For the nozzle configurations test, the results illustrated using multinozzle set poses advantages in the water conservation and the improvement of dilution capacity. This study, to some extent, fills the gap of reducing the hazard caused by releases of H$_2$S that few researches have focused on previously.

Nomenclature

Roman Symbols

$A$: Area of the spray tower (m$^2$)

$a$: Volumetric interfacial area (m$^2$ m$^{-3}$)
\[ C_{H_2S}: \quad \text{H}_2\text{S concentration (mol-m}^{-3}\text{)} \]
\[ C_{Na_2CO_3}: \quad \text{Na}_2\text{CO}_3 \text{ concentration (g-L}^{-1}\text{)} \]
\[ d: \quad \text{Diameter of column (m)} \]
\[ E: \quad \text{Enhancement factor (–)} \]
\[ f: \quad \text{Inertial forces of gas flow (Kg-s}^{-1}\text{-m}^{-3}\text{)} \]
\[ H: \quad \text{Solubility coefficient (mol-m}^{-3}\text{-kPa}^{-1}\text{)} \]
\[ h: \quad \text{Height of sampling ports (m)} \]
\[ K_g: \quad \text{Overall gas-side mass transfer coefficient (kmol-m}^{-2}\text{-s}^{-1}\text{-atm}^{-1}\text{)} \]
\[ k_g: \quad \text{Gas phase mass transfer coefficient (kmol-m}^{-2}\text{-s}^{-1}\text{-atm}^{-1}\text{)} \]
\[ k_{g,a}: \quad \text{Gas phase volumetric mass transfer coefficient (kmol-m}^{-3}\text{-s}^{-1}\text{-atm}^{-1}\text{)} \]
\[ k_l: \quad \text{Liquid phase mass transfer coefficient (m-s}^{-1}\text{)} \]
\[ Q_G: \quad \text{Release flow rate (m}^3\text{-s}^{-1}\text{)} \]
\[ Q_L: \quad \text{Water flow rate (m}^3\text{-s}^{-1}\text{)} \]
\[ R: \quad \text{Universal gas constant (m}^3\text{-atm-kmol}^{-1}\text{-K}^{-1}\text{)} \]
\[ Re: \quad \text{Reynolds number (–)} \]
\[ T: \quad \text{Temperature (K)} \]
\[ u: \quad \text{Gas velocity (m-s}^{-1}\text{)} \]

Greek Symbols

\[ \tau: \quad \text{Viscous forces of gas flow (Pa)} \]
\[ \rho: \quad \text{Gas density (Kg-m}^{-3}\text{)} \]
\[ \mu: \quad \text{Gas viscosity (Pa-s)} \]

Subscript

\[ I: \quad \text{Inlet} \]
\[ D: \quad \text{Dilution} \]

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgments

The authors gratefully acknowledge the financial support of the National Key Technology R&D Program (2008BAB37B04) and the Fundamental Research Funds for the Central Universities (24720122043).

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Research Article

Influence of OH\(^-\) Ion Concentration on the Surface Morphology of ZnO-SiO\(_2\) Nanostructure

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Received 23 July 2015; Revised 2 September 2015; Accepted 3 September 2015

Academic Editor: Yuxin Zhao

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The influence of varying OH\(^-\) ion concentration on the surface morphology of chemically deposited ZnO-SiO\(_2\) nanostructures on glass substrate was investigated. The morphological features, phase structure, and infrared characteristics were examined by scanning electron microscopy (SEM), X-ray diffraction (XRD), and Fourier transform infrared spectroscopy (FTIR), respectively. Results revealed that silica significantly changes the hexagonal morphology of bare ZnO rod to "pointed tips" when using low initial OH\(^-\) precursor concentration. Increasing OH\(^-\) ion concentration resulted in a "flower-like" formation of ZnO-SiO\(_2\) and a remarkable change from "pointed tips" to "hemispherical tips" at the top surface of the rods. The surface capping of SiO\(_2\) to ZnO leads to the formation of these "hemispherical tips." The infrared spectroscopic analysis showed the characteristics peaks of ZnO and SiO\(_2\) as well as the Si-O-Zn band which confirms the formation of ZnO-SiO\(_2\). Phase analysis manifested that the formed ZnO-SiO\(_2\) is of wurtzite structure. Furthermore, a possible growth mechanism is proposed based on the obtained results.

1. Introduction

Zinc oxide (ZnO) is a widely known \(n\)-type semiconductor that attracted research interest due to its properties like wide energy band gap of 3.37 eV and high exciton binding energy of 60 meV [1] which makes it suitable for many applications like in solar cells [2], photodetectors [3], and gas sensors [4]. Another interesting aspect of ZnO growth is its ability to be engineered to different structural features by changing some parameters during synthesis. Tailoring the morphology, shape, and size of ZnO could be a way of expanding its potential especially in solar cell and sensor technologies where reaction at the surface is very crucial. Works have been reported for controlling size and shape of ZnO nanostructures like varying the initial zinc and hydroxyl ion concentrations [5, 6] and also by introducing silica (SiO\(_2\)) to ZnO as a concept of composite material [7, 8]. With good mechanical resistance and high dielectric strength, SiO\(_2\) is likely to be an ideal component to enhance the properties of ZnO. ZnO-SiO\(_2\) is seen to have significant potential application as an antibacterial coating [9], luminescent material [10, 11], photocatalyst [12], and also as gas sensor [13] because of the good sensing capability of ZnO which could be enhanced more with the presence of SiO\(_2\) for size and shape control that could lead to better chemical activity at the surface. However, understanding the mechanism for the growth of ZnO-SiO\(_2\) nanostructures is still a formidable task particularly on controlling its surface morphology. Aside from these, most works related to ZnO synthesis use complex processes and sophisticated equipment like PLD [14], CVD [15, 16], and vapor phase transport process [17–19] among others which is not practical and economical in nature.

Recently, we reported preliminary investigations on the synthesis of ZnO-SiO\(_2\) both in powder form [20] and deposited on glass substrates [21] by using simple wet chemical deposition process. It is also worth mentioning that the SiO\(_2\) from rice husk ash, a naturally occurring material, was used as an alternative to the expensive liquid tetraethyl orthosilicate (TEOS). We found out that SiO\(_2\) modifies the surface of ZnO from hexagonal into pointed tips.
and confirms the attachment of SiO$_2$ to ZnO through FTIR spectroscopy. In this current contribution, the influence of initial OH$^-$ ion concentration on the surface morphology of ZnO-SiO$_2$ is presented. Moreover, a proposed mechanism for the growth of ZnO-SiO$_2$ on glass substrates is also presented based on the evolution of morphology of ZnO-SiO$_2$ with varying initial OH$^-$ ion concentration. Results of this work would pave the way for the control of the morphology of the nanostructures and for its possible use as methane gas detector.

2. Experimental Procedure

2.1. Wet Chemical Deposition Process. ZnO-SiO$_2$ nanostructures were synthesized through low temperature chemical deposition process using zinc sulphate (ZnSO$_4$) and ammonium hydroxide (NH$_4$OH). First, 0.03 M ZnSO$_4$ aqueous solution and varied ammonium hydroxide (NH$_4$OH) concentrations (1.0 M, 2.0 M, and 3.0 M) were prepared separately in a beaker. The ammonium hydroxide was then added dropwise to the ZnSO$_4$ solution and magnetically stirred while subsequently placing the precleaned glass substrates. After 30 minutes’ stirring of the mixed precursors, 0.1 grams of laboratory (in-house) prepared amorphous silica powder was then added and then the solution was continuously stirred for 3 hours while maintaining the bath temperature at 70°C. After 3 hours of constant stirring and heating, the substrates were washed with distilled water in order to remove loosely attached residues present and were allowed to dry at ambient room temperature. Table 1 shows the parameters considered for the synthesis of ZnO-SiO$_2$ where fixed concentration of ZnSO$_4$ was used at varying NH$_4$OH concentrations. The amount of amorphous silica powder used was the same for all samples.

| Sample | ZnSO$_4$ concentration | NH$_4$OH concentration | SiO$_2$ |
|--------|------------------------|-------------------------|--------|
| 1      | 0.03 M                 | 1.0 M                   | 0.1 grams |
| 2      | 0.03 M                 | 2.0 M                   | 0.1 grams |
| 3      | 0.03 M                 | 3.0 M                   | 0.1 grams |

2.2. Characterization of Materials. The morphological characteristics of the samples were studied using JEOL JSM-6510LA analytical scanning electron microscope at low and high magnifications. Functional groups were determined by using Perkin Elmer Spectrum 100 infrared spectrometer from 4000 to 650 cm$^{-1}$ over 32 scans with 4 cm$^{-1}$ spectral resolution. Phase analysis of the samples was studied by X-ray diffraction analysis using Shimadzu XRD-7000 diffractometer from 5 to 40° (2θ) with step scanning mode of 0.02° (2θ).

3. Chemistry of Precursors for the Synthesis of ZnO-SiO$_2$

To understand the mechanism for the deposition of ZnO-SiO$_2$, it is better to look first on the growth of ZnO prior to addition of SiO$_2$. The reaction between zinc sulfate and ammonium hydroxide upon dissociation in aqueous solution results in the formation of Zn(OH)$_2$ which acts as seed nuclei for the growth of ZnO. The reaction is expressed in

$$\text{ZnSO}_4 + 2\text{NH}_4\text{OH} \rightarrow \text{Zn(OH)}_2 + (\text{NH}_4)_2\text{(SO)}_4 \quad (1)$$

The formation of Zn(OH)$_2$ induces rapid nucleation and further addition of ammonia dissolves the solid Zn(OH)$_2$ to form ammonium-zincate bath shown in

$$\text{Zn(OH)}_2(s) + 4\text{NH}_4\text{OH}(aq) \rightarrow (\text{NH}_4)_2\text{ZnO}_2(aq) + 2\text{H}_2\text{O}(aq) \quad (2)$$

On further reaction with water in the active solution during deposition, ZnO forms according to this chemical reaction:

$$(\text{NH}_4)_2\text{ZnO}_2(s) + \text{H}_2\text{O}(aq) \rightarrow \text{ZnO}(s) + \text{NH}_4\text{OH}(aq) \quad (3)$$

Upon addition of SiO$_2$ to the solution, the silica particles in the solution might interact with the OH$^-$ group of Zn(OH)$_2$ because the surface of silica is composed of functional groups, namely, siloxane (Si-O-Si) bridges and silanol groups (Si-OH) where the OH$^-$ group acts as the center of adsorption. Thus, a competition of attraction to OH-group of the Zn(OH)$_2$ seed nuclei between silica and the formation of ZnO is possible to happen.

4. Results and Discussions

4.1. Characteristics of ZnO-SiO$_2$. Using 1.0 M NH$_4$OH. To show that indeed ZnO-SiO$_2$ can be synthesized using silica from rice husk ash via chemical deposition process, a figure of bare ZnO is presented first to have an idea on what would be the effect of SiO$_2$ on ZnO. Figure 1(a) presents a typical micrograph of ZnO grown on glass substrate. It was observed that dense and well-defined hexagonal nanorods were present and preferentially grow perpendicular to the glass substrate, though some were tilted. The hexagonal feature of the micrograph is a characteristic of a wurtzite structure which is the more stable phase of synthetic ZnO. Figure 1(b) meanwhile shows the corresponding IR spectra of bare ZnO. The peaks observed at 779 cm$^{-1}$ and 3279 cm$^{-1}$ are attributed to the stretching mode and hydroxyl group of ZnO, respectively [22]. On the other hand, Figure 2 shows the micrograph of amorphous SiO$_2$ and its FTIR data. It can be seen in Figure 2(a) that the SiO$_2$ particles were agglomerated and were found to have micron size (>3 μm). Additionally, Figure 2(b) presents the characteristic infrared spectra of amorphous SiO$_2$. Peak observed at 474 cm$^{-1}$ is for the bending vibration of Si-O-Si bond while 804 and 1098 cm$^{-1}$ are the vibrational bonds of Si-O. The peak at 3470 cm$^{-1}$ is for both the Si-OH and the O-H vibration of physically adsorbed water [23].

Figure 3 on the other hand shows the micrographs using the same concentration of precursors as in Figure 1 but added with amorphous SiO$_2$ powder grown also on glass substrates. It can be observed that the micrographs have uniform growth of dense ZnO rods. The surface morphology...
shows the preferential growth at $c$-axis having pointed tips of approximately 250 nm in average diameter and 2 $\mu$m in average length which is far different compared to the morphology of bare ZnO. The modification at the surface of ZnO from hexagonal to pointed tips is due to the presence of SiO$_2$ where it attaches to the nonpolar facets of ZnO which hinders the formation of hexagonal structure at its metastable facet. To maintain a much stable structure, the polar facets of ZnO may undergo surface reconstruction during the chemical deposition process resulting in the pointed tips of ZnO rods. Using low OH$^-$ ion concentration enables the growth of the mostly $c$-axis oriented ZnO-SiO$_2$ rods. This
growth habit is due to the higher growth rate along the (0001) plane compared to other growth faces of ZnO.

To confirm ZnO-SiO$_2$ formation, the infrared spectrum of ZnO-SiO$_2$ using 1.0 M NH$_4$OH is shown in Figure 4. Characteristic peak at 746 cm$^{-1}$ indicates the presence of ZnO [22]. The peaks at 832 cm$^{-1}$ and 888 cm$^{-1}$ are for the Si-O-Si asymmetric stretching vibrations while peak at 1063 cm$^{-1}$ is for the Si-O-Si symmetric stretching. Peaks observed at 1500 cm$^{-1}$ and 1553 cm$^{-1}$ are for the Si-OH stretching vibration and the peak at 1393 cm$^{-1}$ is for the Si-O-Si bending. All of these characteristic peaks indicate the presence of the functional groups of amorphous silica from RHA. Furthermore, peak at 1600 cm$^{-1}$ and a broad absorption band situated at 3000 cm$^{-1}$ to 3600 cm$^{-1}$ are attributed to the O-H bending and O-H stretching vibrations of ZnO-SiO$_2$, respectively, which reveals the presence of physically adsorbed water. Moreover, the peak at 1045 cm$^{-1}$ is assigned for the Si-O-Zn stretching which confirms the formation of ZnO-SiO$_2$ [24, 25].

4.2. Characteristics of ZnO-SiO$_2$ Using Higher NH$_4$OH Concentration. Increasing the ammonium hydroxide concentration resulted into much larger diameter but shorter rods. Flower-like formation and apparent change from pointed tips to hemispherical tips on the surface of the structures were observed as shown in Figure 5 for ZnO-SiO$_2$ deposited on glass substrate using 2.0 M NH$_4$OH. On the other hand, Figure 6 shows the micrographs of ZnO-SiO$_2$ using 3.0 M NH$_4$OH where much shorter (~0.850 μm) rods are present together with flake-like structures. The formation of flower-like structures using high NH$_4$OH concentration was due to the sufficient amount of OH$^-$ which was necessary for the nucleation and subsequently growth of anisotropic ZnO-SiO$_2$. The amorphous silica added to the ammonium-zincate bath solution causes the formation of hemispherical tips of the flower-like structures and is also the reason for having shorter and thicker rods. It is believed that, in higher OH$^-$ ion concentration, the SiO$_2$ capped the surface of ZnO rods leading to the formation of these hemispherical tips. This is due to enough OH$^-$ ions that interact with the silanol group of silica in the solution. The notable flakes observed in Figure 6 (encircled) are associated with the excess OH$^-$ ions and may form Zn complexes.

Figure 7 shows the infrared spectra of the chemically deposited ZnO-SiO$_2$ nanostructures prepared using high OH$^-$ ion concentration together with the spectra of ZnO-SiO$_2$ prepared using 1.0 M NH$_4$OH for comparison. It was observed that intensity of the peaks at 1500 cm$^{-1}$ and 1553 cm$^{-1}$ attributed to the Si-OH (silanol) stretches of silica decreases while peak at 1045–1050 associated with the Si-O-Zn band has a more pronounced intensity as OH$^-$ ion concentration is increased. This observation might suggest that the silanol group interacts with the OH$^-$ ions in the solution and that prolonged stirring resulted in the surface capping of SiO$_2$ to ZnO resulting in the formation of flower-like ZnO-SiO$_2$ with hemispherical tips.

The X-ray diffraction diagram of the bare ZnO and amorphous SiO$_2$ and the chemically deposited ZnO-SiO$_2$ nanostructures at varying OH$^-$ ion concentration are presented in Figures 8 and 9, respectively. A broad peak is observed centered at 21.6° (2θ) which is attributed to the amorphous nature of SiO$_2$ [26] while the diffractogram of bare ZnO showed the (100), (002), and (101) reflections indicating the formation of ZnO. Presence of sulfides and hydroxides of zinc was also observed which is due to the precursors used as depicted in Figure 8. Figure 9, on the other hand, shows the diffractogram of the prepared ZnO-SiO$_2$ samples. Phase analysis revealed that the peaks correspond to wurtzite structure of ZnO as indexed to PDF 36-1451. The broad hump observed at 15–30° (2θ) was associated to the amorphous silica added in the ammonium-zincate bath for the synthesis of ZnO-SiO$_2$; the same diffractogram was observed as in the work of [27]. Presence of hydroxide of zinc was also observed.

4.3. Proposed Mechanism for the Growth of ZnO-SiO$_2$. Following the chemistry of solution as previously discussed, the dropwise addition of NH$_4$OH to aqueous solution of ZnSO$_4$ produces Zn(OH)$_2$ precipitate. For ZnO-SiO$_2$ prepared using 1.0 M NH$_4$OH, the Zn(OH)$_2$ produces Zn$^{2+}$ and OH$^-$ ions upon dissociation and induces the formation of ZnO nuclei. Based on the growth habit of ZnO, using low initial OH$^-$ ion concentration (1.0 M) resulted in a slow rate of ZnO nuclei formation leading to the creation of flat end-rods with hexagonal shape as observed in Figure 1. This can be explained by the high growth rate along the (0001) plane of ZnO compared to the other growth faces resulting in a rod-like structure. Upon addition of amorphous silica to the solution, the silanol functional group of silica attaches to the nonpolar facets of ZnO and, to maintain a stable structure, the metastable polar facet of ZnO exhibits surface reconstruction resulting in the pointed tips of ZnO-SiO$_2$ rods.

However, using high initial OH$^-$ ion concentrations (2.0 M and 3.0 M) resulted in the flower-like formation of ZnO-SiO$_2$ with hemispherical tips. Based on the micrographs, hydroxide cluster formation might be favourable for the growth of flower-like structures. Since there are sufficient OH$^-$ ions, more Zn(OH)$_2$ clusters were formed and subsequently adhere on the glass substrates which serve as seed nuclei while some may dissociate to Zn$^{2+}$ and OH$^-$ ions. Further addition of NH$_4$OH triggers more formation of Zn(OH)$_2$ which tends to continuously produce free Zn$^{2+}$ and OH$^-$ ions and starts to form ZnO rods on the Zn(OH)$_2$...
Figure 5: Micrograph of ZnO-SiO$_2$ using 2.0 M NH$_4$OH showing flower-like ZnO-SiO$_2$ nanostructures having hemispherical tips. At (a) 10,000x magnification and (b) 13,000x magnification.

Figure 6: Micrograph of ZnO-SiO$_2$ using 3.0 M NH$_4$OH showing flower-like ZnO-SiO$_2$ nanostructures having shorter rods and more pronounced hemispherical tips. At (a) 10,000x magnification and (b) 13,000x magnification. Encircled are the flake-like structures.

Figure 7: Infrared spectra of the as-grown ZnO-SiO$_2$ on glass substrate using 1.0 M (black), 2.0 M (red), and 3.0 M (green) NH$_4$OH.

seed nuclei. When amorphous silica was added, its silanol group attaches to the free OH$^-$ ions competing against the Zn$^{2+}$ ions leaving more Zn$^{2+}$ resulting in the formation of thicker and shorter ZnO-SiO$_2$ rods. Excess OH$^-$ ions, especially using 3.0 M NH$_4$OH, lead to the formation of zinc complexes as evidently suggested by the flake-like structures. As deposition time is prolonged, ZnO-SiO$_2$ structures were slowly deposited on the substrate having already seed nuclei and, consequently, the neighbouring ZnO from the solution adheres on the seed nuclei that were already deposited on the substrate and forms the flower-like structure. The formation of hemispherical tips is believed to be due to enough OH$^-$ ions present in the solution that attaches to the silanol group (Si-OH) of silica and then subsequently caps the surface of ZnO rods resulting also in a much bigger but shorter rod.
5. Conclusion

In conclusion, the control of the morphology of ZnO-SiO$_2$ was presented by changing initial OH$^-$ ion concentration. For a better understanding of the growth of ZnO-SiO$_2$, we demonstrated first the effect of SiO$_2$ on the morphology of ZnO followed by the influence of varying OH$^-$ ion concentration on its size and shape. It was found that bare ZnO rods exhibit hexagonal morphology having a c-axis preferred growth direction. Addition of amorphous silica to the ammonium-zincate bath for ZnO-SiO$_2$ synthesis resulted in a remarkable change of morphology from hexagonal to “pointed tip” rods. Increasing initial OH$^-$ ion concentration produces "flower-like" structure having hemispherical top surface but shorter rods due to surface capping of silica to ZnO. Infrared spectroscopic study confirms the formation of ZnO-SiO$_2$ from the functional groups present. Phase analysis by XRD suggested a wurtzite crystal structure of ZnO-SiO$_2$ was developed. Preliminary studies on the gas sensing capability and testing of the optical and electrical properties for solar cell application of the produced ZnO-SiO$_2$ are currently being conducted.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgment

The authors would like to thank the Commission on Higher Education-Philippine Higher Education Research Network (CHED-PHERNet) through the Office of the Vice Chancellor for Research and Extension of MSU-IIT for the financial support of this research study.

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