Atrazine Removal Using Nano-Zero Valence Iron and Granular Activated Carbon Mixture

Kawintra Kongka, Wuttiwat Chawkorash, Budsakorn katkaew, Wut Dankittikul, and Apichon Watcharenwong

***Abstract*—This research aims to synthesizes nano-zero valence iron coated on activated carbon (nZVI/GAC). Characteristics of the synthesized materials were investigated. The morphology was examined using scanning electron microscope (SEM). The synthesized material was used as the adsorbent material for atrazine removal. The comparisons of removal efficiency were studied in both cases of adsorption and Fenton-like reaction. The results showed that nZVI/GAC adsorbent materials can achieved 96% atrazine removal efficiency compared to GAC adsorption. The factors influencing the atrazine removal were the amount of material and the initial concentration of atrazine. Mixture ratios of Fe/GAC were also investigated for atrazine removal. The appropriate ratio for atrazine removal was 3:1.**

***Index Terms*—Activated carbon, adsorption, nano zero valence iron, atrazine.**

I. Introduction

At present, environmental issues are big and people are more interested in them. One interesting point is that pesticide residues in the crop area. Residues of these substances may contaminated raw water.

Atrazine is one of the most widely used plant nutrients. It is also related to the chemical industry. Which can be a precursor substances and products. It also has a molecular structure that cannot be degraded by enzymes in nature. It can also change the form so slowly that it tends to accumulate in the environment. In the present study, several researchers have studied the method of atrazine removal. One of the methods was to study the adsorption capacity of natural materials such as soybeans (SBB), corn stalks (CSB), rice stalks (RSB), poultry manure (PMB), cattle manure (CMB), and pig manure (PgMB). The adsorption capacity depends on the temperature and the initial concentration of atrazine, the adsorption capacity of the natural material as follows SBB> RSB> CMB> CSB> PMB> PgMB, which depends on the pore on the absorbent material [1]. In addition, the adsorption activity of activated carbons (SAC) and carbonate-induced activated biochar (CAB) was also investigated. CAB is 4 times more efficient than SAC, as well as an increase in temperature [2]. There is also a comparative study of the adsorption of atrazine in the presence of sodium chloride using hydrous iron oxide (HIOD301), hydrous aluminum oxide (HAOD301) and polymeric adsorbent (D301). HIOD301 and HAOD301 showed higher adsorption capacity than D301. Both adsorbents had an adsorption efficiency of more than 95% [3]. Another study also used the activated carbon (AC), nMgO and nZnO, and the composite of AC/MgO/ZnO to adsorb atrazine [4]. The effects of different operational parameters on the adsorption were evaluated. The pH of the solution had no significant effect on atrazine adsorption. The AC removed atrazine very well, while MgO and ZnO nanoparticles had low removal efficiency. The results of this study indicated that the prepared AC and AC/MgO/ZnO composite can be good alternative adsorbents for the removal of atrazine. Atrazine removal was also investigated by advanced oxidation process with the use of solar-sunlight Fenton-like processes with sulfate and iron ions to remove atrazine [5]. The atrazine oxidation by solar-sunlight with the addition of persulfate and iron ions (Solar/$S_2O_8^{-2}/Fe^{2+}$) gave the highest removal efficiency compared to the others (Unactuated $S_2O_8^{-2}$, Solar-sunlight only, $S_2O_8^{-2}/Fe^{2+}$, Solar/$S_2O_8^{-2}$).

Nano zero valence iron (nZVI) has a size in nano scale which is non-toxic and can act as potential alternative source of Fe^{2+} through the dissociation of ZVI by the following reactions.

$$Fe^0 \longrightarrow Fe^{2+} + 2e^- \quad (1)$$

ZVI had been successfully used to remove 2, 4-dinitrotoluene [6], 4-chlorophenol [7], aniline [8], [9], and alachlor [10] by Fenton-like process involving persulfate. Consequently, the objectives of the study described here were to compare the abilities of granular activated carbon (GAC) and mixture of nZVI/GAC to remove atrazine from contaminated water. The atrazine removal efficiency by Fenton-like process was also investigated using persulfate. The appropriate ratios of Fe:GAC for atrazine removal were also examined.

II. Materials and Methods

A. Synthetic of nZVI/GAC

$FeSO_4 \cdot 7H_2O$ was used to prepare the precursor solution at a concentration 0.054 M in volume of 250 ml. Then the pH was adjusted to pH 5 with hydrochloric acid and follow by addition of 0.756 g GAC. The solution was stirred for 1 hour at room temperature. Then nitrogen gas was purged into a

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The authors are with School of Environmental Engineering, Institute of Engineering, Suranaree University of Technology, Nakhon Ratchasima, 30000, Thailand (e-mail: kawintra.saiparn@gmail.com, wuttiwat.chaw@gmail.com, Kornbudsakorn22@gmail.com, wut@sut.ac.th, w.apichon@sut.ac.th).

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solution for 1 hours to eliminate the oxygen gas out of the solution. Then 0.108 M $NaBH_4$ was dropwise added to the solution and was kept stirring the mixture at room temperature for another 100 minutes. Then, the precipitates derived from the reaction were filtered with a 45 µm filter paper using vacuum filtration and rinsed with ethanol and deionized water, respectively. Finally, the precipitates were dry in an oven at 60° C for 24 hours. [8]

B. Removal of Atrazine

For the removal of atrazine, the experiments were divided into 2 parts. Part 1, the effect of the amount of absorbent on atrazine removal was studied. The amount used is as follows: 0.05, 0.1, 0.2, 0.4, 0.8 and 1.6 g / 20 ml of atrazine. The initial atrazine concentration was 25 mg/l and during the experiment the solution was stirring at 150 rpm for 6 hr. Part 2, the experiment for determine the optimal Fe:GAC ratio for the atrazine removal was conducted, by using the following Fe:Ac ratios of 1:1, 1:3, 1:5, 3:1, 5:1. Besides, the effect of initial atrazine concentration on removal efficiency was also investigated using material dosage of 5 g/1000 ml of atrazine solution. In this study, atrazine concentrations were measured with a UV-VIS spectrophotometer measured at 220 nm.

III. Results and Discussion

A. Materials Characterization

Morphologies of materials used to remove atrazine in this study were characterized by scanning electron microscope (SEM). The images of SEM show in Fig. 1. were measured in different magnification. Fig. 1a. shows the morphology of GAC at magnification of 22X. Fig. 1b. shows the morphology of pure nZVI at magnification of 50000X. The nZVI were round shape particles with average diameter of 110 nm. Finally, for Fig. 1c. shows the morphology of nZVI/GAC at magnification of 15000X.

B. Removal of Atrazine by Adsorption and Fenton-Like on Fe:GAC 1:1

In this experiment, the atrazine removal was compared with two different materials, GAC and nZVI/GAC. The effect of addition of persulfate on atrazine removal efficiency was also examined. From Fig. 2a., during the first 200 minutes, atrazine adsorption rates of nZVI/GAC was found to be faster than the one which was adding persulfate. This phenomenal occurred maybe due to the underdoes of persulfate added. However, pure GAC achieve fastest atrazine removal efficiency compared with the others during the first 200 minutes. The mixture material between nZVI and GAC has less specific surface area than the pure GAC due to small particle of nZVI was occupied the adsorption site of GAC. Fig. 2b. shows the effect of material dosage on atrazine removal efficiency. With small dosage of material (< 0.8g in 20 ml of solution), GAC shows highest atrazine removal efficiency. While the atrazine removal efficiencies of nZVI/GAC and nZVI/GAC with persulfate were comparable. With the higher material dosage (>0.8 g in 20 ml of solution), the composite material shows better atrazine removal efficiency than bare GAC. The atrazine removal efficiency of nZVI/GAC can reach 96% higher than that of other cases using the same material dosage of 1.5 g. This trend coincided with the removal of atrazine by using graphite (GR) and nZVI/GR as an absorbent material with the addition of persulfate. It was found that the removal of atrazine by GR showed better efficiency than nZVI/GR. [11]

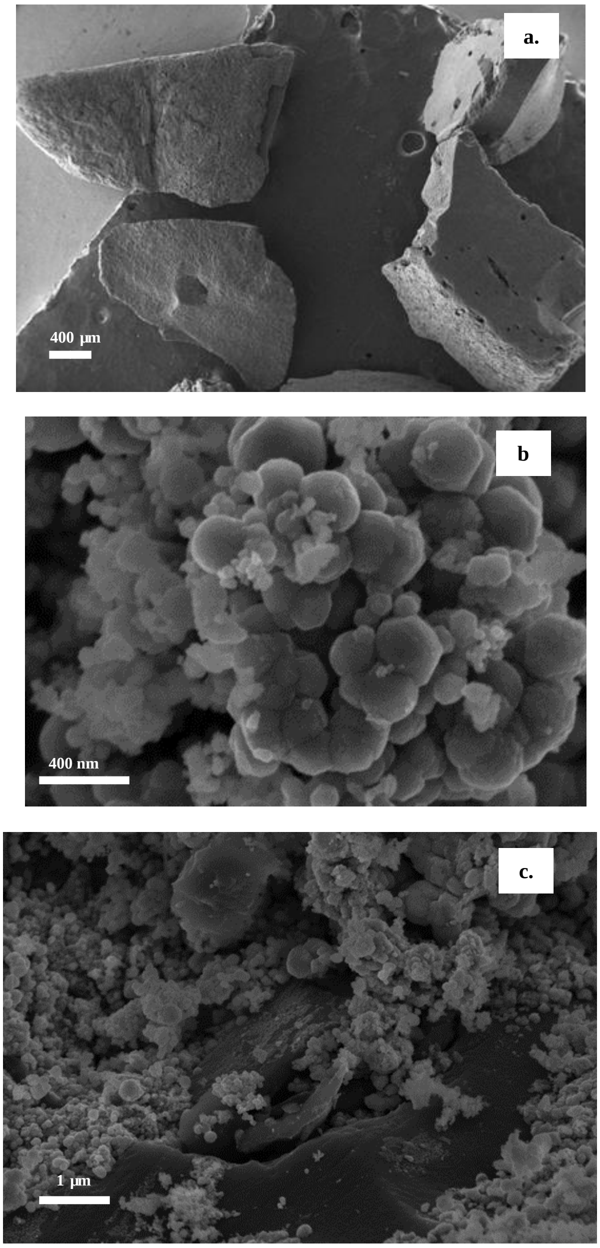
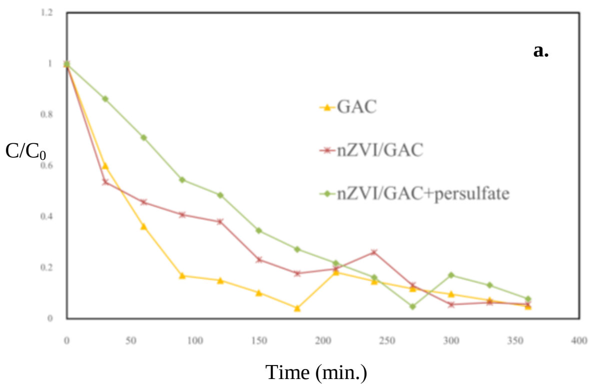


Fig. 1. SEM images of the a) GAC, b) pure nZVI, and c) nZVI/GAC.



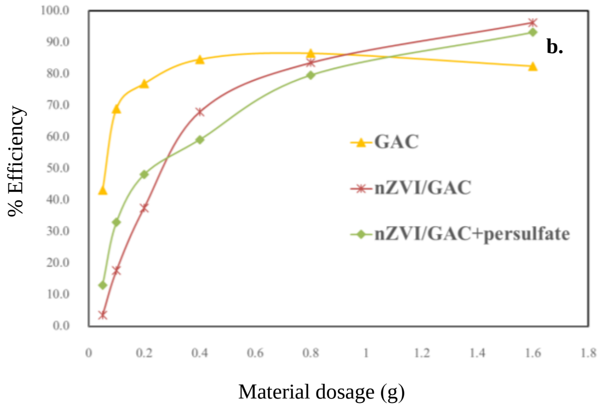


Fig. 2. Removal of atrazine by the Fe:GAC ratio of 1:1, by a) relationship between C/C$_0$ with time and b) relationship between the removal efficiency with the materials dosage.

Fig. 3 shows the effect of Fe:GAC ratios on C/C$_0$ values along with the reaction time. When increase amount of GAC with the constant amount of Fe, the atrazine removal efficiencies were gradually increased. But when amount of GAC were fixed and increase amount of Fe from 1 to 3 or to 5, the atrazine removal efficiencies were dramatically increased. This occurred because Fe or nZVI play a key role by Fenton-like reaction for atrazine removal. It was found that Fe:GAC ratio of 3:1 gave the best atrazine removal performance.

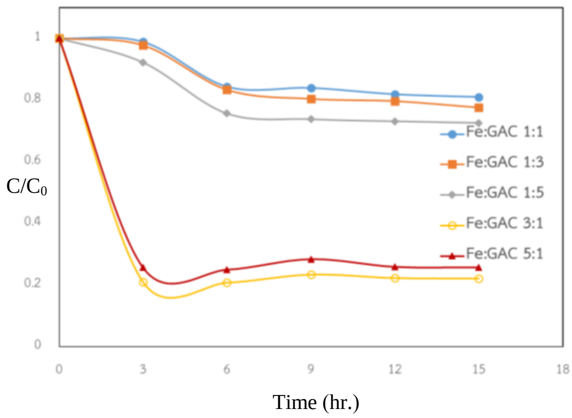


Fig. 3. Relationship between C/C$_0$ and reaction time by different ratios of Fe:AC.

With the ratio Fe:GAC of 3:1, amount of atrazine removed per gram of materials were shown in Fig. 4a. For the first 3 hours of the experiments, the amount of atrazine removed was increased. After that it was constant even the reaction time get longer up to 50 hours. Wei *et al.* 2018 examined the adsorption of atrazine with apricot shells activated carbons (ASAC), wood activated carbons (WAC), and walnut shells (WSAC). It was found that during the first hour had fastest atrazine adsorption rate. After that the adsorption rate gradually increased (2 to 6 hours) and finally reached equilibrium. (6 to 12 hours) [12]. The initial concentration of atrazine was the factor that influence the amount atrazine removed, as shown in Fig. 4b. It was found that the initial atrazine concentration of around 15 to 20 mg/l can achieved the maximum amount of atrazine removed. The lower initial atrazine concentration than 15 mg/l or higher than 20 mg/l gave less amount of atrazine removed.

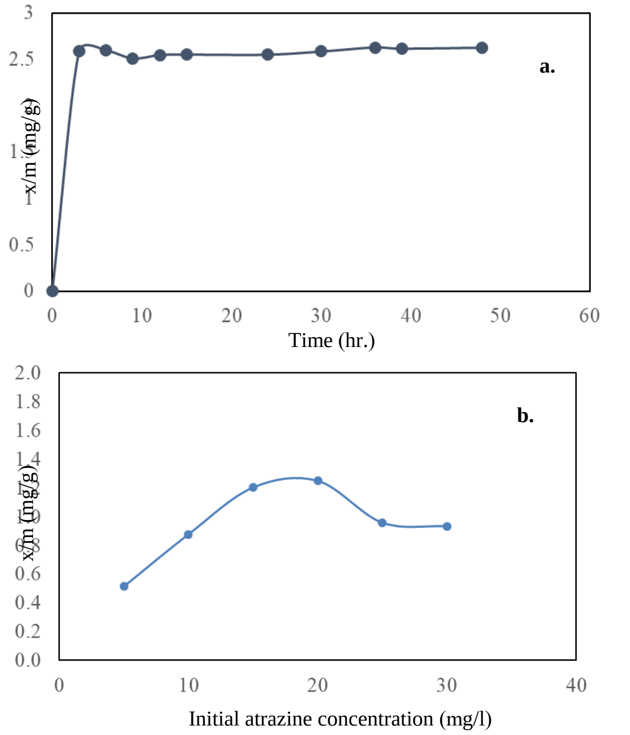


Fig. 4. The effect of atrazine removal at Fe:GAC ratio was 3:1 by a) Relationship between the amount of atrazine removed per gram of material with time. b) Relationship between the amount of atrazine removed per gram of material with initial atrazine concentration.

IV. Conclusion

In conclusion, atrazine adsorption efficiency of GAC better than nZVI/GAC. Since after mix nZVI with GAC the specific surface area of GAC was reduced. However, the atrazine removal performance by Fenton-like reaction gave better removal efficiency with the higher material dosage. The optimum Fe:GAC ratio for the removal of atrazine was 3:1. In this study, the material dosage and the initial concentration of atrazine had an effect on the atrazine removal efficiency. However, there are other important factors that this study does not investigate, such as temperature and pH, which should be further studied in the future.

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Apichon Watcharenwong was born in August 1978. He got his bachelor degree in civil engineering from Khonkaen University, Thailand in Apirl 2001. He got his master degree in environmental engineering from King Mongkut's University of Technology Thonburi, Thailand in October 2003. He graduated from Chulalongkorn University, Thailand where he obtained his Ph.D degree in environmental management in April 2008.

He is lecturer at school of environmental engineering, institute of engineering, Suranaree University of Technology, Thailand since 2008. His current research interests are in the area of waste utilization, nanomaterial preparation, environmental technology, and hazardous and solid waste management.

Kawintra Kongka was born in November 1995. She obtained bachelor degree in Environmental Engineering at Suranaree University of Technology, Nakhon Ratchasima Thailand in 2018. She has got a cooperative education internship at Consultants of Technology Co., Ltd.. One project which she contributed to have been finished. It is study of appropriateness in the design of wastewater treatment system for condominium.

Wuttiwat Chawkorash was born in December 1994. He obtained bachelor degree in environmental engineering at Suranaree University of Technology, Nakhon Ratchasima Thailand in 2018. He has got a cooperative education internship at Thai Environmental Technic Limited. One project which he contributed to have been finished. It is assessing the adequacy of the water treatment system of sugar factory.

Budsakorn katkaew was born in August 1995. She obtained bachelor degree in environmental engineering at Suranaree University of Technology, Nakhon Ratchasima Thailand in 2018. She has got a cooperative education internship at the Nawaloha lndustry. One project which she contributed to have been finished. It is the design of the ventilation system to reduce air pollution form automotive painting process.