Comparison of Different Methods and Treatment on Arsenic Removal from Wastewater

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ABSTRACT: Since arsenic pollution from industry occurs everywhere around the world, it causes a serious problem to the environment. People are trying to find effective arsenic removal methods to reduce the adverse impact caused by arsenic release. There are many technologies and biotreatments used to dispose arsenic pollution, such as polyacrylonitrile-based ultra filtration (UF) membrane method, chemically modified lactic acid bacteria method, iron oxide-coated fungal biomass method, pretreated waste tea fungal biomass method and chemically modified biomass method to remove arsenic. Due to the high removal efficiency of biosorbent on heavy metal, more biomass systems are applied in arsenic removal area recently. This paper will introduce some biological technologies to remove arsenic from wastewater, especially some biosorbent technologies based on certain kind of biomass (e.g. tea fungus). Compared with the conventional systems, biomass processes can decrease capital costs by 20\%, operating costs by 36\% and total treatment costs by 28\%. In the other hand, biomass methods are the environmentally friendly technologies. Compare with other treatment, using biomass as the raw materials for arsenic and other heavy metals treatment does not add any other pollutants into environment. Due to above advantages, biomass methods on arsenic removal are worthy to develop and investigate in the future, and can widely be applied in the wastewater treatment industry.

INTRODUCTION

Arsenic is known as a natural toxic semi-metallic element in both organic and inorganic forms in the world [1–4], and it can cause many adverse effects on human health [5]. Compared with organic form of arsenic, its inorganic form is more toxic for human being [6–8]. A lot of inorganic arsenic species are found in the surface water and groundwater source all over the world. A research report indicated that organic arsenic pollutants exist in a great number of water resources in the North America (especially, United States and Canada) [9]. Arsenic is naturally found in water, soil, air, rocks, and also plants and animals [10–13]. However, arsenic can be further released to the environment through anthropogenic activities (such as agricultural activities and industrial activities), and some natural events (such as forest fires, volcanic actions and rock erosion) [14–18]. Arsenic is widely used in metals, drugs, paints, and semi-conductors. Nowadays, using arsenic as a wood preservative is very popular in the U.S. Industry activities and practices, such as mining, coal burning, and copper smelting also contribute to the release of arsenic to environment [19–21].

Arsenic pollution in water resource, especially in groundwater resource, is very common in some developing countries, such as India, Bangladesh, Argentina, Mexico, China, Nepal and Vietnam [22], and also occurred in some rural area of developed country, including Japan, New Zealand, Germany, and the U.S. [4]. There are some pieces of evidence showing that the varieties of adverse impacts caused by arsenic have been observed at endemic arsenic poisoning areas such as some provinces of Mexico, Chile, and China, especially in Bangladesh, India and West Bengal.

When people began realizing the toxicity of arsenic in last few years, strict regulations and laws were

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made in effort to reduce arsenic pollution. According to the European Commission, the World Health Organization (WHO) in 1993, and U.S Environmental Protection Agency (EPA) in 2001 [7], the acceptable concentration of arsenic in drinking water resource was decreased from 50 μg/L to 10 μg/L [22]. The feature that arsenic is odorless and tasteless indicating it is difficult to recognize this contaminant easily and quickly [23—26]. People might take in a certain amount of this contaminant without realizing the pollution and this can cause serious problems on human health. According to the analysis results of U.S. EPA, people who are exposed to arsenic for a long time may have diseases such as cancers of the lungs, bladder, kidneys, nasal passages, skin, etc. [27]. The most severe arsenic pollution occurs in Bangladesh and India, and some research showed that that about 60 to 100 million people suffer from arsenic because of consumption of drinking water contaminated by arsenic in these two Asian countries [28].

Given the toxicity of arsenic, removal of arsenic from the polluted groundwater is necessary and also a big challenge to meet the requirement of the drinking water standard at 10 μg/L. For years, people have been trying to find effective arsenic removal technologies to reduce the adverse impact of arsenic. Several decades ago, arsenic has been fortuitously removed from wastewater by using coagulation process, and coagulation method is demonstrated as an economical and effective technology in recent years. Nowadays, there are many developed technologies and methods for removal of arsenic from wastewater, such as polyacrylonitrile-based ultrafiltration (UF) membrane method, chemically modified lactic acid bacteria method, iron oxide-coated fungal biomass method, pretreated waste tea fungal biomass method and chemically modified biomass method [29].

There are a few problems associated with the current treatment technologies for heavy metals removal in wastewater from industrial effluents. Effective removal of trace metals and huge capital investment control is a bottleneck problem. Therefore, it is imperative and necessary to further develop the current techniques to find more effective means. Through implementing these developed technologies and new technologies, the heavy metal can be removed at a low price. Recently, the search of new treatment techniques has paid attention on the microbial metal binding capacity (e.g. algae, yeast, bacteria or fungi) [22]. Some studies have shown that biosorption play important part in improving the usability of industrial wastewater [29]. As far as now, biosorptive methods can not completely replace the existing common technical methods which are only fitted in dispose low concentration grade. However, this method may conduct as polishing systems for processing technology, which are partly effective. Many studies were implemented and all have emphasized that the biosorption of metal ions mainly rely on the interaction with certain substances on the surface of biosorbent [22]. The interests of recent research focus on finding different biosorbents to remove heavy metals including arsenic removal. The fact that arsenic pollution is occurring everywhere in the world meant that it is necessary and urgent to find a suitable biomass biosorbent to remove arsenic in a competitive and cost-efficient way. Due to the high removal efficiency of biosorbent on heavy metal, more biomass systems can be applied in arsenic removal area [30]. This study aims to introduce, compare and discuss the different biomass technologies, and provide recommendations from the potential development of current biomass removal systems.

**MATERIALS AND METHODS**

**Iron Oxide-coated (IOC) Biomass**

IOC adsorbents methods are categorized as emerging techniques for arsenic removal. Some studies showed that the IOC sand was beneficial for removing arsenic from wastewater, and using other IOC or loaded materials were proved to be an efficient method to remove arsenic in aqueous solution as well. Loukidou et al. obtained the results that using chemically modified *P. chrysogenum* method which also will be shown in this paper could increase arsenate removal rate compared with unmodified *P. chrysogenum* biomass [5]. However, among the various pretreatment studies, IOC *A. niger* biomass was reported to be one of the best methods due to its high efficiency of removing arsenic [27]. Dimethylarsinic acid (DMA) is a major metabolite found in human beings and rodents that are exposed to arsenic [8,10]. DMA can be used as the indicator to determine the arsenic removal rate from aqueous solution.

**Preparation of Standard Reagents, *A. niger* and IOC Biomass**

Distilled deionized water was used to prepare other standards, modifier and wash solution, which was obtained from a local supplier. The volume of 200 ml
DMA (1000 mg/L) solution was made by dissolving 0.4426 g of cacodylic acid in deionized water. *A. niger* biomass grew in aerobic conditions, and was maintained on potato dextrose agar plates [10]. And then some standard solution was prepared in certain conditions, which was inoculated by *A. niger* biomass. The solution of Fe(NO₃)₃·9H₂O and NaOH, and biomass powder were put into porcelain pot, and then keep the pot with mixture in an oven at 80°C for 3 hours. After this, the temperature of the oven was increased to 100°C for another 24 hours, and then the IOC *A. niger* biomass can be used for experiment [27].

**pH and Equilibrium**

As pH is an important and sensitive parameter, this study was controlled by different pH values to determine the removal rate of arsenic. All experiments were made in duplicate, and the average value was used to analyze. A 100 ml of the DMA solution with the concentration of 100 μg As/L was put with 0.1 g of biomass in a number of conical flasks with pH between 5 and 8, and the samples were taken once per hour [10].

**RESULTS AND DISCUSSION**

Figure 1 showed the results that the higher DMA removal rate by IOC *A. niger* biomass occurred at pH value of 6 and equilibrium time of 7 hours respectively, and DMA removal rate was more than 50% at pH 6 after 2 hours. In the previous research regarding to the As(III) and As(V) removal, the results showed that nearly 95% of As(V) and 75% of As(III) were removed by IOC biomass while the DMA removal by the same biosorbent was only 50% or less [10]. The results demonstrated that using IOC *A. niger* as the biomass can get high removal efficiency of arsenic due to the removal rate of DMA. Through the experiment, removal capacities of As(III) and As(V) using *A. niger* biomass were demonstrated to be similar to those of other IOC materials, but much less than activated carbon and activated alumina, which was shown in Figure 2.

The reasons for this difference may be concluded to the different initial concentration of arsenic. The initial arsenic concentration of 100 μg/L was used for experiment of IOC biomass, whereas the arsenic concentration for activated carbon and activated alumina studies was 100 mg/L [29]. This study also demonstrated that the removal rate of As(III) was increased when temperature increased from 5–30°C; Similarly, an increase was found in As(V) removal when temperature increasing from 5–10°C, but keeping a constant thereafter until 30°C [27].

**Biomass as Biosorbent**

*P. chrysogenum*, a type of wasted by-product came from antibiotic output, was studied for removal of cationic metal pollutants for many years. Some experiments are used to test and try to enhance the efficiency of biosorbent by various chemical pre-treatment. In this study, the modification or preconditioning of biomass was executed by hexadecyl-trimethylammonium bromide (HDTMA-Br), dodecylamine (DA) and cationic polyelectrolyte, Magnafloc-463 [28]. The possible of *P. chrysogenum* biomass for As(V) dislodge from aqueous solution using closed to perfect operating conditions was tested by following experiments [8].

Previous researches have carried out that using *P. chrysogenum* as the biomass to remove Zn, Cu and Ni from wastewater is practicable. These experiments stated that the dead fungal biomass can be regarded as an adsorbent for removing toxic heavy metal from wastewater [29]. The study was to determine whether this biomass can remove arsenic and what the efficiency is. This biomass specimen was comprehensively washed by deionized water to remove different soluble residues, and then dried at indoor temperature (25°C). The pH value of aqueous suspensions is around 6 [28].

**Biomass Pre-treatment**

Three solutions were selected and used to modify the *P. chrysogenum* biomass surface, including 1% w/v of polyelectrolyte magnagloc 463, 10% w/v of cationic...
surfactants HDTMA-Br and dodecylamine (DA). The dry weight of 10 g biomass was used to cure with 30 ml of chemicals in a vibrating screen with the velocity of 180 rpm for 24 hours at 25°C [8,28]. And then the biomass was washed twice with distilled water and did the air dehumidification process after that [30].

**Biosorption Experiments**

The operating conditions of experiments were suggested by previous research [6,31]. To determine the effluence of pH values, the batch scale of biosorption tests were applied to conical flasks which stirred in a reciprocating oscillating sieve with the velocity between 180 and 190 rpm at indoor temperature (25°C) in various pH levels. The As(V) solution with the reference concentration (using Na₂HAsO₄·7H₂O) was appended to biomass suspension (normally 1g/L), dispersed by using a hand homogenizer to produce the desired level of concentration of biomass suspension. The mixture solution pH can be modified by the addition of sodium hydroxide or nitric acid. The range of concentration is from 0.2–2 mg/L. The electrokinetic measurement were implemented by using a Rank Brothers Mark II microelectrophoretic apparatus, and using a Perkin-Elmer FT-IR spectrum 1600 instrument to get fourier transform infrared spectra of the biomass samples [22]. The solution of 100 mL of HCl (0.1N) was used to wash the biomass for four times, and the obtained waters were analyzed for determination of alkaline and alkaline earth metals which were shown in the process of cultivated solution. Sodium hydroxide (0.1N) was used as titrant for potentiometric titration of biomass, and the pH value of suspension was measured using a pH-meter after titrant addition [5,32].

**Results of Experiment**

The previous studies showed that the most important aspect for biosorption methods is to select the appropriate microorganisms which are capable of removing large numbers of heavy metals from wastewater [22]. During the experimental procedures, the four different biomasses can be roughly characterized, especially when ionic interactions are popular for removing heavy metals from wastewater [33]. The Figure 3 shows the ionic characterization of modified and unmodified biomasses, considering the release of alkaline and alkaline earth cations (including Na⁺, K⁺, Mg²⁺ and Ca²⁺) and total ionic contents of different biomasses. From the table, it is easy to find that 0.57 meq/g of HDTMA-Br modified Mycan biomass was the highest ionic content of resulting biosorbent. Through this table, the pre-treatment of biomass was demonstrated to enhance the ionic content of biomass, because comparing with the unmodified Mycan biomass with total ionic content of 0.43 meq/L, the total ionic content of modified biomass raised to 0.51 meq/L for Magnafloc-Myan and 0.45 meq/L for DA-Mycan. These values can be determined as an approximate method for determining the ionic exchange capacity of the different examined biomasses [5,9,28]. The bigger the value of total ionic content is, the better removal efficiency of the biomass can achieve. Therefore, HDTMA-Br modified Mycan biomass had the best removal efficiency.

**Tea Fungal Biomass Method**

The tea fungus (or called as Kombucha) is a waste product which is formed in the fermentation of black tea. The experiment is to determine the possible mea-
sure for removing arsenic with tea fungal biomass. The pre-treatment was found to improve the performance of arsenic removal by using Ferric trichloride (FeCl₃) [34]. The brief procedures were shown in following part.

**Experimental Method**

Preparation of tea fungus is the first step for the experiment. Usually, the tea fungus biomass was prepared in several processes, and was obtained from perfumery of Tehran city and cultivated for 10 days at 28 ± 2°C to get a new fungal mat. Secondly, the tea fungal mat was washed using deionized water and then was dried at 75°C for 24 hours. Then a part of the dried and ground mat was immersed in FeCl₃ solution (15 ml/L) for 1 hour, using these two modified fungal mats to test the efficacy of arsenic removal from an aqueous solution. Thirdly, they prepared some synthetic solution, and use electrical pH meter to adjust the pH value to a desired value. The optimum speed of agitation was adjusted about 50–300 rpm, and the authors chose the 160 rpm for rotary rate at room temperature (22 ± 4°C). In the next few processes, the authors do some pretreatments and analysis on biosorption isotherms, effect of pH on biosorption, and effect of background ions, metal analysis, kinetic modeling and isotherm modeling [8].

**Results of Experiment**

From the kinetic study, the results showed the arsenic biosorption by tea fungus, and yjr arsenic uptake was at relatively high rate. According to results and some analysis, the experiment also showed that the system can reach to equilibrium phase within 90 minutes at the initial arsenic concentration of 4 mg/L, and the authors also supplied many values of $q_e$, $k_1$, $R_2$, $K$, $K_0$ for their experiment. One of conclusions they got is that kinetic analysis of arsenic biosorption by pretreated waste tea fungal biomass can better represent the pseudo first-order rate equation than others. According to the analysis of pseudo second-order rate equation, they thought there was no direct correlation between initial concentration (IC) of arsenic and the rate of arsenic biosorption using tea fungal biomass. In isotherm study part, Langmuir and Freundlich isotherms have been applied. Through the comparison, The Langmuir equation described the isotherm arsenic biosorption by tea fungal biomass with higher correlation coefficient ($R^2 > 0.99$), which was better than the results from the Freundlich model ($R^2 > 0.95$). The optimum initial pH values for arsenic biosorption and removal were showed to be between 6 and 8 in those experiments. In the next few experiments, they demonstrated that increasing the IC of background ions to more than 500 mg/L caused the decrease on arsenic removal, and they also found the there is no obvious increase in uptake when the agitation speed is above 150 rpm [8].

**Discussion and Comparison**

The results of these three techniques for arsenic removal from aqueous solution by six different biomasses were shown in previous content respectively. They all got the high removal efficiency in certain conditions, such as optimal pH, temperature and background ions.

![Figure 3. Ionic characterization of modified and unmodified biomass.](image)
In these studies, using biomass as biosorbent to remove arsenic was demonstrated as an effective method and can be implemented into wastewater treatment field.

These three technologies have some common points in their experimental processes. Firstly, all the six kinds of biomasses were pre-treated by certain solution and cultivated in certain condition. These pre-treatment are necessary and play important roles in whole procedure and the final arsenic removal rate. Secondly, these studies all focused on analyzing the different factors which effluent the arsenic removal and finding an optimal condition for biomass. Thirdly, excluding these experiment, there are a great of evidence showed that the ferrous solution can enhance the efficiency of arsenic removal. Therefore, using ferrous solution for pre-treatment of biomass is potential method to improve the arsenic removal capacity of biomass. The last but not the least, all the biomass is very cheap and easy to obtain. Most of biomasses can be got from food, pharmacy and industrial waste. Due to the capacity being as biosorbent of arsenic removal, the biomasses are cost-effective materials which are valuable in recent and future wastewater treatment industry.

There are also some different results in the previous three experiments. The pH is the most obvious aspect showing the difference of results. In the first experiment, as can be seen in figure 1, pH value of 5 was the lowest performance of DMA removal (arsenic removal). The pH value of 6 is the optimal condition, in other hand, the pH value of 7 and 8 also showed the good performance of DMA removal. The figure 4 showed the effect of pH on equilibrium capacities of biosorption by tea fungus biomass in the third experiment. The pH value of 5 to 8 did the best performances on equilibrium capacities and arsenic removal. However, unlike the other two experiments, the As(V) removal rate decrease with an increase of pH value from 3 to 8. Some studies [6] gave some reasons for that: when pH values are low (3-4), H₃AsO₄ and H₂AsO₄⁻ are existing species of arsenic solution, and would be expected to interact more strongly with the respective ligands which carry positive charges. When the pH value grew, the amount of negatively arsenic species increases, and it will affect the removal rate of arsenic. The results are shown in Figure 5.

There are some improvements of these biomass methods in the future according to recent research. Because all these studies and experiments were done by in small scale and at low concentration of arsenic, if these biosorption technologies are applied into practice, the more real concentration and scale should be considered. Those experiments also lack of determination of combined conditions. In the real case, the removal rate of arsenic is related to combined conditions. Therefore, it is necessary to design a more actual and practical model to simulate the real case. Through this type of experiment, people can get a more reliable remove rate of arsenic by biomass methods.

CONCLUSIONS

Biosorption of arsenic and other heavy metal is promising key technology including the removal of toxic heavy metals from industrial effluents and natural

![Figure 4. Effect of pH on equilibrium capacities of As (V) biosorption by tea fungus.](image)

![Figure 5. Effect of pH on As(V) adsorption removal.](image)
waters. Implement of biomass methods could be concluded as an eco-friendly and cost-effective process. Because most of biomass comes from industrial waste, the cost of biomass is very low. Generally, compared with the conventional systems, these kinds of methods can decrease capital costs by 20%, operating costs by 36% and total treatment costs by 28% [22]. In the other hand, biomass methods are the environmentally friendly technologies. Compare with other treatment, using biomass as the raw materials for arsenic and other heavy metals treatment does not add any other pollutants into environment. Due to above advantages, biomass methods on arsenic removal are worthy to develop and investigate in the future, and can widely be applied in the wastewater treatment industry.

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