

Original Research

Removal of Boron and Arsenic from Petrochemical Wastewater by Using Aquatic Booster as Adsorbent

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Abstract

The potential to remove boron and arsenic from petrochemical wastewater by using aquatic booster was investigated in batch experiment process and the results were measured by inductively coupled plasma mass spectrometry (ICPMS). The main parameters influencing arsenic and boron adsorption onto the aquatic booster were contact time, size of particle, agitation speed, and dosage. The initial concentration of boron and arsenic was fixed by changing contact time (120-480 minutes), agitation speed (0-120 rpm), aquatic booster dosage (0-55 g/L), and size of particle (2 mm, 1 mm, and 0.60 mm). The adsorption efficiency of arsenic and boron increases with longer contact time as well as more aquatic booster dosage and higher agitation speed. However, it tends to achieve equilibrium once the active sites of the adsorbent are fully occupied. On the other hand, adsorption efficiency decreases with larger adsorbent particle size. The equilibrium time for both boron and arsenic is 390 minutes. The removal efficiency for boron is around 60.36% by 35g/L dosage, 80 rpm and a particle size of 0.60 mm at of 390 minutes. As for the arsenic, the condition where it gives the removal percentage around 71.83% is that particle size of 0.6 mm, 300 minutes contact time, agitation speed of 80 rpm and dosage of 45g/L. The modeling study shows that the adsorption isotherms for both metals onto aquatic booster are Freundlich type.

Keywords: mixed agricultural waste adsorbent, petrochemical wastewater, heavy metal adsorption

Introduction

Many concerns about heavy metals contaminating our wastewater rise nowadays and discharge a large amount of metal-contaminated wastewater usually come from industries, commercial, and domestic areas. Generally, wastewaters generated from industrial and domestic consist of several types of heavy metals such as boron, arsenic, cadmium, chromium, cuprum, nickel, lead, and zinc, which all

are most hazardous from the chemical-intensive industries. It is due to their high solubility in aquatic environments that heavy metals can be absorbed by living organisms. Once they enter the food chain, large concentrations of heavy metals may accumulate in the human body. If the metals concentrations are ingested beyond the permitted value, they can cause serious health disorders. Heavy metal removal from inorganic effluent can be achieved by conventional treatment processes such as chemical precipitation, ion exchange, and electrochemical removal. These processes have significant disadvantages, including com-

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plex equipment, high energy consumption, and the generation of toxic sludge [1]. Adsorption has become one of the alternative treatments. In recent years, the search for low-cost adsorbents that have metal-binding capacities has been investigated [2]. The adsorbents may be of mineral, organic or biological origins, zeolites, industrial by-products, agricultural wastes, biomass, and polymeric materials [3]. There are many adsorbents that can be used for the removal of metal ions from wastewater and, certainly, cost plays an important role for determining which one is applicable. Consequently, in the last few decades, alternative adsorbents like the most popular microbial biomass and lignocelluloses materials were studied. These are natural materials available in large quantities and with a low price. For examples, it was reported that copper can be removed by sunflower leaves up to 89.37 mg/g [4]; lead removal efficiency can reach more than 95% by spent black and green tea leaves [5]; and Cr and Cd can be removed by 71.4% and 54.3% separately by *Salvinia* biomass [6].

In this research, organic compost compounds, which are agricultural waste products, were used to replace the expensive commercial adsorbents. The main components in the organic compost mixture are rice husk, peat soil, and cow dung, and rice husk is an abundant agricultural waste with a world production of 132 million tons in 2008 [7]. In terms of metal binding capacity rice husks have the potential to be inexpensive adsorbents for the recovery of cations like nickel, zinc, copper, cadmium, antimony, and lead. The organic compost mixture or compounds usually are used as aquatic boosters, and adsorptions of heavy metals like arsenic and boron onto aquatic boosters are rarely studied, unlike copper, lead, and cadmium, etc.

Materials and Methods

The organic compost (aquatic booster) was obtained from a company in Johor and later underwent a process that screened the compost through a mesh and gave the particle sizes of 0.6, 1, and 2 mm by a sieve shaker. Three types of sieved adsorbents are each designated as most fine, medium, and coarse. After sieving and screening, the aquatic booster was first washed with deionized water for a few times in order to remove impurities and then filtered. The residues were then dried in an oven at 120°C for 24h and most soluble and volatile organic components are removed to prevent the competitive chelation process with metal ions in the solution, which would reduce the adsorption efficiency. Such an impediment phenomenon was observed in a nickel adsorption experiment in other research [8]. The wastewater was collected from a petrochemical plant in Port Dickson, used in the experiments without any dilution with initial 27.66 ppm boron and 0.9174 ppm arsenic at pH 8.24. Jar test equipment was used to agitate the adsorbent in the wastewater. That pH was measured by a pH meter (Brand Mettler, Toledo).

Inductively coupled plasma mass spectrometry (ICPMS, Agilent 7700 Series) with argon gas was used to analyze the boron and arsenic concentrations in the petro-

chemical wastewater. ICP-MS can detect boron down to 0.15 µg/L and arsenic down to 0.2µg/L. Pore structure characterization of 3 different sizes of aquatic booster particles was performed by a computer-controlled automated porosity analyzer (Micrometrics ASAP-2020M) at 423 K. The specific surface area was calculated by using the Brunauer Emmett Teller (BET) equation [9]. Total pore volume (V_{total}) and the average pore diameter (d_{av}) were derived from the Barret-Joyner and Halenda (BJH) method [10].

All the experiments were carried out at ambient temperature (25°C) in batch mode. All the adsorbents of three types of sizes were separately studied by varying the adsorbent dosage, contact time, and agitation speed as a variable control method. The remaining solution after adsorption was analyzed by ICPMS. The average amount of metal adsorbed was calculated three times for each sample. The removal percentage (%) of boron and arsenic was calculated according to equation (1):

$$R (\%) = \left\{ \frac{C_i - C_e}{C_i} \right\} \times 100 \quad (1)$$

...where C_i and C_e were the initial and final concentrations of boron and arsenic in the wastewater. And the adsorption capacities of adsorbents for boron and arsenic at equilibrium were calculated by:

$$q_e = \left(\frac{C_i - C_e}{W} \right) V \quad (2)$$

...where W (g) is the mass of adsorbent and V (L) is the volume of the solution.

Results

Characterization of Porous Structure

The surface area of adsorbent with particle sizes of 0.6, 1 and 2 mm are separately 21.2831, 17.5158, and 12.8592 m²/g. Average pore volume for three adsorbent particle sizes are as same as 0.003422 mL/g. And the average pore diameter of different adsorbent sizes are all 19.725 Å, which is bigger than the molecular size of arsenic (2.49Å) and boron (1.59Å). This means that boron and arsenic atoms can be adsorbed into the aquatic booster pore.

Effect of Contact Time on Boron and Arsenic Removal

As shown in Fig. 1, it demonstrates that with the contact time increases, the percent of metal adsorption also increases. The equilibrium time was found to be 390 minutes. Boron adsorption rate rapidly increased in the beginning and slowed down during the end of the process. Even though the removal efficiency of boron keeps increasing as time goes on. The best contact time selected for removing

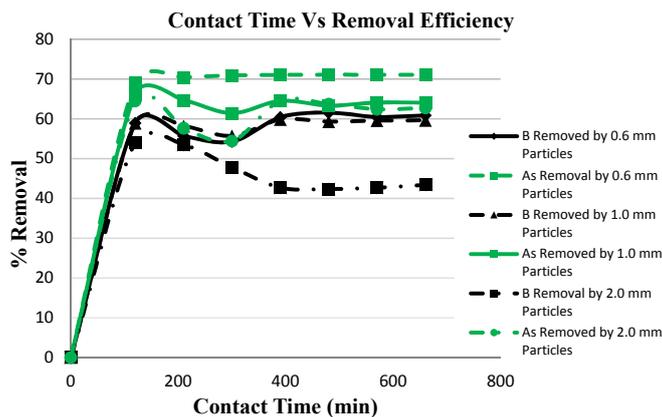


Fig. 1. Adsorption of boron and arsenic under different contact times.

boron in wastewater in this treatment is 390 minutes. The removal percentage of boron after 390 minutes is 61.50%, close to 60.36% at 390 minutes, so contact time does not need to be longer than equilibrium time for time efficiency concerns. For comparison, the saturated contact time for boron adsorption is 1 hour by palm oil mill boiler bottom ash [11] and 8 hours by activated sludge.

It is similar that the removal efficiency of arsenic increases with time and starts to approach its equilibrium at 390 minutes, and it is the superior contact time selected in this study for the arsenic removal percentage of 71.10%. As some literatures have reported, the equilibrium time for arsenic adsorption can be as long as 6 hrs [12]. Conclusively, at the beginning of adsorption, fast diffusion on the external adsorbent surface into the intra pores of it and a large number of available active sorption sites cause the relatively high adsorption rate.

Experimental conditions for data in Fig. 1 are 35 g/L aquatic booster in 250 mL volumetric flasks at 80 rpm at room temperature.

Effect of Dosage on Boron and Arsenic Removal

In this experiment, five different concentrations of aquatic booster are 15 g/L, 25 g/L, 35 g/L, 45 g/L, and 55 g/L. Fig. 2 shows that boron removal in petrochemical

wastewater increases with increasing adsorbent amount. It also shows that the adsorption efficiency of arsenic increases rapidly with increases in dosage of aquatic booster from 15 g/L to 45 g/L. At 45 g/L of aquatic booster, the maximum removal efficiency is 55.96% for boron and 72.83% for arsenic. The increase in the efficiency of removal is because of the increase of adsorbent contact surface and active sites for adsorption [13]. However, adsorptive capacity of aquatic booster does not increase a lot at higher adsorbent dosage compared to lower dosage because there no more metal ions for surplus adsorbent particles to adsorb exists, and also that lower driving force for adsorption at higher adsorbent dosage occurs [14]. Thus, the low dosage of aquatic booster is more preferable for adsorption. Based on this result, the dosage of 45 g/L of aquatic booster was chosen as the optimum for arsenic removal.

Experimental conditions for data in Fig. 2 are 300 minutes contact time in 250 mL volumetric flasks at 80 rpm at room temperature.

Effect of Agitation Speed on Boron and Arsenic Removal

The speeds of agitation are 40, 60, 80, 100, and 120 rpm. Fig. 3 shows the removal percentage of boron and arsenic. The removal percentages on boron and arsenic were found to increase with the increase of agitation speed and the

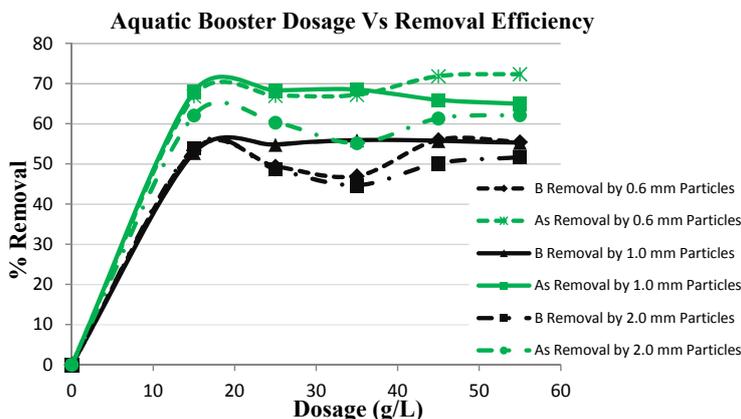


Fig. 2. Adsorption of boron and arsenic under different adsorbent dosages.

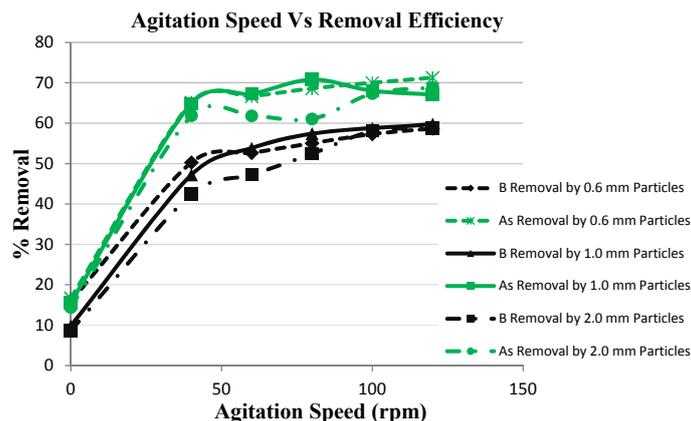


Fig. 3. Adsorption of boron and arsenic under different agitation speed.

removal efficiency rises only 0.26% for boron and 1.3% for arsenic by 0.6 mm particles from 80 rpm to 100 rpm. Raising agitation speed is more profitable when larger adsorbent particles are applied, since higher increased value in removal efficiency (which is 5.67% for boron and 5.28% for arsenic) by 2 mm particles was recorded. Increasing agitation speed reduces the boundary film layer of adsorbent particles, thus resulting in a higher external film mass transfer rate as reported in the removal of copper by using sawdust [15] and study on the sorption of lead by peat [16]. Usually, increase of the agitation speed also improves the diffusion of ions into the pores of the adsorbents. As a result, the agitation speed of 80 rpm was selected as the optimum speed for boron and arsenic removal by 0.6 mm adsorbent particles. Similarly, research reported no significant increase in uptake above 150 rpm agitation speed [17].

Experimental conditions for data in Fig. 3 are 300 minutes contact time in 250 mL volumetric flasks with 35 g/L dosage at room temperature

Effect of Particle Size on Boron and Arsenic Removal

Adsorption capacity of rice husk is very dependant on surface characteristics. It is expected that the adsorption capacity will be increased with a larger surface area associated with a smaller particle size [18, 19]. As illustrated in Fig. 4, it shows that the coarse aquatic booster with particle

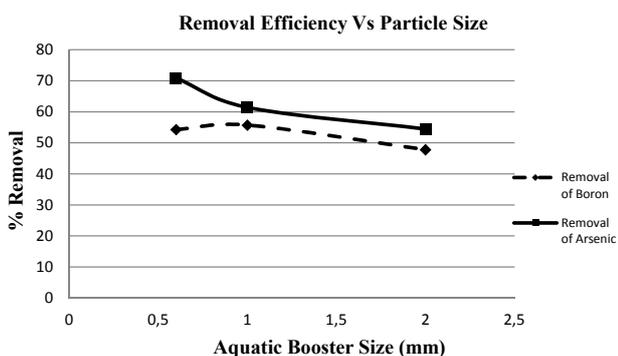


Fig. 4. Adsorption of arsenic and boron by different particle sizes.

size of 2 mm is only able to remove 47.80% of boron and 54.43% of arsenic. The medium size of aquatic booster, which is 1 mm in size, can remove about 55.71% of boron and 61.38% of arsenic. The aquatic booster with particle size of 0.6mm gives the best adsorption result on arsenic, which is 70.89%, but 54.27% for boron. This means further reduction on particle size below 1 mm does not have a significant effect on boron removal efficiency.

Experimental conditions for data in Fig. 4 are 80 rpm agitation speed, and 300 minutes contact time in 250mL volumetric flasks at dosage 35 g/L at room temperature.

Adsorption Isotherm

In the study, Langmuir and Freundlich isotherms were used to describe the relationship between the amount of boron and arsenic adsorped and their concentrations at equilibrium in solution. Langmuir isotherm is a monolayer represented by equation (3) [20]:

$$q_e = \frac{C_e q_m K_L}{1 + K_L C_e} \tag{3}$$

...where C_e (mg/L) is the equilibrium concentration of adsorbate, q_e (mg/g) is the amount of adsorbate adsorbed at equilibrium per unit mass of adsorbent, q_m (mg/g), and K_L (L/mg) are the Langmuir maximum adsorption capacity and energy-related constant, respectively, with respect to certain adsorbents. Langmuir model is suitable for monolayer chemical adsorption description [21]. The linear plot of C_e/q_e against C_e as shown in Fig. 5 demonstrates a fair fitting of the experimental data with the Langmuir isotherm. The regression factors are 0.8397 for boron and 0.8228 for arsenic, respectively. Hence, the adsorption behaviors of boron and arsenic onto aquatic booster can be only fairly described by Langmuir isotherm model. The boron and arsenic adsorption onto aquatic booster was also investigated by using Freundlich isotherm, a multilayer adsorption model that does not consider the interaction between adsorbate molecules and adsorbent's surficial active sites given by equation (4) [22]. Where K_f (mg/g) and n are the Freundlich constants regarding adsorption capacity and

Table 1. Langmuir and Freundlich constants for boron and arsenic adsorption.

Langmuir Isotherm				Freundlich Isotherm			
Boron		Arsenic		Boron		Arsenic	
q_m (mg/g)	K_L (L/mg)	q_m (mg/g)	K_L (L/mg)	n	K_f ($\text{mg}^{1-n} \cdot \text{L}^n / \text{g}^{1-n}$)	n	K_f ($\text{mg}^{1-n} \cdot \text{L}^n / \text{g}^{1-n}$)
1.42	1.6	0.085	0.97	1.6	0.11	1.33	0.047

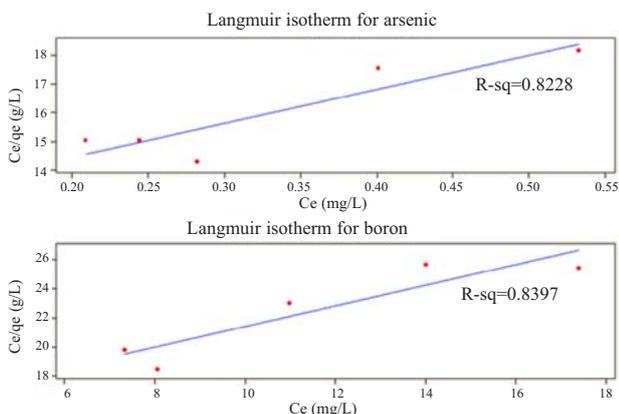


Fig. 5. Langmuir adsorption isotherms for arsenic and boron.

intensity, respectively. By plotting $\log q_e$ against $\log C_e$, linearization of the equation is obtained.

$$q_e = K_f C_e^{1/n} \quad (4)$$

The data can be described well by Freundlich model for boron and arsenic with R-square, which is 0.9488 for boron and 0.9706 for arsenic in Fig. 6, better than Langmuir isotherm fits. The better fitting of Freundlich is attributed to the fact that Freundlich isotherm is an empirical equation based on adsorption by heterogeneous surfaces like the aquatic booster surface, while Langmuir model assumes that the adsorption of metals occurs on a more homogeneous surface. Moreover, they are both frequently suitable and used for short-term and mono component adsorption process by different materials [23]. Table 1 lists the isotherm constants calculated from plots.

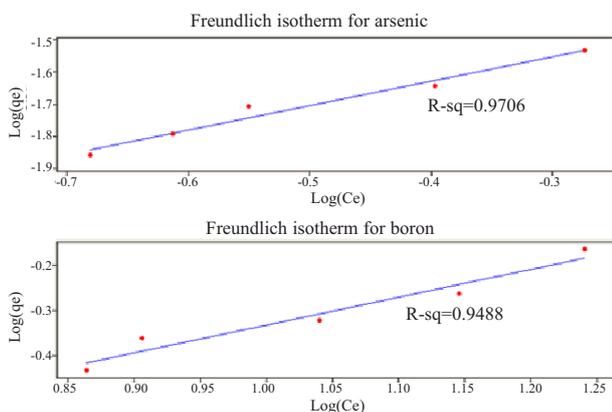


Fig. 6. Freundlich adsorption isotherms for arsenic and boron.

Conclusion

Aquatic booster can adsorb boron and arsenic in petrochemical wastewater with particle size of 0.60 mm, and it gives the highest removal efficiency compared to particles of larger sizes. The amounts of boron and arsenic adsorbed increase with decrease in particle size. The particle size of adsorbent is an essential factor for the enhancement of the removal of arsenic and boron. The efficiency of aquatic booster in removing arsenic and boron increases along with increase in adsorbent dosage, but it will approach the equilibrium. Optimum dosage appropriate for boron removal is 35 g/L and 45 g/L for arsenic. And it finds that the greater the amount of aquatic booster was added, the less the removal rate is enhanced. The equilibrium of contact time for boron to achieve is at 390 minutes, almost the same for arsenic. The superior parameters for removal percentage of 60.36% for boron are 35 g/L dosage, 80 rpm 390 minutes contact and 0.60 mm particle size. As for arsenic, the superior conditions for removal percentage of 71.83% include 0.6 mm size of particle, 300 minutes contact, 80 rpm agitation speed and 45 g/L dosage. Moreover, increase in agitation speed also can raise the removal percentage to 100 rpm. Boron and arsenic adsorption isotherms are better described by the Freundlich model.

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