Adsorptive Behavior of Arsenic(III) Ions from Aqueous Solution onto Forestry and Agricultural Waste Biochar Pyrolyzed at 400°C

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Abstract

Sorption capacity of two different biochar (saw dust and rice straw) was evaluated in the recovery of arsenic from aqueous solutions. Biochar from rice straw and saw dust were obtained from pyrolysis of biomass at 400°C. The optimum sorption conditions were studied for different concentrated monometallic system. Sorption studies were performed at different pH, contracting time and different initial metal ion concentration in the batch mode. The optimum pH was 3 for recovery of As(III) and kinetic studies yielded an optimum equilibrium time of 50-60 minutes with an adsorbent dose of 1 g/L and initial concentration ∼20 mg/L for As(III) ions. As(III) ions in aqueous solution were transported to biochar surface through adsorption and intra-particle diffusion process. Experimental data for As(III) ions was fitted a Langmuir model with R^2 value for As(III) 0.969, 0.879 for saw dust and rice straw respectively. The Freundlich constant, K_F values for removal of As(III) ions by saw dust and rice straw were 0.9127, 0.8951 respectively. The 1/n value for arsenic ions obtained from saw dust and rice straw were 0.209, 028 and indicate the normal sorption of As(III). The values indicated the affinity of the sorbent towards the uptake of As(III) ions were favorable and rice straw and saw dust biomass can be used to remove Arsenic(III) ions from aqueous phase.

Keywords: *biochar, adsorption capacity, heavy metals, Arsenic(III)*

Introduction

Recent years, biosorption methods were extensively used for removal of heavy metals from aqueous phase since such methods have been proven to be an efficient technique for the sequestration of pollutants in wastewater . Such methods are usually low cost as the absorption materials are mostly by-product of agricultural and other industrial wastes. Most of the studies related with biosorption were aiming towards the optimizing different physicochemical parameters to obtain the highest removal efficiency while

the others were concerned the biosorption mechanism. From among these low cost biosorption materials, application of biochar is becoming extremely popular due to their high sorption capacity and availability of materials in almost unlimited amounts . Biochar, that pyrolyzed from biomass under no or very low oxygen condition are mostly stable and having a superior ability to retain heavy metals. Therefore such materials are beneficial in decreasing the bioavailability of pollutants and mitigate their ecological toxicities . Biochars made from agricultural wastes, including fruit peels , pine needles , grass , hardwood , crop straw and woodchip have been widely investigated for removing toxic heavy metals from aqueous solution replacing costly chemisorption methods.

From among different biochars obtained from agricultural byproducts, sawdust and rice straw are used extensively for heavy metals sequestration studied. Sawdust in their raw or burned form were shown excellent adsorptive behavior for heavy metals such as Cu, Pb, Cd and Ni from aqueous solution . Waste rice straw was also used as a biosorbent to remove heavy metals such as Cu(II), Zn(II), Cd(II) etc. from contaminated water and have shown excellent adsorptive behaviors .

Inorganic arsenic that exist in different oxidation states are highly toxic when present in water . The most important inorganic species are arsenite (AsO_3^{3-}) and arsenate (AsO_3^-), referred to as arsenic (III) and arsenic (V). The pentavalent arsenic is most stable in oxygen-rich aerobic aqueous environments while trivalent arsenite is predominate in moderately reducing anaerobic environments such as in deep groundwater. As(III) is more toxic and more mobile than As(V) . Arsenic compounds are widely used as pharmaceuticals, agrochemical, and wood preservation. It is also apply in light emitting diodes (LED), glass making and semiconductor industries and wastewater of such industries may contain high content of As . The World Health Organization (WHO) guideline of 10 ppb (0.01 mg/L) has been adopted as the drinking water standard for As. Arsenic is a well known carcinogen but also attack other organs in the human body .

Since As species is highly toxic when present in water bodies, more attention were given to remove such contaminants using commonly available materials such as biochars from agro and other industrial wastes. This study was aimed to investigate the efficiency of different bio-residues to remove arsenic (III) from contaminated water. Biochar that produced from sawdust and rice straw were used as the adsorptive material in this study. Pyrolyzing temperature was selected as 400°C since it considered as an optimal condition that producing biochar for effective sorbent .

Materials and Methods

The biochars used in this work were obtained from rice straw (*Oryza sativa* L.) and from saw dust (*Artocarpus heterophyllus*). Rice straw was collected from the field and then chopped into small pieces (< 2mm). Saw dust was collected from wood mills. All materials were then dried in air for 48 hours. The pyrolysis was performed in a small stainless steel pyrolyser vessel (1200 cm^3) with a screw tight lid that fixed with 2 mm diameter steel tube. Pyrolyser was filled with material and flushed with nitrogen gas prior to plug the lid. The pyrolyser was kept inside a pre-heated (100 ± 5 °C) muffle furnace (Thermolyne- type 6000). Pyrolysis temperature was raised to 400 °C at a rate of approximately 20 °C min^{-1} and held constant for four hours. After heating for 4 hour at 400 ± 5 °C, the pyrolyser was quickly taken out from the muffle furnace and was rapidly quenched in a distilled water bath at room temperature.

Pyrolyzed materials were then washed thoroughly with deionized water in order to remove any remaining dirt. Dried material were then grounded and mechanically sieved to a particle size of <0.125 mm that were used for the adsorption experiments. Adsorption experiments were carried out by using batch technique to obtain equilibrium data that were performed at different pH, contacting time and initial concentrations to obtain equilibrium isotherms for known concentrations of As(III) solutions. A stock solution of 1000 mg/L As(III) were prepared using As(NO$_3$)$_3$ and diluted to various initial experimental concentrations. The experimental procedure was done as follows: 0.1 g of the powdered samples was shaken with 100 ml of a metal ion solution whose concentration was 5 mg/L. All adsorption experiments were performed at room temperature (27±1.0°C) and 0.1 g of biochar were added to 250-ml Stoppard flasks containing 100 ml As(III) solutions and agitated at 600 rpm. All batch isotherm tests were replicated three times and all the observations were recorded in triplicate and average values are reported. The solutions were then filtered using 0.45 μm nylon fiber membrane filters and the total As(III) concentration in solution was determined by hydride generator atomic absorption spectrophotometer.

To observe the effect of pH for the adsorption, the solution pH were change from 3.0 to 9.0 using either 0.1 M NaOH or 0.1M HCl. Initial concentrations of solution were set from 5 mg/L to 30 mg/L in order to evaluate the effect of initial concentration for the adsorption on to biochar.

Large-scale adsorption processes for water treatment demand inexpensive, nontoxic, available adsorbents of known kinetic parameters and sorption characteristics. Therefore the knowledge of optimal conditions would be enabling a better process design and modeling. Thus absorption experiment variables were set as a function of initial pH of the solution, contact time

and initial metal concentrations in order to obtain the optimum adsorption conditions. After selecting the optimum conditions, the amount of As(III) removed or adsorbed and the removal percentages (%) of As(III) were calculated using mass balance equations;

$$q = \frac{(C_0 - C_f)v}{m}$$

----------(1)

$$Removal\ Percentage\ (\%) = \frac{(C_i - C_f) \cdot 100}{C_i}$$

----------(2)

where the q is the amount mg/g of As(III) adsorbed, C_0 and C_f are the initial and final concentrations of As(III) (mg/L), V is the volume of solution and m is the weight of the biochar used for the experiment.

Results and Discussion

Influence of contacting time to As(III) ions

It was observed that adsorption capacity about 6.8 mg/g of As(III) ion from saw dust biochar was attained in first 35 minutes and concentration became almost constant after 40 minutes (Figure 1). Adsorption of arsenic onto rice straw biochar was optimum around 50 minutes duration and adsorption capacity was 5.7mg/g.
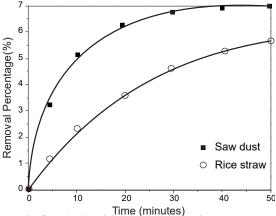

Figure 01: Removal of As(III) with Contacting Time

The fast initial uptake was observed for As(III) ions onto saw dust biochar surface due to more functional groups in the biomass. More time was consumed on diffusion of metal ions to binding sites which remains in rice straw biochar. It was concluded that 50 minutes was sufficient for sorption to attain equilibrium.

Effect of pH on As(III) adsorption

The pH of a solution consider as an important parameter in the adsorption of As (III) ions onto various adsorbents. The effect of pH on the adsorption of As(III) ions onto biochars were investigated at initial pH ranging from 3.0 to 9.0. The results revealed that As(III) adsorption by biochars were highly pH-dependent. The amount of As(III) adsorption on to rice straw biochar was increased with decreased in pH values. The effect of pH values on As(III) adsorption was more evident when rice straw biochar was used as adsorbent compared to that of sawdust (Figure 2). For instance, As(III) removal percentage (%) for rice straw biochar was 53 at the pH of 3 and decreased to 17 at the pH of 7 when initial concentration was 10.55ppb, whereas for sawdust the values were 35 at the pH of 2.5 and increased upto 59.9 at the pH of 7.
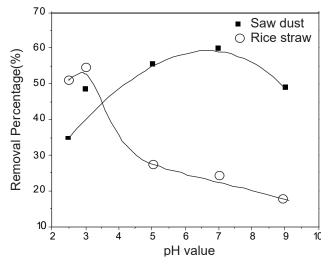

Figure 02: Variation of Removal Percentage(%) of As(III) with pH

For the As (III), the sorptions were 53% and 59% for biochars from rice straw and sawdust respectively. When pH close to 5, the binding sites of sawdust biochar became negatively charged due to presence of amino groups on the surface hence, the higher removal was recorded. Higher adsorption of As(III) ions onto rice straw biochar at lower pH may be due to attracting AsO_3^{3-} ion onto higher positively charged metal binding sites.

Influence of initial ion concentration on As (III) adsorption

Removal percentages of arsenic ions onto saw dust and rice straw biochar were gradually increased with increased initial concentration of the metal solution (Figure 3). It was observed as a general trend that there is a decrease of the removal percentage with increase in initial concentration from 22 mg/L. These results may be explained on the basis that the increase in the number of

ions competing for the available binding sites and also because of the lack of active sites on the adsorbent at higher concentrations.
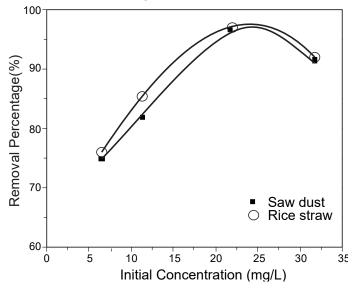

Figure 03: Variation of Removal Percentage(%) of As(III) ions with Initial Ion Concentrations

Sorption dynamics of As (III) ions

Kinetics of adsorption is an important characteristic in defining the efficiency of adsorption. In order to explain the kinetics of biosorption pseudo second order kinetics model also was applied.

$$\frac{dq_t}{dt} = K_2(q_e - q_t)^2 \frac{dq_t}{dt} = K_2(q_e - q_t)^2 \qquad \text{------------------ (3)}$$

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e}\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e}t \qquad \text{------------------ (4)}$$

Where, K_2 is the pseudo-second order rate constant. The slope and intercepts of the plot of t/q_t vs t (Figure 4) for adsorption of As (III) ions on saw dust and rice straw biochar were used to determine the value of K_2 and q_e respectively. Values of correlation coefficient (R^2) and calculated values of K_2 and q_e were (Table 01) indicated that pseudo-second order model is suitable to explain our experimental data. Values of K_2 for removal of As(III) ions for rice straw and saw dust biochar were 0.086 and 0.004.
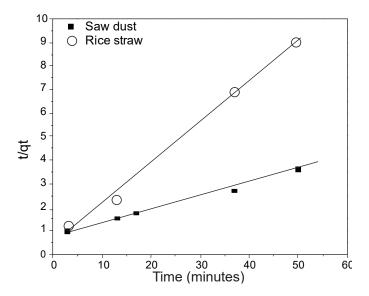
Figure 04: The graph of Time t vs t/qt for As(III) ions

Table 01: Isotherm Parameters of different isotherms

isotherm models	Parameters	Rice straw	
		As (III)	As (III)
Pseudo 2nd	K_2	0.004	0.086
	q_e	1.38	5.78
	R^2	0.998	0.998
Langmuir	K_L	2.19	12.07
	q_{max}	8.89	9.09
	R^2	0.814	0.969
	R_L	0.995	0.999
Freundlich	K_F	0.0018	0.0137
	N	0.491	0.714
	R^2	0.987	0.990

Adsorption Mechanism

Also the metal ions can be transported from aqueous phase to the solid phase by the intra-particle transport phenomenon. The intra-particle transport is supposed to be the rate controlling step. The rate of particle transport through this mechanism is slower than adsorption on the exterior surface site of the adsorbent. The amount of adsorbed species varies proportionately with a function of retention time. The equation can be expressed as .

$$q_e = K_d t^{1/2} + C q_e = K_d t^{1/2} + C \qquad \text{-------------(5)}$$

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Where K_d is the constant coefficient, the initial rate of intra-particular diffusion (mg/L. $min^{1/2}$). The transport of the adsorbents in aqueous solution through the biochar particle interface into the pores of the biochar particles, surface of the adsorbents, is responsible for adsorption.

Figure 5 illustrates the diffusion of As(III) ions within the saw dust and rice straw biomass as a function of time and shows that intra-particle diffusion occurred in adsorption process for saw dust and two stages for rice straw. The arsenic ions diffused quickly among the saw dust particles till the end. But it showed that the adsorption process at the beginning for movement of ions through rice straw particles and then intra-particle diffusion slowed till end. The slight deviation of these lines from origin indicates that As(III) removal controlled by both physical and chemical process.
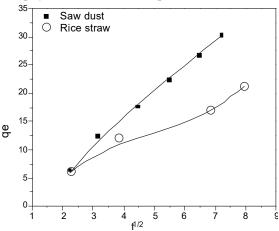

Figure 05: The graph of qe vs $t^{1/2}$ for As(III) ions

Conclusion

The results of this study reveals that the percentage removal of As(III) ions were dependent on the pH of the solution and the initial metal concentration. The contact time necessary for maximum adsorption was ranged between 50-60 minutes for both materials. The optimum pH was 3 for recovery of As(III) ions. Kinetic studies yielded an optimum equilibrium time of 50 minutes with an adsorbent dose of 1 g/L and initial concentration ~20 mg/L for both ions. It can be concluded that metal ions in aqueous solution were transported to biochar surface through adsorption and intra-particle diffusion process. The sorption values indicated the affinity of the sorbent towards the uptake of As(III) ions and adsorptions of the metal ions were favorable.

Acknowledgement

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