

Removal of Arsenic(III) from Aqueous Solutions by Used Black Tea Leaves

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Abstract

The present work investigates the possibilities of used black tea leaves (UBTLs) without any pretreatment in the removal of As(III) from aqueous solutions. Adsorption column with UBTLs have been used in the removal of arsenic(III) under various conditions: adsorbent amount, particle size, treatment flow rate, initial arsenic(III) concentration, and pH. No secondary-pollution problem will arise, as desorption of the arsenic (As) is possible. It is observed that UBTLs have good potential in the removal of arsenic from aqueous solutions. Few experiments with real life As contaminated ground water samples show arsenic removal upto 90%. The present study might provide new avenues to achieve the arsenic concentrations required for drinking water standards recommended for Bangladesh by WHO.

Keywords: Adsorption; Arsenic(III); Used black tea leaves; Column method; Groundwater

I. Introduction

Arsenic (As) contamination is one of the most challenging environmental problems today. Millions of people worldwide are affected by As-contaminated groundwater as it is their only source of drinking water¹. Elevated concentrations of arsenic in groundwater are found in many countries such as Bangladesh, India, Vietnam and Chile². Increased usage of As contaminated groundwater for drinking has caused serious health problems^{3,4}. Furthermore, it is reported⁵ that As acts as an endocrine disruptor at very low concentrations. In the recent past, because of its high nuisance value various regulatory agencies have revised the maximum contaminant level of arsenic in drinking water from 50 µg/L to 10 µg/L^{6,7}. This situation demands the development of simple, low cost methods for the removal of As from groundwater.

Two forms of arsenic are common in natural waters: arsenite (AsO_3^{3-}) and arsenate (AsO_4^{3-}) referred to as As(III) and As(V). The As(V) species exists as oxyanions (H_2AsO_4^- and HAsO_4^{2-}) at neutral pH, whereas the predominant As(III) species is neutral H_3AsO_3 ^{8,9}. As(III) is more toxic and more difficult to remove with the conventionally applied physicochemical treatment methods than As(V). Therefore, a preoxidation step is usually required to transform the trivalent to the pentavalent form. The oxidation procedures are performed by the addition of chemical reagents, such as potassium permanganate, chlorine, ozone, hydrogen peroxide, or manganese oxide^{10,11}. Although these reagents are effective for the oxidation of trivalent arsenic, they can also cause several secondary problems, arising from the presence of residual reagents and the formation of side products. This process can result in a significant increase in operating costs. So, As(III) is selected as the removal target in this study.

The principal methods¹²⁻¹⁶ used for arsenic removal from contaminated water sources are coagulation/direct filtration, ion exchange, adsorption on iron oxides or on activated alumina, iron-oxide coated sand and reverse osmosis. Of these, the adsorption techniques¹⁷ are simple and convenient and no need for complicated regeneration process. Few studies have been reported regarding sorption of different metal ions using UBTLs^{18,19}. The present work investigates the possibility of the use of UBTLs without any pretreatment as an effective adsorbent for removing As(III)

from aqueous solutions in a single-step column operation. Finally the proposed method was applied for the removal of total arsenic from the highly real arsenic contaminated groundwater for drinking water.

II. Materials and Methods

All reagents used throughout this work were of AR grade. Potassium arsenite (KAsO_2) was procured from Wako Pure Chemical Industries Ltd., Osaka, Japan, and NaOH, KOH, HCl, HNO_3 , and H_2SO_4 were obtained from Nacalai Tesque Inc., Kyoto, Japan. Stock solutions (1000 mg/L) of As(III) were prepared in distilled pure water from solid KAsO_2 . Dilute fresh standard solutions were prepared daily before use. Water was purified using an ultrapure water system (Advantec MFS, Inc., Tokyo, Japan) resulting in a resistivity of $>18 \text{ M}\Omega \text{ cm}$.

UBTLs used in the present investigation were obtained from local market after extracting tea liquor from fresh black tea leaves. The material was then boiled in distilled water for 8 h. Elemental analysis shows that UBTLs contain 65.3 % carbon, 32.2 % oxygen, 0.1% calcium and less than 0.1% sulphur and phosphorus^{18, 19}. The collected UBTLs were washed with pure water several times to remove dust and fines. The washing process was continued till the wash water contains no color. The washed materials were then dried in a hot-air oven at 105 °C for 24 h. The dried material was sieved and 780 µm, 510 µm, 390 µm, 525 µm and 250 µm fractions were separated for the adsorption studies. The materials were then stored in polyethylene bottles (high density) and used for the removal of As(III) without any other physical or chemical treatment.

UBTLs were added to the adsorption column (2 x 30 cm) made of glass. After the pH had been adjusted to the desired value with HCl and NaOH solutions, the sample solution (100 mL) containing 100 µg/L As(III) were passed through the adsorption column at a given flow rate. The adsorption experiments were carried out in columns that were equipped with a stopper for controlling the column eluate flow rate (treatment rate). The experiments were accomplished at room temperature. Each experiment on the removal of As(III) was repeated more than five times. A graphite furnace atomic absorption spectrometer (GFAAS) (GFS 97, Thermo Electron Corp., England) was used for the determination of arsenic. The removal (adsorption) efficiency was calculated using the equation¹⁷

removal (adsorption) efficiency = $(C_0 - C_e)/C_0 \times 100$ (1)

where C_0 and C_e are the concentration of As(III) in the sample solution before and after treatment, respectively. The total As were measured by GFAAS using nickel nitrate (10 mg/L)¹⁷ as a matrix modifier.

III. Results and Discussion

For a comparison, we have taken used news papers (UNPs) as another adsorbent. The performance of two adsorbents (UBTLs and UNPs) was evaluated for the removal of As(III) from aqueous solutions. Preliminary studies showed that the As(III) removal efficiencies with UBTLs and UNPs were 57% and 18%, respectively, under the following conditions: initial concentration, 100 $\mu\text{g/L}$; amount of adsorbents, 2 g; average particle size, 780 μm ; and treatment flow rates, 6.7 mL/min. As UNPs show rather low removal efficiencies as compared to UBTLs, the UNPs are not considered further in the present study.

Effect of adsorbent amount on As(III) adsorption

The effect of the amount of UBTLs on the removal of As(III) was studied by varying the amount of UBTLs under the reported experimental conditions. The results are illustrated in Figure 1. The removal efficiency of As(III) is increased gradually with the increasing amount of UBTLs. The result indicates that the adsorption capacity of UBTLs very much depends on the surface activities. Surface interaction increases with specific surface area which is readily accessible to the arsenic species. It was expected that increasing UBTLs amount would increase removal capacity of As(III).

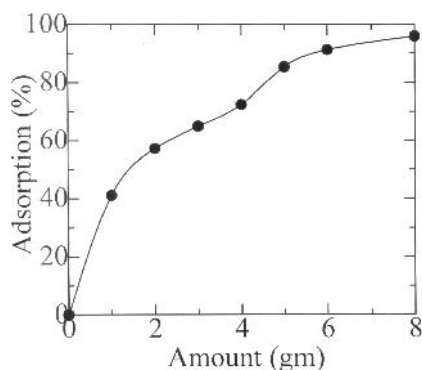


Fig. 1. Effect of adsorbent amount on the removal of As(III) by adsorption onto UBTLs.

Initial As(III) concentration, 100 $\mu\text{g/L}$; average particle size, 780 μm ; treatment flow rate: 6.7 mL/min.

Effect of particle size on As(III) adsorption

The column adsorption experiments were carried out for the removal of As(III) from aqueous solution using five different particle sizes (average diameters of 225, 325, 390, 510, and 780 μm). These findings are presented in Fig. 2. The figure shows that the highest removal capacity is achieved within the particle size range between 225 to 300 μm . Within 300–400 μm range, the percent adsorption falls and attains a plateau around 60%. These data show that a decrement in particle size increases the percent adsorption of As(III). This fact is in agreement with an earlier

communication where it is reported that when the size of particles increases, metal ions adsorption decreases¹⁷. Similar trends have also been reported by Wong et al.²⁰. These phenomena might be due to the fact that the smaller particles offer comparatively large surface areas and greater numbers of adsorption sites.

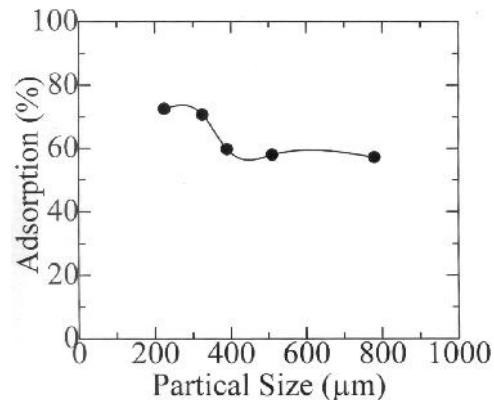


Fig. 2. Effect of particle size on the removal of As(III) by adsorption onto UBTLs.

UBTLs amount, 2 g; Initial As(III) concentration, 100 $\mu\text{g/L}$; treatment flow rate, 6.7 mL/min.

Effect of flow rate on As(III) adsorption

The effect of the treatment flow rate on the removal of As(III) are illustrated in Figure 3. The flow rate is varied to achieve the maximum removal of the adsorbates, and it is observed that the removal decreases with increasing flow rate. In other words, the removal efficiency for As(III) gradually increases with decreasing flow rate down to 0.6 mL/min. 70% removal of As(III) with 2 g of UBTLs was observed at 0.6 mL/min.

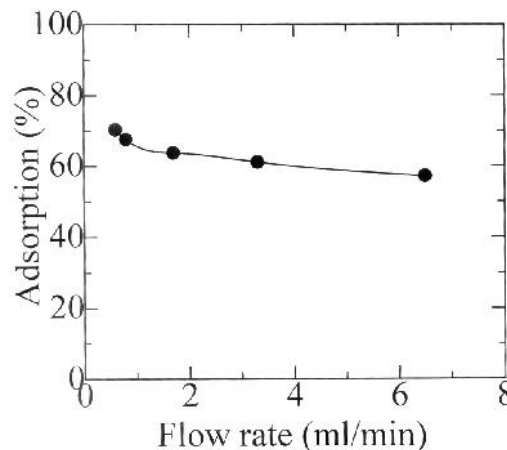


Fig. 3. Effect of treatment flow rate on the removal of As(III) by adsorption onto UBTLs.

UBTLs amount, 2 g; average particle size, 780 μm ; Initial As(III) concentration, 100 $\mu\text{g/L}$.

Effect of initial As(III) concentration

The removal efficiency is highly dependent on the initial concentrations of As(III) in the sample solution. The effect of variation of initial As(III) concentration (50–400 $\mu\text{g/L}$) on the removal by UBTLs is illustrated in Figure 4. Perusal of Fig. 4 reveals that the removal efficiencies decrease with increasing adsorbate concentration of the solution. This is

due to the fact that in lower concentration, the adsorbate could adequately occupy the active sites on the carbon surface. However, with the increase in adsorbate concentration, the number of active adsorption sites is not enough to accommodate arsenite ions.

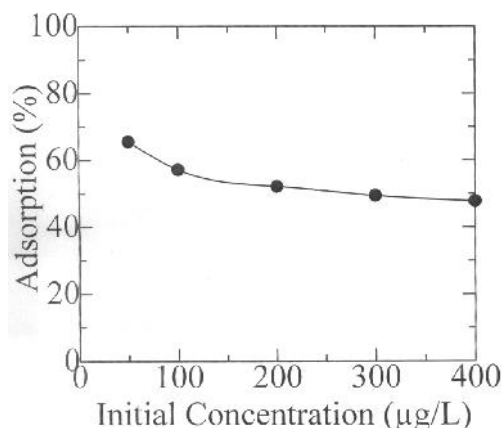


Fig. 4. Effect of initial adsorbate concentration on the removal of As(III) by adsorption onto UBTLs.

UBTLs amount, 2 g; average particle size, 780 µm; treatment flow rate, 6.7 mL/min.

Effect of pH on As(III) adsorption

pH is one of the most important parameters controlling the metal ion sorption process^{21,22}. Figure 5 depicts the effect of pH on As(III) removal with UBTLs. The effect of pH on As(III) adsorption by UBTLs was studied throughout the pH range between 3 and 14. It is observed from the figure that % adsorption increase with pH, reaches a maximum at pH 7.5 and then decreases sharply upto pH 12. The decrease in As(III) removal at high pH could be attributed to the interionic repulsion of the different types of oxyanions of arsenic and hydroxyl ions. These results show that As(III) are not favorably removed by UBTLs in basic medium above pH 8.5. The maximum removal efficiencies for As(III) were observed in the neutral region (at pH 7.5, Fig. 5). These results should be of immense importance to the practical implementation of arsenic removal from groundwater.

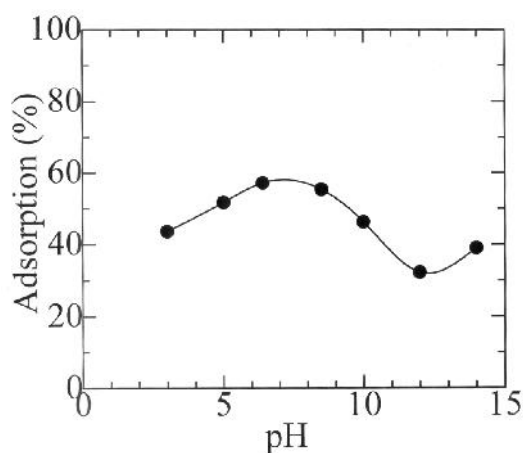


Fig. 5. Effect of pH on the removal of As(III) by adsorption onto UBTLs.

UBTLs amount, 2 g; average particle size, 780 µm; treatment flow rate, 6.7 mL/min; Initial As(III) concentration, 100 µg/L.

Desorption

Recovery of the adsorbed material as well as the regeneration of adsorbent is also an important aspect in the realm of wastewater treatment. Attempts were made to desorb As(III) from UBTLs surface with a number of eluents, such as acids like HCl, H₂SO₄ and HNO₃ and bases like NaOH and KOH. 50 mL volume of each eluent were poured into the column and allowed to stand for fixed time, and then passed through the column under gravity. This desorption process was performed using batch method. The results are presented in Table 1. Lorenzen et al.²³ have reported that arsenic elution can be achieved by using either strong acidic or alkaline solutions. In the present study, it is observed effective desorption with alkaline solutions (Table 1). These findings are consistent with the results observed for the effect of pH. In general, desorption of As(III) increases with increasing desorption time. Among the desorption agents used, KOH shows highest desorption capacity for As(III) from the surface of UBTLs.

Table 1. Influence of the eluent on the desorption of As(III)

Desorption agent	Standing time (h)	Desorption % of As (III)
KOH (1 M)	8	61.5
	16	62.0
	20	69.0
	36	70.0
KOH (2 M)	8	59.0
	12	62.5
	18	66.5
	24	69.0
NaOH (1 M)	8	49.0
HCl (1 M)	8	13.0
HNO ₃ (1 M)	8	7.0
H ₂ SO ₄ (1 M)	8	12.0

Adsorption process: initial As concentration, 100 µg/L; UBTLs, 20 g; average particle size, 780 µm; treatment flow rate, 6.7 mL/min; efficiency, 79%.

Desorption process: Volume of desorption agent, 50 mL

Application of the developed treatment system

It has been reported²⁴ that the total arsenic concentration in the tubewell water samples (which were collected from Sonargaon, Dhaka, Bangladesh) is in the range 0.25-1 mg/L, with 60-90% of the arsenic present as As(III) species. The utility of the waste UBTLs were tested with another two real life As contaminated groundwater samples from Sonargong, Dhaka, Bangladesh. The concentrations of total arsenic in the samples were 270 and 595 µg/L. The treatment results are presented in Table 2. 30 g of adsorbent was applied in the treatment. The concentrations of arsenic in the treated water samples could be lowered to 50 and 59 µg/L. The desorption efficiencies with 100 mL of 1 M KOH were 55% and 49%. These results show that the arsenic could be successfully removed from practical As-contaminated groundwater, and the adsorbed As could be recovered from the surface of UBTLs.

Table 2. Removal and desorption of As from the contaminated groundwater

	sample 1	sample 2
pH	7.8	7.6
initial As concentration ($\mu\text{g/L}$)	270	595
final concentration ($\mu\text{g/L}$)	50	59
removal ^a (%)	81	90
desorption ^b (%)	55	49

^aRemoval: UBTLs amount, 30 g; average particle size, 780 μm ; flow rate, 0.6 mL/min.

^bDesorption: 1 M KOH, 100 mL; standing time, 8 h.

IV. Conclusions

The proposed column treatment system might be appropriate and suitable towards home made approaches for arsenic removal in the rural areas due to its simplicity, ease of operation and handling, and regeneration capacity. The present method is effective for a wide range of concentrations (i.e., 50-400 $\mu\text{g/L}$), which are within the range to those generally observed in contaminated Bangladeshi groundwater and wastewater. The proposed cost-effective As removal technique using UBTLs is quite appropriate and safe in the sense that no other harmful chemicals or substances are introduced into the water while arsenic is being removed. Further study is in progress in order to achieve the arsenic concentration required for drinking water recommended by WHO and the full regeneration process of adsorbent.

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