Use of Activated and Modified Pumice Stone for Removal of Mercury (II) and Arsenic (III) Ions from Aqueous Solution

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Abstract

The removal of Hg (II) and As (III) ions from aqueous solutions using activated and modified pumice stone was investigated. The pH, temperature, and initial metal ion concentration, which are very important for removal studies, were investigated by batch method. The experiments showed that the equilibrium adsorption data fit well with the Freundlich isotherm model well for Hg (II) and As (III) ions. The negative values of $\Delta H^{\circ} = -$ 199.92 kJ mol⁻¹ and -78,15 kJ mol⁻¹ for mercury (II) and arsenic (III) ions indicate that the adsorption process is exothermic. ΔS° was calculated as -267.85 J K⁻¹ mol⁻¹ for As (III) ions and the positive value of $\Delta S^{\circ} = 0.69$ kJ K⁻¹ mol⁻¹ for Hg (II) ions. The negative value of ΔG° = -405.14 kJ mol⁻¹ for Hg (II) ions and -1.67 kJ mol⁻¹ for As (III) ions indicates that the adsorption is spontaneous. EDTA was found to be a good desorbent in desorption studies for the recovery of arsenic and Hg ions. The experiments show that pumice stone can be used for the removal of Hg (II) and As (III) in aqueous solution.

Keywords Adsorption, Arsenic, Mercury, Pumice stone, Wastewater

Sulu Çözeltiden Cıva (II) ve Arsenik (III) İyonlarının Uzaklaştırılması için Aktifleştirilmiş ve Modifiye Edilmiş Pomza Taşının Kullanımı

Öz

Aktifleştirilmiş ve modifiye edilmiş pomza taşı kullanılarak sulu çözeltilerden Hg (II) ve As (III) iyonlarının giderimi araştırılmıştır. Giderim çalışmaları için çok önemli olan pH, sıcaklık, başlangıç metal iyonu konsantrasyonu kesikli yöntemle araştırılmıştır. Deneyler, denge adsorpsiyon verilerinin Hg (II) ve As (III) iyonları için Freundlich izoterm modeline iyi uyduğunu göstermiştir. Cıva (II) ve arsenik (III) iyonları için $\Delta H^{\circ} = -199.92$ kJ mol⁻¹ ve -78,15 kJ mol⁻¹ değerlerinin negatif olması adsorpsiyon sürecinin ekzotermik olduğunu göstermektedir. ΔS°, As (III) iyonları için -267,85 J K-1 mol-1 ve Hg (II) iyonları için ΔS° = 0,69 kJ K⁻¹ mol⁻¹ pozitif değeri olarak hesaplanmıştır. Hg (II) iyonları için ΔG°=-405.14 kJ mol⁻¹ ve As (III) iyonları için -1.67 kJ mol-1 negatif değeri adsorpsiyonun istemli olduğunu göstermektedir. Arsenik ve Hg iyonlarının geri kazanımı için yapılan desorpsiyon çalışmalarında EDTA'nın iyi bir desorbent olduğu bulunmuştur. Deneyler, pomza taşının sulu çözeltide Hg (II) ve As (III) giderimi için kullanılabileceğini göstermektedir.

Anahtar Kelimeler: adsorpsiyon, arsenik, cıva, pomza taşı, atık sular

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1. Introduction

Hg, a liquid metal, and organic mercury compounds (i.e. methylmercury chloride [MeHg(I)], C_2H_5CHg , Me₂Hg and C_6H_5CHg) have toxic effects on both the environment and humans [1]. Even at very low concentrations, mercury is hazardous to living organisms due to its accumulation in the food chain. Accumulation in animals and humans poses serious risks. The distribution of Hg in the environment is due to industrial activities such as mining, use of fossil fuels, use of mercury-containing raw materials containing mercury [2]. According to the European Union, the maximum permissible limit for mercury in drinking water is $1\mu g L^{-1}$ and the limit for wastewater discharge is $5\mu gL^{-1}$, as Hg (II) is considered a priority and hazardous pollutant [3]. Hg has adverse health effects such as direct effects on the central nervous system and kidney system, developmental movement and brain function disorders, muscle weakness, chest pain, shortness of breath, diarrhoea, vomiting [4,5]. Because of its high toxicity, mercury (As (III)) is receiving increasing attention worldwide. As (III) causes very serious problems in the body such as aspigmentation disorder, skin thickening, stomach pain, skin, lung, bladder and kidney cancer, and neurological disorders [6,7,8,9].

In the last century, the provision of clean water to people has become the most serious environmental problem due to the contamination of surface and wastewater with toxic metals [10]. Therefore, it is of great importance to carry out various studies to remove toxic metals such as Hg (II) and As (III) from water. It has also been reported that Hg (II) and As (III) have been removed from surface waters by various methods [3-11]. In recent years, several low-cost natural or modified mineral sorbents, such as activated alumina, red mud, quartz and fly ash, etc., have been investigated for the removal of toxic metals from water by adsorption [12]. One such inexpensive material is pumice. Pumice stone (PS) is a lightweight volcanic rock with a pore volume of up to 85% formed during explosive eruptions [13]. As pumice is an inexpensive, naturally abundant and porous material with a large surface area, it is thought to be very suitable as an adsorbent [14,15]. PS was activated with H₂SO₄ (APS). For the removal of As (III), PS was modified with FeCl₃ + pumice, $FeCl₃ + NaOH (MPS)$. In this study, activated pumice stone (APS) and modified pumice stone MPS were investigated for the removal of Hg (II) and As(III). Several studies were carried out on the effect of agitating time, pH, temperature, initial concentration, isotherms, and kinetics on adsorption. Freundlich and Langmuir isotherm models were applied to elucidate the adsorption. Desorption studies were carried out for the to evaluate the possible metal recovery from APS and MPS by EDTA, HCl and HNO₃. Surface morphology characterization was carried out by FTIR and SEM analysis. These results indicate the possibility of using APS and MPS for the removal of Hg (II) and As (III) ions in aqueous solution.

2. Materials and Methods

2.1.Reagent

All reagents were of analytical grade. Hg was purchased from Merck, $HNO₃$ (Merck), $K₂Cr₂O₇$ (Carlo Erba), DW (Milipore), SnCl2 (Merck), As2O3 (Merck), NaOH (Sigma-Aldrich), NaBH⁴ (Merck), Na₂HPO₄ (Merck), NaH₂PO₄ (Merck), NH₃ (Merck), NH₄Cl (Merck).FeCl₃(Merck).1g

of Hg was dissolved in 10 mL of concentrated HNO₃, 0.3 mL of 5% K₂Cr₂O₇ solution was added to prevent adsorption of glass and diluted to 1 L with DW to give 1000 mgL^{-1} of Hg (II) solution. Dilutions of 1000 mg L^{-1} solution were made to obtain standard solutions for Hg (II) measurements. 3% w/v solution of SnCl₂ solution was freshly prepared to reduce Hg (II) ions. To prepare a 1000 mg/L As (III) stock solution, 0.3301 ± 0.0002 g As₂O₃ was weighed. After adding 10% NaOH until As₂O₃ dissolved, it was acidified with concentrated HCl solution. 1 g of NaBH₄ was dissolved in 0.5% NaOH solution, and the volume was made up to 100 mL with the same solution. This solution was freshly prepared for each analysis. The following buffer solutions were used at a concentration of 0.1 mol L^{-1} were used to adjust the pH: acetic acid/sodium acetate (pH 4.0–6.0), Na₂HPO₄-NaH₂PO₄ (pH 6.0-7.0) and NH₃-NH₄Cl (pH 8.0-9.0). The water used to prepare of the solutions and as carrier solution was DW. All glass containers were soaked in 10% nitric acid for 24 hours and rinsed with DW to remove Hg (II) and As (III) and to prevent crosscontamination.

2.2.Instruments

Hg (II) and As (III) concentrations were measured using a Varian 220 FS atomic absorption spectrophotometer (AAS). The AAS equipped with a Hg and As Hallow cathode lamp at the 253.7 nm, 217.6 nm wavelength was used for the determination of Hg (II) and As (III) in sample solutions. VGA-77 model hydride system with quartz cell was used for cold generation of Hg vapour and hybrid generation of arsine vapor. Hanna P211 microprocessor pH meter was used to measure the pH of the solutions.

2.3.Preparation of APS and MPS

PS samples were obtained from the Isparta region of Turkey. Prior to use in the experiments, the PS samples were crushed and sieved through a 200 mesh sieve. It was observed that some colouring substances in the structure of the adsorbents dissolved and leached into the water, and to remove this, they were washed and dried with DW until no longer gave off colour. PS was refluxed with 1 M 250 mL of H_2SO_4 at 80 °C for 8 hours, filtered, washed with DW, and dried to complete the activation process.10 grams of the washed PS was taken and treated with 0.5 M 50 mL FeCl₃ solution for 12 hours for arsenic (III) adsorption. FeCl₃ is a dark brown-yellow acidic crystalline substance (pH<3). FeCl₃ has good solubility in water and undergoes hydrolysis to hydrochloric acid and iron hydroxide when in solution. The other modification process for arsenic adsorption was carried out by taking 10 grams of adsorbent and using $0.5 M 25 mL FeCl₃$ and 0.2 M 25 mL NaOH solutions together. All modified adsorbents were decanted from the solution, washed with DW and dried.

2.4.Batch Adsorption Experiments

Adsorption experiments were performed using the batch technique. For Hg (II) adsorption, 0.10 \pm 0.02 g APS was added to a beaker containing 25 mL of 100 mg L⁻¹ Hg (II) solution and the suspension was mixed. For As (III) adsorption studies, 0.10 ± 0.02 g MPS was added to another beaker containing 25 mL of 50 mg L^{-1} As (III) and the suspension was mixed. After decantation, the concentration of Hg (II) and As (III) ions was analyzed by AAS using the vapour generation method. The effect of agitating time was studied at 5-150 min. for Hg (II) and 5-120 min for As

(III) ions. The effect of pH was studied in the pH range of 3.0-8.0 for Hg (II) ions and As (III) ions. Isotherm studies were performed with a constant APS and MPS weight of 0.10±0.02 g and varying initial concentrations in the range of $25-1000$ mg L⁻¹ for Hg (II) ions, 20-1500 mg L⁻¹ for As (III) ions. All the experiments were performed in duplicate.

The percentage adsorption of Hg(II) and As(III) ions on APS and MPS from aqueous solution was calculated according to equation (1):

% = − 100 … … … … … … ….………...…………………………………………… (1)

 C_{int} is the initial concentration of Hg(II) and As(III) (mg L⁻¹), C_{fin} is the final concentration of $Hg(II)$ and As(III) (mg L^{-1}).

2.5. Desorption and Regeneration Studies

When equilibrium was reached, the Hg (II) saturated APS and As (III) saturated MPS were decanted from the solution and placed in 50 mL beakers containing 25 mL (0.05-0.15 M) HCl, HNO₃ and EDTA solution and shaken at 150 rpm for 30 min at 35 °C. The APS and MPS were then decanted by centrifugation. The concentrations of Hg (II) and As (III) in aqueous solution were determined by CVAAS.

3. Results and Discussion

3.1 Characterizations Studies

3.1.1.FTIR spectroscopy

The FTIR spectra of the APS and MPS adsorbents are shown in Figure 1. The peak at 3545 cm⁻¹ in Figure $1(a)$ is related to the O-H stretching vibration [16]. The peaks at 1118 cm⁻¹ belong to the stretching vibrations of C-O [17]. The peaks at 2239 cm⁻¹ are characteristic bands belonging to the C-N bending vibration in Figure1(b), a peak at 800-400 cm⁻¹ can be associated with Si-O stretching [18], bending and Al-O stretching, bending and bending, respectively.

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Figure 1. The FTIR spectra of APS and MPS

a) APS b) MPS

3.1.2. Surface morphology

The differences in the scanning electron microscope images of Hg (II) and As (III) adsorbed and desorbed APS and MPS are shown in Figure 2. The surface variation in the SEM micrographs showed the structural changes in the adsorbent before and after the Hg (II) and As (III) adsorption process. The general morphology of the PS before adsorption and after desorption could be characterized as much asperity. It was found that the surfaces of the Hg (II) loaded APS and As (III) loaded MPS were found to be rough layered.

Figure 2. Scanning electron microscope images of PS, APS, MPS, Hg (II) and As (III) adsorbed and desorbed PS, APS and MPS a)Activated pumice stone b)FeCl3 modified pumice stone $(c)FeCl₃ + NaOH$ modified pumice stone (d) Hg (II) loaded activated pumice stone (e) As (III) loaded pumice stone f)As (III) loaded FeCl₃ pumice stone (g) As (III) loaded FeCl₃ + NaOH pumice stone (h) Hg (II) desorbed activated pumice stone (I) As (III) desorbed pumice stone i)As (III) desorbed FeCl₃ pumice stone, (j) $FeCl₃ + NaOH$ desorbed pumice stone

3.2. Effect of agitating time on sorption of Hg (II)and As (III) ions

Stirring time is one of the most critical parameters for the successful utilization of adsorbents [19,20]. Figure 3 shows the effect of agitating time on the adsorption of Hg (II) ions on APS. It can be seen that the percentage removal increases rapidly with increasing agitation time up to 120 minutes and measurements at 150 minutes show that equilibrium is reached after 120 minutes. Therefore, an optimum agitating time of 120 minutes was chosen for further studies. For the arsenic ion agitation time studies, 5, 10, 20, 30,40,60 and 120 minutes were determined (Figure 3). 50 mL of 50 mg L⁻¹ As (III) solution was added on 0.5 g of MPS (PS, FeCl₃ + PS, FeCl₃ + NaOH + PS) and stirred for the indicated times, and the solutions were filtered and analysed. The optimum was found to be 60 minutes for PS, $FeCl₃ + PS$, and $NaOH + FeCl₃ + PS$.

Figure 3. Effect of agitating time on sorption of Hg (II) and As (III) (0.10±0.02 g of APS, 25 mL of 100 mg L⁻¹ Hg (II) solution; 0.5 g of MPS, 50 mL of 50 mg L⁻¹ As (III) solution) (\bullet : PS, \blacktriangle : $FeCl₃ + PS$, \blacksquare : $FeCl₃ + NaOH + PS$, \blacklozenge : APS)

The adsorption capacities of PS and $FeCl₃ + PS$ are close to each other. When the adsorption capacities of PS, $FeCl_3 + PS$, $FeCl_3 + NaOH + PS$ were examined, it was found that the adsorption capacity of $FeCl₃ + NaOH + PS$ was higher. When NaOH is used, there is probably an adsorption mechanism in the form of (Fe-O-As) as the coordination of hydroxyl groups of ferrous hydro(oxides) with OH-ligands in the arsenite molecule [21]. Therefore, higher adsorption capacity was obtained when $FeCl₃ + NaOH + PS$ was used as adsorbent.

3.3. Effect of pH on sorption of Hg (II) and As (III) ions

In order to study the influence of pH on the adsorption capacity of APS for Hg (II), experiments were carried out with an initial concentration of 100 mg L^{-1} over the pH range 3.0–8.0 and the results are shown in Figure 4. During the pH experiments, analyses were carried out with and without adsorbent (blank). The maximum adsorption percentage of Hg (II) was observed at the pH 5.0. It is reported that, in the presence of Cl⁻, the species such as $HgCl_2$, $(HgCl_2)_2$, $Hg(OH)^+$ and HgOHCl are also present in small amounts between pH 4.0 and 6.0 [22]. The lower adsorption of Hg (II) at acidic pH is due to the presence of excess H^+ ions competing with metal ions for the sorption sites. At high pH values (7.0-9.0), the decrease in adsorption is due to the formation of soluble hydroxylated compound (Hg(OH)2). Similar pH values have been observed for adsorption of Hg (II) from aqueous solution in other studies [23-25]. In this study, the change in adsorption as a function of pH change was investigated for As (III) adsorption (Figure 4). The maximum adsorption percentage of As (III) was observed at the pH 6.0. The adsorption of the adsorbed

substance depends on the pH of the medium. Since the structure of the adsorbed substance can change with pH.

Figure 4. Effect of pH on sorption of Hg (II) and As (III) (0.10±0.02 g of APS, 25 mL of 100 mg L^{-1} Hg (II) solution; 0.5 g of MPS, 50 mL of 50 mg L^{-1} As (III) solution) $(•: PS, △: FeCl₃ + PS, □: FeCl₃ + NaOH + PS, •: APS)$

If OH \cdot or H₃O⁺ ions are formed in the pH-dependent solution, these ions compete with the adsorbed material and therefore greatly affect the adsorption efficiency. Anions of acids and cations of bases used to adjust pH can compete with metal ions. The pH-dependent adsorption of substances on the surface of solids is a complex reaction. For these reasons, pH has a major effect on adsorption performance. When the effect of pH on the As (III) adsorption of the adsorbents used was investigated, no adsorption was observed at pH=7.0. This may be due to the more selective adsorption of $H_2PO_4^-$ / HPO_4^2 anions used as buffers in this study than As (III) species found in uncharged H_3AsO_3 and anionic H_2AsO_3 structures at this pH. The increase in As (III) adsorption observed at low pH can be explained by the increase in positively charged centres on the adsorbent surface, and the increase observed at high pH can be explained by the formation of negatively charged anionic structures of adsorbed As (III).

3.4. Effect of temperature on sorption of Hg (II) and As (III) ions

Temperature is an important parameter in explaining the energy dependent mechanism of adsorption. Temperature changes the equilibrium capacity of the adsorption process. It is generally known that the change in temperature is directly proportional to the reaction rate. It is therefore expected that the reaction rate will increase as the temperature increases. The adsorption reaction is classified as either endothermic or exothermic. Temperature affects the rate and amount of adsorption. Adsorption experiments were carried out at 20-35 °C for Hg (II) adsorption and the results are shown in Figure 5. Subsequent studies were carried out at 30 °C.

For As (III) adsorption, the effect of temperature was tested at 20, 25, 30, 35 °C (Figure 5). 50 ml of 50 mgL⁻¹ As (III) solution was added to 0.5 grams of adsorbent (PS, FeCl₃ + PS and NaOH + $FeCl₃ + PS$) and mixed at the indicated temperatures for the indicated time and filtered. The optimum was found to be 30 °C for PS, $FeCl_3 + PS$ and NaOH + $FeCl_3 + PS$.

Figure 5. Effect of temperature on sorption of Hg (II) and As (III) (0.10±0.02 g of APS, 25 mL of 100 mg L⁻¹ Hg (II) solution; 0.5 g of MPS, 50 mL of 50 mg L⁻¹ As (III) solution) \bullet : PS, \blacktriangle : FeCl₃ + PS, \blacktriangleright : FeCl₃ + NaOH + PS, \blacklozenge : APS)

3.5. Thermodynamics of adsorption

The temperature dependent coefficient of dispersion was calculated using the following formula (Eq .2)

$$
K_d = \frac{c_{Ad}}{c_e} \qquad \qquad (2)
$$

 K_d is the equilibrium constant, C_{Ad} and C_e are the equilibrium concentrations (mg L^{-1}) of Hg (II) and As (III) ions on the APS and MPS in the solution (Equation 2). As shown in Figure 5, the adsorption process was evaluated between 20-35 \degree C for Hg (II) and As (III) and it was observed that adsorption increased with temperature. Thus, the adsorption Hg (II) and As (III) adsorption are endothermic in nature. Thermodynamic parameters such as the change in the values of ∆G°, ∆H° and ∆S° were calculated (Table 1, Eq. 4). The values of ∆G° for the adsorption process obtained from Eq. 3 are listed in Table 1. The negative value of ΔH° (-199.919 kJ mol⁻¹ the positive value of $\Delta S^{\circ} = 688.032$ J K⁻¹ mol⁻¹ for Hg (II)) indicates that the adsorption processes are

exothermic and spontaneous at high temperatures. The negative value of ΔG° (-405.137 kJmol⁻¹) indicates that the adsorption process is spontaneous. In arsenic studies, when pumice was used as an adsorbent, the ΔH° value was 37.739 kJ mol⁻¹, $\Delta S = 127.944$ J K⁻¹ mol⁻¹, ΔG° value = -1.668 kJ mol⁻¹. For the FeCl₃ modified pumice the ΔH° value was 13.35 kJ mol⁻¹, $\Delta S^{\circ} = 37.268$ J K⁻¹ mol⁻¹, and the ΔG° value was 1.871 kJ mol⁻¹. The ΔH° value for As (III) adsorption on pumice modified with NaOH and FeCl₃ was found to be -78.148 kJ mol⁻¹, ΔS° = -267.85 J K⁻¹ mol⁻¹, ΔG° $= 3010.28$ J mol⁻¹.

3.5 Adsorption isotherms

The relationship between the equilibrium concentrations and the amount of adsorbed material per unit adsorbent has been shown by isothermal models. The binding between adsorbent and adsorbate can be explained by adsorption models [26]. The best known isotherm models, Langmuir and Freundlich, were applied (Eq 3,5). In this study, Langmuir and Freundlich isotherms were used to determine the adsorption mechanism of APS for Hg (II) ions. 25 mL of Hg (II) ions at different concentrations (25, 50, 75, 100, 125, 125, 150, 175, 175, 200, 400, 600, 800, 1000,1500 mg L^{-1}) were treated with APS for 60 min (Figure 6).

Figure 6. Effect of Hg (II) and As (III) ions concentration on the adsorption by APS, PS, PS + FeCl₃, PS + NaOH + FeCl₃ (0.10 \pm 0.02 g of APS, 0.5 g of MPS) \bullet : PS, \blacktriangle : FeCl₃ + PS, \blacktriangleright : FeCl₃ + NaOH + PS, \blacklozenge : APS)

Compliance with the Freundlich isotherm indicates that the adsorbate is heterogeneously coated on the surface [27-29]. The equations for Freundlich, and the calculated parameters are given in Table 1. Since the correlation coefficient of the plot of Freundlich model plot is higher than that of Langmuir, it can be said that the Freundlich type adsorption isotherm is suitable for Hg adsorption. In concentration change studies for As (III) and Hg (II) adsorption, values of 20, 50, 100, 200, 400, 800, 1000 and 1500 mg L^{-1} were determined. As a result of the experiments and the isotherm graphs drawn, the Freundlich isotherm for PS, APS, $FeCl₃+PS$, and NaOH+FeCl₃+PS seems to be more appropriate than the Langmuir isotherm. It can be said that the adsorption has a heterogeneous structure for As (III) and Hg (II) ions.

Table 2 shows the capacities of some adsorbents used for the adsorption of As (III) and Hg (II) ions from the literature. As can be seen, many adsorbents have been used. The pumice stone used in this study has the advantages of being widely available in nature and having a very good capacity.

3.6 Desorption and reusability studies

The percentage desorption of Hg(II) and As(III) from the sorbent is shown in Figure 7,8.

Figure 7. Desorption (%) results of Hg (II) ions from activated pumice stone by using different eluents (0.1 M HCl, 0.5 M HCl, 0.1 M HNO₃, 0.5 M HNO₃, 0.1 M EDTA)

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Figure 8. Desorption (%) results of As (III) ions from modified pumice stone by using different eluents (0.1 M HCl, 0.5 M HCl, 0.1 M HNO3, 0.5 M HNO3, 0.1 M EDTA)

Figures 7 and 8 show the results of 4 consecutive desorption treatments with 0.1 M and 0.5 M HCl, 0.1 M and 0.5 M HNO₃ and 0.1 M EDTA. 0.1 M EDTA seems to be suitable for both metal ions and has good reproducibility (% 99-98). 0.1 M EDTA is considered as a suitable eluent due to its tendency to form complexes with heavy metals. The fact that the desorbent still works with 98% efficiency even after 4 consecutive treatments is very important for the reusability of the desorbent.

4. Conclusion

In this study, APS and MPS were used to remove Hg (II) and As (III) ions from aqueous solution. APS and MPS could be effectively used to remove Hg (II) and As (III) ions. PS, FeCl₃ + PS, FeCl₃ + NaOH + PS adsorption capacities were found to be 52.0, 57.5, 65.7 mg g⁻¹ for As (III) ions respectively, and APS adsorption capacity was found to be 155.75 mg g^{-1} for Hg (II) ions, respectively. The adsorption capacities of PS and $FeCl₃ + PS$ are close to each other. When the adsorption capacities of PS, $FeCl_3 + PS$, $FeCl_3 + NaOH + PS$ were examined, it was found that the adsorption capacity of $FeCl_3 + NaOH + PS$ was higher. Since metals can be recovered with EDTA, pumice stone is very advantageous in terms of reusability. Pumice stone is an economical adsorbent low cost and effective adsorbent for the removal of Hg (II) and As (III) ions from water. The use of pumice stone, which is very common and abundant in nature, as an adsorbent in the removal of As (III) and Hg (II), which are highly toxic metals, from aqueous environments can be recommended as an economical and simpleadsorption method.

Ethics in Publishing

There are no ethical issues regarding the publication of this study

Author Contributions

Vedia Nüket Tirtom: Designed and wrote the manuscript, carried out the experimental studies, conclusions and interpretation of the experiment.

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