Improved Mercury Removal from Water by Activated Ceramic: Sorption Isotherm

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Abstract: - Mercury (Hg) is widely known toxic metal contaminant posing severe thread in the aquatic environment. The aim of present investigation was to improve the Hg adsorption capacity of akadama volcanic ash soil derived ceramic (AVAS-ceramic) by chemical activation and optimize the process parameters required in sorption. Chemical activation of AVAS-ceramic was performed by 1 and 5% sodium carbonate (Na₂CO₃) and process parameters, contact time, solution pH, adsorbent dosage and adsorbate concentration were optimized using the batch operation studies. The activated AVAS-ceramic showed 25% (1% Na₂CO₃) and 127% (5% Na₂CO₃) elevated amounts of Hg²⁺ adsorption compared to the control AVAS-ceramic. Results also clearly revealed 270 min contact period is required to achieve the equilibrium state of Hg²⁺ adsorption. The adsorption was highly pH dependent and pH 7.5 was determined as optimum. Adsorption data was well described by the Langmuir sorption isotherm model. It can be concluded that the Na₂CO₃ activated AVAS-ceramic was capable of adsorbing elevated amount of Hg²⁺ by the effects of surface adsorption with enhanced ion exchange mechanisms due to Na₂CO₃ impregnation. Therefore, the Na₂CO₃ activated AVAS-ceramic could be applied as a low-cost environmentally sound adsorbent in removing Hg from water phase.

Key-Words: - AVAS-ceramic, Activation, Sodium carbonate, Adsorption, Mercury, Isotherm

1 Introduction

Mercury (Hg) is one of the well-known serious human health risk posing toxic metal pollutants commonly found in lithosphere, hydrosphere, atmosphere and biosphere of the global environment. Its nonessential and hazardous properties severely affect not only to the human health but also to the broader ecosystem components. No metabolic function, transformation of lower to higher toxic forms, bioaccumulation, biomagnification and severe health effects on animal systems (mutagenic, teratogenic, carcinogenic, embryocidal, cytotoxic, and histopathological effects) are the significant criteria of Hg [1]. The toxicity of monomethylmercury (MeHg⁺) or dimethylmercury (Me₂Hg) is associated with ability to penetrate membranes within seconds and to cross the blood-brain barrier. Mercury and its derivatives recognized as dangerous and insidious poisons, can be adsorbed through the gastrointestinal tract, skin and lungs [2], and responsible for the development of carcinogenic, mutagenic, teratogenic, tyrosinemia, paralysis, serious neural, intestinal and renal problems [3],[4]. The U.S. Environmental Protection Agency (EPA) estimated 630,000 newborns in America are at risk of unsafe levels of Hg exposure [5].

Natural, anthropogenic and re-emitted sources are the principal origin of Hg emissions [6]. Annual emissions of Hg from anthropogenic sources are to be over 2000 tonnes, of which about 30% are from coal-fired power plants [7]. Coal burning, municipal solid waste incineration, electronic, paper, pharmaceutical industries [8]–[10] and tailings of gold mines are the major anthropogenic sources of Hg emission. Besides, indiscriminate application of Hg in industries (Like; chlor-alkali, paint, oil refining, rubber processing, fertilizer, barometers, thermometers, pumps, lamps) also substantially contaminates the environment [11]–[13].

Since, Hg persists for decades in global environment with above serious impacts by means of continuous cycling between air, water, and land, therefore, Hg removal from polluted environment and contaminated effluents is a growing challenge to the scientist. Various methods, sulphide precipitation, membrane filtration, iron and alum coagulation, ion exchange and activated carbon adsorption are commonly practiced in this context. Recently, though natural and refuse derived materials have been tested as alternative low-cost
sorbents [14]–[16], but activated carbon and zeolites are used as typical sorbents for removing Hg ions from aqueous phase by adsorption process [17], [18]. Inspite of these, adsorption and ionic exchange capacities of several minerals and soils [19]–[21] have been suggested to possible use for the remediation of natural water bodies. Adsorption of Hg by solid materials is a suitable choice for final purification of wastewater with appreciable removal efficiency [22]. Various low cost clay/soil based ceramic pot filter [23] and membrane filters [24], [25] have been developed to treat the wastewater by removing various metals, nutrients and dyes [26]. Ceramic derived from the clay is an alternative adsorbent media to remove mercury [27], arsenic and lead from water [28], [29].

Generally, the ceramic has no specific chemical structure and consists of various metal oxides in different proportion to accentuate the strengths of the materials in which the atoms of metal and oxygen usually form a crystal, where the positions of the atoms are very regular, producing edges and facets. In traditional ceramics, small and variously sized metal oxide crystals containing alumina and silica (the oxide of silicon) exist in clays. Ceramics are usually ionic or covalent bonded materials, and can be crystalline or amorphous. The present study used akadama volcanic ash soil derived ceramic (herein called as AVAS-ceramic) is derived from akadama volcanic ash soil, which has also been characterized as a good Hg removing agent by Bhakta and Munekage [30]. Salim et al. determined the chemical properties of the AVAS-ceramic by SEM-EDS analysis and showed its arsenic removal potentiality from aqueous phase [28]. Therefore, the present study considered AVAS-ceramic for the development of Hg removing activated ceramic-based adsorbent media.

On account of the above points of view, though varieties of adsorbent media have been developed to remove Hg from water but many of them are costly and inaccessible in the underdeveloped countries and in some cases having negative environmental impact in practical field. In this regard, therefore, the development of low cost materials and simple methods are still required. Understanding of these facts, the present study attempts (1) to improve the Hg\(^{2+}\) adsorption capacity by chemical activation and (2) to determine the process parameters through sorption isotherm study of low-cost AVAS-ceramic.

## 2 Materials and Methods

### 2.1 Activation of AVAS-ceramic

The study used sodium carbonate (Na\(_2\)CO\(_3\)) to activate the AVAS-ceramic for improving the Hg removal capacity. Na\(_2\)CO\(_3\) (purity 99.5\%) was dissolved in 8 ml distilled water @ 1 and 5\% of the ceramic weight, 2 g AVAS-ceramic was added to each solution and mixed properly to make a homogenous solution. Likewise, 2 g AVAS-ceramic was treated with only distilled water for control. The Na\(_2\)CO\(_3\) treated ceramics and control ceramic were allowed for 4 h at room temperature and oven dried at 100°C for 6 h. The dried activated AVAS-ceramic granule was used for adsorption experiment.

### 2.2 Adsorption experiment

To determine the mercury removal capacity, 12 glass bottles (100 mL) were randomly divided into four groups having three replicates each (4 x 3) and filled with 50 ml of 0.2 mg/L Hg solution prepared from the standard stock solution of mercuric chloride (HgCl\(_2\); Cica-Reagent, Kanto Chemical Co., Inc., Tokyo, Japan). Two (1 and 5\% Na\(_2\)CO\(_3\)) activated and one control ceramics were employed @ 1 g/L in three groups and remaining one group used as control of only Na\(_2\)CO\(_3\) @ 1 g/L received no ceramic. Bottles were shaken at 200 excursion/min by a mechanical shaker for sufficient contact period 6 h at 25°C. Hg\(^{2+}\) removal capacity of ceramics was determined by calculating the mercury removal percentage (MRP) following the equation (1):

$$\text{MRP} = \frac{C_0 - C_e}{C_0} \times 100$$  \hspace{1cm} (1)

Where, \(C_0\) and \(C_e\) are the initial and final concentrations (mg/L), respectively. The studies on effect of process parameters were performed with highest Hg\(^{2+}\) removing activated ceramic.

### 2.3 Effect of process parameters

Hg\(^{2+}\) adsorption studies were performed in capped glass bottles (100 ml) using known weight of Na\(_2\)CO\(_3\) activated AVAS-ceramic following the batch operation mode. All experiments were conducted using the known volume of adsorbate (50 ml) with known weight of adsorbent and concentration of Hg within temperature controlled mechanical shaker at 25°C. The effect of contact periods was determined maintaining the initial concentration 0.4 mg/L and adsorbent dose 1 g/L. The experiment was carried out in different pH values 2.9, 4.3, 5.3, 7.5, 9.1 and 11.0 to determine
the specific pH required for optimum Hg\(^{2+}\) adsorption. The initial Hg concentration was varied from 0.203 to 0.438 mg/L to examine the effects of initial adsorbate concentration, whereas the effect of adsorbent dosages was found maintaining the ceramic weights ranged from 0.4 to 2.4 g/L. Each experiment was performed at least twice following the identical conditions using controls of only Hg solution and adsorbent without Hg in solution.

The Hg\(^{2+}\) adsorption onto the activated AVAS-ceramic at the equilibrium, \(q_e (\text{mg/g})\) was calculated by following the equation (2) of mass balance relationship:

\[
q_e = \frac{(C_0 - C_e) V}{M}
\]

Where, \(C_0 (\text{mg/L})\) and \(C_e (\text{mg/L})\) are the initial and the equilibrium water-phase concentration of Hg, respectively, \(V (\text{L})\) the volume of the solution and \(M (\text{g})\) the mass of ceramic. The percentage of Hg removal from water phase was calculated using above mentioned equation (1).

2.4 Analysis
The water sample was collected from the glass bottle, centrifuged and supernatant was used for analysis using the RA-3 Mercury Analyzer (Nippon Instruments Corporation, Japan). Hg removed from water was calculated by quantifying the residual Hg content in water phase.

3 Results and Discussion
3.1 Adsorption experiment
MRP varied from 11.5 to 93.7% in four groups of the experiment. 1% Na\(_2\)CO\(_3\) and 5% Na\(_2\)CO\(_3\) activated ceramic showed 25 and 127% elevated MRP, respectively compared to that of ceramic only (Fig. 1). Results clearly revealed higher Hg\(^{2+}\) removal from water was due to the effect of activation of ceramic by Na\(_2\)CO\(_3\) impregnation.

AVAS-ceramic is constituted by varieties of metal oxides, therefore, elucidation of the exact mechanism of the elevated Hg removal by Na\(_2\)CO\(_3\) activation was not clear from the present study. The probable mechanism might be explained as follows: (i) As ceramic is composed of metal oxides as a major constituents, therefore, activation process incorporates the Na\(_2\)CO\(_3\) in the ceramic surface by forming the ion complexes with the metal oxides and (ii) Hg\(^{2+}\) ions of solution replaces the Na\(^+\) and forming the bonds with CO\(_3^{2-}\) in ceramic by ion exchange process, which resulting in the decrease of higher amount of Hg in water (Equation 3).

\[
\text{[Ceramic + Na}_2\text{CO}_3\text{]} + \text{HgCl}_2 = \text{[Ceramic + HgCO}_3\text{]} + \text{NaCl} \quad (3)
\]

Due to highest Hg adsorption capacity, the 5% Na\(_2\)CO\(_3\) activated ceramic was considered for further study to determine the optimum process parameters.

3.2 Effect of process parameters
3.2.1 Effect of contact time
Fig. 2 depicting the effect of contact time on the removal of Hg\(^{2+}\) from water phase. The activated AVAS-ceramic showed the rapid adsorption rate until 210 min, followed by slow adsorption and equilibrium state was achieved at 270 min of the contact time. The Hg\(^{2+}\) adsorption capacity increased sharply from 0 to 64% in first 30 min, and then gradually increased to 89%.

![Fig. 2 Effects of contact time in the Hg\(^{2+}\) adsorption of AVAS-ceramic (initial concentration 0.4 mg/L, dosage 1 g/L and pH 7.5)
3.2.2 Effect of pH
The pH of solution plays an important role in the adsorption mechanism of adsorbent media. The effect of pH on the Hg^{2+} adsorption process of activated AVAS-ceramic was shown in Fig. 3. The increasing Hg^{2+} adsorption trend was pronounced with increasing pH and maximum adsorption was found at pH 7.5 (82.3%), whereas adsorption rate was in decreasing trend with further increasing pH. Results clearly revealed that neutral pH is optimum for adsorbing the Hg^{2+} from aqueous phase in activated AVAS-ceramic. It has been shown that pH 7 is the optimum for Hg^{2+} adsorption [27] and highest arsenic adsorption was also reported at pH 7.5 [28] by some ceramics. Above proposition suggested that neutral pH influence significantly over acidic and alkaline pH in the surface adsorption as well as ion exchange processes at the functional groups of Na_2CO_3 activated AVAS-ceramic by sponsoring the lower H^+ conditions in removing Hg^{2+}. As H^+ ions are preferentially adsorbed on the surface of the adsorbents, therefore, higher H^+ ions concentration prevent the positively charged metal ions to reach at the binding surface of the adsorbent. The effects of initial pH on Hg^{2+} removal may be explained as follows: both the adsorbent and the adsorbate are positively charged (M^{2+} and H^+) consequently the net interaction is electrostatic repulsion in the acidic condition [31]. The concentration of protons is reduced with increasing pH which resulting in the formation of surface metal-adsorbent complex or higher removal of metal ions [32].

3.2.3 Effect of initial Hg concentration
The effect of initial Hg^{2+} concentrations on the adsorption process of activated AVAS-ceramic was shown in the Fig. 4. The Hg^{2+} adsorption was enhanced with increasing the initial concentration of Hg^{2+} by per gram of employed ceramic. The maximum Hg adsorption percentage in the highest initial concentration (0.438 mg/L) was higher (5 – 100%) than that of the remaining initial concentrations. Obtained results implied that the saturation rate of Hg^{2+} binding onto the functional groups of ceramic was greater in the higher concentrations by means of increasing electrostatic interactions which resulting in the increasing rate of adsorption.

3.2.4 Effect of adsorbent dosage
Fig. 5 elucidates the effect of adsorbent dosages on the Hg^{2+} adsorption of AVAS-ceramic. Though total Hg^{2+} adsorption increased with increasing the dosages but the amount of adsorption per gram of ceramic showed a reverse response with dosages. The rates of adsorption were 20, 55.5, 88, 88.5, 88.3 and 88% in 0.4 mg/L, contact time 270 min and pH 7.5, respectively. Results revealed that adsorption
rate was increased up to dosage 1.2 g/L and steady thereafter, therefore this dosage would be optimum. The decrease in adsorption amount with the increasing adsorbent doses may result from the electrostatic interactions, interference between binding sites, and reduced mixing for higher densities at higher doses of adsorbent [33], [34]. This is supported by the metal removal results of sequential adsorbent treatment using solid adsorbs (such as sand, silica, coal and alumina) proposed by Yabe and de Oliveira [35].

3.3 Adsorption isotherms
The effectiveness of adsorbent is the important facts for applying in the practical fields. According to Benguella and Benaissa [36] and Yalcinkaya et al. [37], the relationship between the adsorbate and adsorbent under different operation conditions of the batch experiments helps to understand the effectiveness of various adsorbent materials. In adsorption process, the relationship between the amount of adsorbate adsorbed and remaining adsorbate in the solution is explained by an isotherm. Generally, Langmuir and Freundlich models are widely used models for the single and binary cases among various isotherm equations. To ascertain the Hg\(^{2+}\) adsorption capacity of activated AVAS-ceramic, the present investigation followed the Langmuir and the Freundlich models. The Langmuir isotherm was derived with the basic assumption that the sorption takes place at specific homogenous sites within the adsorbent. Following equations were used to describe the Langmuir (Equation 4) and Freundlich (Equation 5):

\[
q_e = \frac{K_Lq_mC_e}{1 + K_LC_e}
\]

Where, \(K_L\) is constant related to free energy of adsorption. \(C_e\) (mg/g) is the equilibrium concentration in solution. \(q_m\) (mg/g) indicates the adsorption capacity corresponding to the complete monolayer coverage.

\[
q_e = K_F C_e^{1/n}
\]

Where, \(K_F\) (L/mg) is the Freundlich constant, \(C_e\) (mg/g) is the equilibrium liquid phase concentration and \(1/n\) is the heterogeneity factor. Generally, the parameter \(n\) is greater than unity. A high \(K_F\) and high \(n\) value is an indication of high adsorption throughout the concentration range. In general, it is stated that the \(n\) values in the range of 1 to 10 represents good adsorption [38].

Fig. 6 illustrated the Hg\(^{2+}\) adsorption equilibrium curve of activated AVAS-ceramic. The calculated fittings parameter of the experimental results for the Langmuir and Freundlich isotherm models were shown in Table 1. The \(R^2\) values of Langmuir (0.956) and Freundlich (0.851) clearly indicating that Langmuir isotherm is well fitted with the experimental data rather than the Freundlich isotherm. Accordingly, it can be explained in favour of monolayer coverage of Hg\(^{2+}\) ions on ceramic. Besides, it is also obviously considered that the Freundlich constant \(1/n\) is an indicator to evaluate the adsorption strength and the deviation from linearity of the adsorption. Therefore, the favorable adsorption may be described due to having the \(n\) value of Freundlich constant between 1 and 10.

![Equilibrium curve of AVAS-ceramic for the adsorption of Hg\(^{2+}\)](image)

**Table 1. Langmuir and Freundlich isotherm parameters for AVAS-ceramic in removing Hg\(^{2+}\)**

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Langmuir</th>
<th>Freundlich</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(K_L) (L/mg)</td>
<td>(q_m) (mg/g)</td>
</tr>
<tr>
<td>AVAS-ceramic</td>
<td>28.821</td>
<td>0.518</td>
</tr>
</tbody>
</table>
3.4 Management of spent ceramic
To avoid the further hazardous environmental problems, the Hg loaded spent ceramic should be managed properly following the pollution control measures. The Hg loaded ceramic may be managed by the following ways: (i) desorption of Hg from ceramic and recycled and (ii) extraction of Hg from ceramic by chemical methods. Further experiment is required to determine the Hg desorption efficiency of AVAS-ceramic in order to recycle and reuse for protecting the environment and cost effective benefit.

4 Conclusions
The present investigation improved (1% Na₂CO₃, 25% and 5% Na₂CO₃, 127%) the Hg²⁺ adsorption capacity of AVAS-ceramic by activation with Na₂CO₃. The batch operation studies optimized the contact time 270 min and pH 7.5 for Hg adsorption process. Though the effects of other examined process parameters are interrelated with each other but the results demonstrated adsorption capacity increased with increasing initial concentration of Hg, whereas a reverse response of adsorption capacity was determined in the effect of AVAS-ceramic dosages when the other influencing parameters remain constant. The experimental data is well fitted with Langmuir isotherm model in present study. The effects of surface adsorption with enhanced ion exchange mechanisms is probably to be the driving force for removing higher amount of Hg²⁺ compared to control ceramic. Though activated AVAS-ceramic showed lower Hg removal capacity compared to that of the other few developed adsorbents as published data available so far, but from the viewpoints of economical feasibility, availability and simplicity in preparation method, it might be a low-cost adsorbent for removing Hg from water.

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References:
[14] Y. Kawamura, H. Yoshida, S. Asai and H. Tanibe, Breakthrough curve for adsorption of mercury(II) on polyaminated highly porous...


