

Decontamination of Mercury-containing Water by Pottery

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Summery- The heavy metal removal capability using pottery as a low cost sorbent has been investigated for mercury. The results indicated that mercury is better removed by pottery from neutral to alkaline solutions. The capacity of the used pottery container (100 ml in volume) for complete removal of mercury was found to reach 3×10^{-4} mole/l, and the time needed was 8 hours. The sorption process was suggested to occur via adsorption and ion exchange. The effect of presence of humic or fulvic acid, as ligands abundant in water, is also investigated. The results imply that, in the absence of humic or fulvic acid the sorption follows the expected behaviour, i.e. sorption sites with similar affinity for mercury. In presence of humic or fulvic acid, additional sorption sites are available by the organic molecule when it is associated to the pottery.

Introduction

The look for pure water is a quandary for all people; without water there is no life. In many fresh waters, metals levels are increased by different kinds of sewage or other sources. The existence of heavy metals (HM) and trace elements in drinking waters is of great concern, because of the relation between these elements and the occurrence of human cancer, as well as their toxicity.

Significant concern exists regarding human exposure to Hg. In appreciation of the public health risk, the USA restricts the maximum level of Hg in water to 0.002 mg/l¹. As pointed out by Tseng et al², Hg speciation has been a field of permanent concern over a long period. Such interest is mainly due to toxicological impact, ecological problems and biogeochemical cycling

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of $\text{Hg}^{3,4}$. In soils and waters, volatile forms [e.g., Hg^0 & $(\text{CH}_3)_2\text{Hg}$] evaporate to the atmosphere, whereas solid forms deposit to particulates.

The release of Hg is estimated to be $\sim 2 \times 10^5$ ton/y⁵. It enters water from industrial wastes, mining and pesticides. Generally, most of the Hg released comes from burning coal in power plants⁶. The produced Hg^0 is highly volatile and may move over long distances in the atmosphere. Wet deposition may later occur in the earth's crust or oceans in the form of Hg^{2+} ³. Dissolved Hg^{2+} shows a high tendency to adsorb on suspended matter and, thus, to accumulate in the top sediments of estuaries³. High biological activity in these areas, leads to methylation of Hg^{2+} , by the action of bacteria⁷. The resulting soluble (MeHg^+) is released into water and bioaccumulates in fish tissues⁸. Bacteria can also convert Hg to $(\text{CH}_3)_2\text{Hg}$, which forms a vapor⁹.

The use of pottery for refining of water is a kind of low cost treatment. Pottery is an artificial stone, hard, non-flexible, not affected by heat or cold, fire or water and does not deteriorate with time¹⁰. Pottery wares were used for refrigeration of water. People used pottery for refrigeration didn't know that it is a good purifying sorbent.

The XRD has indicated that the main minerals in pottery are quartz, K-feldspar, plagioclase feldspar, calcite and opal-CT¹¹. The chemical analysis has illustrated that the major components are SiO_2 , Al_2O_3 and Fe_2O_3 , in addition to CaO , TiO_2 , MgO , K_2O , and Na_2O ¹². Since the exchange capacity of clay minerals reaches to 100 meq/100g¹³, it is expected that pottery is an ideal sorbent for the removal of metals. Pottery has a stable structure, as was manifested by the absence of any release of radioactivity of the reactor induced isotopes when it is irradiated and immersed in water (or in dilute acid), for prolonged time¹⁴.

Humic substances are the primary metal-complexing chelates and, thus, achieve a very important function in the environmental, bioavailability, toxicity, and mobility of HM in the biosphere¹⁵. These substances are considered problematical in water because they can readily react with Cl_2 to

form carcinogenic compounds and they can complex/partition HM and hydrophobic polychlorinated organics, affecting their fate and transport⁽¹⁶⁾.

The aim of this work was to study the HM removal capability using a low cost sorbent that can remove the HM and does not alter the water quality. Mercury is selected because of its high toxicity and its easy arrival to water. The parameters affecting Hg removal, such as pH, time of removal and $[\text{Hg}^{2+}]$ were investigated. Possible removal mechanisms were elucidated. The effect of presence humic or fulvic acids, as an environmental ligands present in water, is also investigated.

Experimental

Pottery containers were obtained from local merchant; they are red pottery vessels used as a kind of vases. The volume of each container is about 100 ml, and the thickness of the material is about 1.0 cm. The vessels were washed by water and left to dry before use.

The investigations were carried out using deionised distilled water, at room temperature ($25 \pm 1^\circ\text{C}$) and atmospheric pressure. The pH of water was adjusted to the pH of fresh water (8.0 ± 0.1) by addition of few drops of 1.0 M NaOH. The final pH was around 7.4 ± 0.1 , at the end of the experiment. The pH was measured using a bench top pH-meter model HI 8417. Analytical grade chemicals were employed. A standard stock solution of 0.1 M of Hg^{2+} was prepared and 0.25 ml from this solution was added to each pottery vessel containing 50 ml of water to attain a concentration of 5×10^{-4} M. In the experiments of the effect of pH, the pH was varied in the range 4–9 by addition of HCl or NaOH.

Humic acid (HA) and fulvic acid (FA) were used to investigate the effect of presence of these organic polyelectrolytes on the removal of mercury. Fluka HA is used after purification by a method similar to that previously described¹⁷. FA was extracted and purified by the common method⁽¹⁸⁾. A working solution of 50 mg/l HA or FA was prepared for each pottery vessel and the pH is

adjusted by addition of small drops of HCl or NaOH, for HA and FA, respectively before spiking the solution with mercury.

The final concentration at various time intervals (C_f) of 1 ml aliquot solution was measured using Atomic Absorption Spectrometer (Hitachi Z-6100) by the standard reduction-vaporization method. The percentage of removal of mercury was then calculated from the following relation:

$$\% \text{ Removal} = \frac{C_i - C_f}{C_i} \cdot 100$$

Where C_i is the initial concentration of mercury and C_f is the final concentration, after time t .

Results and Discussion

Fig. (1) displays the effect of time on the removal of Hg^{2+} from water, at $\text{pH } 7.4 \pm 0.1$ (the final pH). Notably, the rate of removal increases sharply, then gradually to reach about 95% after 8 hours, and do not change after that up to 28 hours. The results show that removal of mercury is time dependent. The rapid removal followed by slow removal of Hg^{2+} by pottery suggests two sorption processes; ion exchange and adsorption in the beginning, followed by a slow penetration of mercury into the crystal lattice of minerals forming pottery⁽¹⁹⁾.

Since pottery constituents are mainly SiO_2 , Al_2O_3 and Fe_2O_3 , and to a smaller level CaO , TiO_2 , MgO , K_2O , and Na_2O ¹²; there exists many various adsorption/ exchange sites. Therefore, the metal removal mechanisms may include physical and chemical adsorption and/or ion exchange.

The Hg^{2+} removal through adsorption may be expressed in the light of presence of surface hydroxylated sites, particularly those of silicate and iron, on pottery; as follows:

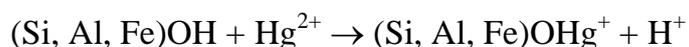
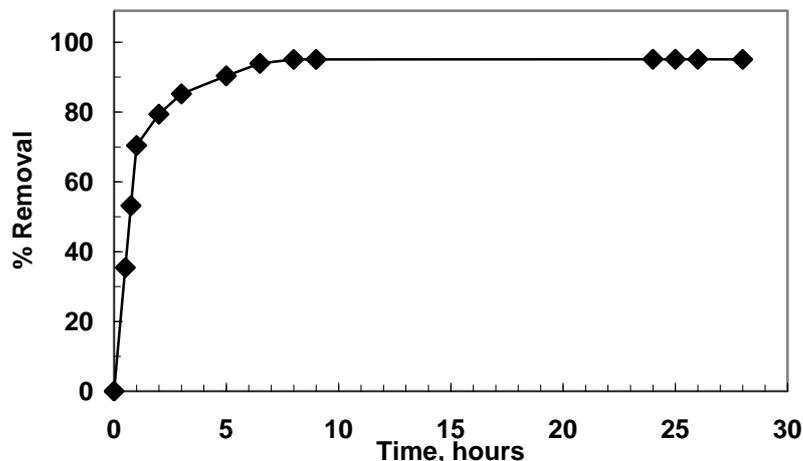
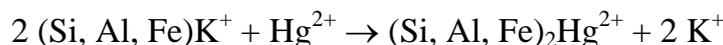


Fig. (1): Removal of Hg^{2+} by pottery, at pH 7.4



where (Si, Al, Fe) denotes the basic surface sites of pottery. The equation indicates that the adsorption of Hg^{2+} on pottery involves a proton release. As indicated above, the final pH was lower than the initial one. This implies that Hg^{2+} removal by adsorption is an acceptable mechanism.

The mercury removal through ion exchange route may be expressed as²⁰:

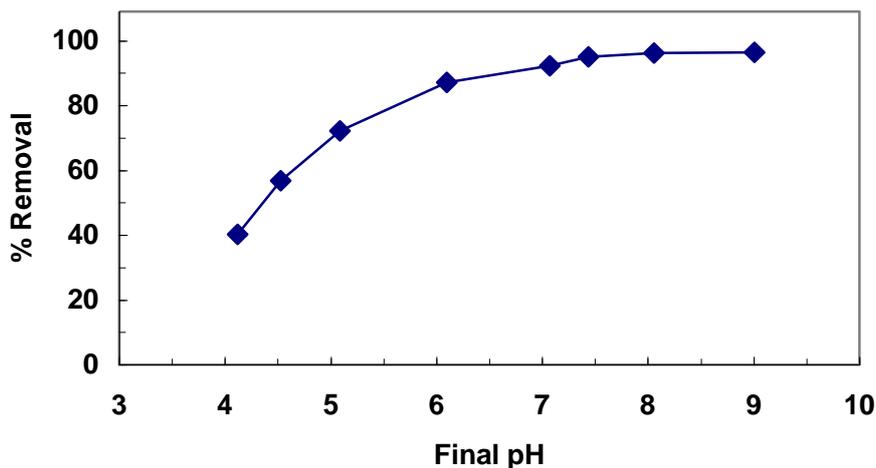


The significant role of ion exchange for Hg^{2+} removal by pottery has been recognized by investigating the release of potassium after removal of mercury. It was reported that ion exchange through constant charge sites of sorbent is responsible for zinc removal by synthetic aluminosilicates¹² and cobalt removal by bentonite¹⁹.

The effect of pH on the removal of mercury from water by pottery was studied by varying the pH from 4 to 9. The results obtained are presented in Fig. (2) and showed an obvious removal dependence on pH. The % removal increases from acidic to alkaline conditions to reach a maximum in neutral to slightly alkaline solution. These results show that mercury is better removed by pottery from neutral to alkaline solutions. This action is a result of the competition with H^+ ions, which can protonate the sorption sites of pottery^{15, 21}. At low pH's, acidic protons compete with the metal ion, thus cause a decrease in removal. At high pH, the reaction sites are deprotonated and negatively charged, so attract the metal and the removal increases. A similar behavior was

obtained previously for Eu^{3+} with pottery²², and comparable results were reported for Eu^{3+} , Co^{2+} and Cs^+ with clay²³ and for Cs^+ , Sr^{2+} , Gd^{3+} ²⁴, Co^{2+} and Zn^{2+} ²⁵ with humin.

Fig. (2): Effect of pH on removal of Hg^{2+} from water by pottery



The effect of Hg^{2+} concentration on its removal by pottery is investigated by varying the metal ion concentration. As Fig. (3) shows, the % removal is around 100% between 10^{-7} and 3×10^{-4} M, away from which it decreases. This decrease means that the Hg^{2+} included in the system, after attainment saturation, stays in solution. The figure illustrates that the capacity of the used pottery container for complete removal of mercury reaches 3×10^{-4} mole/l.

Fig. (4) illustrates the effect of presence of environmental ligands such as HA and FA on mercury removal by pottery. The sorption of mercury is clearly promoted by HA or FA. Theoretically, HA/FA influence the sorption of metal in three compartments¹⁵: First, adsorption of HA/FA increases the negative charge on the sorbent and, hence increases metal adsorption. Second, by competing with the adsorption sites for the metal, in this case the presence of HA/FA may decrease the metal adsorption. Third, the HA/FA-metal complexes in solution also affect metal adsorption onto the sorbent.

Fig. (3): Effect of Hg^{2+} concentration on removal of mercury by pottery, at pH 7.4

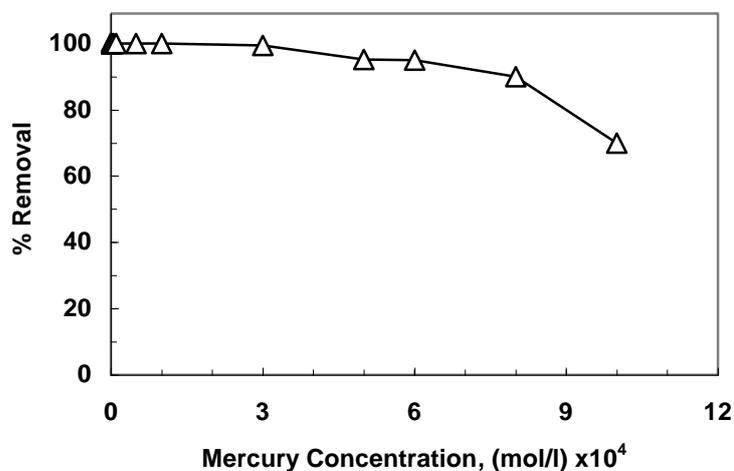
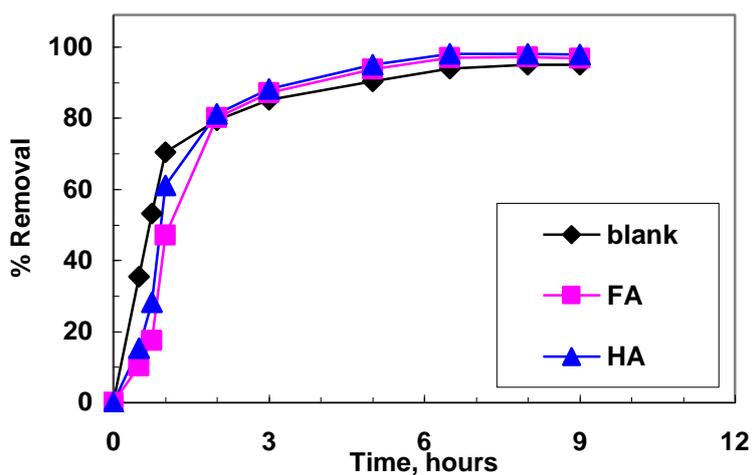


Fig. (4): Effect of humic and fulvic acids on removal of Hg^{2+} by pottery, at pH 7.4



The results indicated in Fig. (4) preponderate the first assumption. It was proposed^{15, 26} that there are two possible structures for the adsorption of the metal and HA/FA on mineral surfaces. One is the S-M-HA and the other is the S-HA-M, where S represents the adsorption site on the surface of sorbent and M is the metal ion. As pointed out by Liu and Gonzalez²⁷, the most possible surface structure of bivalent metal ions between montmorillonite and HA should be S-M-HA.

Thus, Hg^{2+} may be acting as a bridge between HA/FA and pottery. In the presence of HA/FA, additional adsorption sites are available by the organic molecule when it is associated to the sorbent.

Conclusions

- The red pottery has high affinity to remove mercury from water.
- Mercury is better removed by pottery from neutral to alkaline solutions.
- The capacity of the used pottery container for complete removal of mercury reaches 3×10^{-4} mole/l, in 8 hours.
- The sorption process was suggested to occur via adsorption and ion exchange.
- The presence of humic or fulvic acid, enhances the removal of mercury.

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