ABSTRACT

Experiment was performed to draw a mercury adsorption stoichiometry of ceramic and activated carbon from aqueous phase in two parts - first part dealt with the effect of three different pH - 4, 7 and 10, whereas second part was designed to determine the effect of three temperatures - 15, 25 and 35°C. SEM-EDS analysis of adsorbents clearly showed highly uneven and porous surface structure of activated carbon compared to ceramic that contains SiO2 (73.65%) as a major constituent with negligible amount of metals, whereas C (98.46%) is the only constituent in activated carbon. Activated carbon exhibited 15 to 52% (experiment of pH effect) and 49 to 70% (experiment of temperature effect) higher adsorption efficiency than that of the ceramic, which inferred that the activated carbon is a proficient Hg adsorbent compared to the ceramic because of having greater available Hg adsorptive total surface area than ceramic and in contrary, high ionic competition on the surface of ceramic prevents more Hg adsorption from aqueous phase which is entirely absent in activated carbon. PH 7 and pH 4 revealed the highest Hg adsorption in ceramic and activated carbon, respectively. It also signified that pH 7 facilitates Hg adsorption reducing positive ions competition on the ceramic surface which is higher in rest of the pH levels, whereas pH 4 may be optimum to reduce HgCl2 into Hg(I) over the remaining pH in activated carbon for adsorbing maximum Hg. In the experiment of temperature effects, highest temperature (35°C) exhibited a higher rate of adsorption (ceramic 32 - 35% and activated carbon 0.13 - 0.84%) than the remaining temperatures. Therefore, it may also be concluded that highest temperature (35°C) of the medium promotes the used adsorbents to remove higher quantity of Hg from water phase because surface group activity of adsorbents, ionization and movements of Hg ions increases with increasing temperature that leads to the higher rate of Hg adsorption.

Keywords: mercury, adsorbents, SEM-EDS, pH, temperature, adsorption efficiency.

1. INTRODUCTION

Environmentally threatened impacts of metal pollution are a well known fact during last few decades globally. Presently, it is appearing as an increasing and alarming challenge to the researchers and environmental control agencies for polluting the water and soil resources severely through the indiscriminate disposal of metals in the environment. It is also conspicuous that some metals have toxic or harmful effects on many forms of life. Among the most toxic metals, mercury (Hg) is one of the 11 hazardous priority substances in the list of pollutants contained in the Water Framework Directive [1]. It is a naturally occurring trace element found in rocks, soils, sediments and the atmosphere having neurotoxic effects that potentially accumulates to toxic levels in the different food chains and biological tissues of humans and animals alike [2]. Moreover, it may be appeared as a critical and chronic problem because it can easily be transformed into methylmercury, an organic form, by bacteria in bottom-level sediments which is taken up by organisms more rapidly and is much more toxic than inorganic form. Mercury and its compounds recognized as dangerous and insidious poisons and can be adsorbed through the gastrointestinal tract and also through the skin and lungs [3] which is stored in the liver, kidneys, brain, spleen and bone leading to development of carcinogenic, mutagenic, teratogenic and also promotes several health problems, tyrosinemia, paralysis, serious intestinal and urinary

complications, dysfunction of the central nervous system and in more severe cases of intoxication, death. The severity of mercury toxicity was recognized in the late 1950s and 1960s because of an environmental tragedy in Minamata Bay, Japan, where hundreds of individuals suffered from mercury poisoning (Minamata disease) [4].

Nevertheless, mercury is still used worldwide in various anthropogenic activities such as barometers, thermometers, pumps, lamps and in many others. Industries principally responsible for the dispersion of mercury are the chlor-alkali, paint, oil refining, rubber processing and fertilizer industries [5-7], cement plants and also all those used as fossil fuels. Furthermore, once discharged into the atmosphere, mercury persists in the environment for decades and creates long-term contamination problems in the different trophic levels of the food chain through bioaccumulation.

On account of the above awful contamination, accumulation, biomagnification and several health hazards consequences of mercury, as strict control measure of mercury emissions from coal-fired power plants [8] and for its wide application in different industries are required in one hand and relevant studies involving the removal of this pollutant from the environment is also parallelly most essential on the other hand to protect the total environment. Accordingly, various legislative control measures and improved and innovative methods of reverse osmosis, precipitation, coagulation, ion exchange, solvent
extraction, adsorption, membrane filtration and ultrafiltration are continuously being developed for cleaning the water and wastewater contaminated with metal pollutants [9-13]. In this context, adsorption is one of the widely used and promising techniques employing various biomaterials and inorganic materials as sorbent. Commonly applied biomaterial sorbents are algae [14], fungi, sugar cane bagasse [15], rice husk, wheat barn [16], pine bark, olive cake [17], coconut husk and chitin [18]; whereas iron hydroxides and oxyhydroxides [19], aluminium hydroxides and oxides [20], clays, zeolite, calcite, manganese nodule residue [21], perlite [22], peat [23] activated carbon [24], sewage sludge [25], etc. are commonly considered as inorganic sorbents. Various intrinsic and extrinsic factors greatly influence in the metal removal mechanism of these technologies and adsorbents; among these pH, temperature, contact time, adsorbent size and dose etc. are the most important extrinsic factors. It has been reported that cadmium and arsenic adsorption of ceramic is largely regulated by pH, temperature, contact time, initial metal concentrations, adsorbent size and doses [26, 27]. The adsorption of HgCl$_2$ on activated carbons in the liquid phase may take place by two mechanisms, i.e. adsorption of the HgCl$_2$ species and/or reduction to Hg (I) by the surface functional groups [28]. In the above points of view, though activated carbon adsorbs Hg efficiently from aqueous phase but the information regarding the effect of pH and temperature in the Hg adsorption efficiency of ceramic and activated carbon is very scanty. Therefore, the present investigation has been aimed to draw the Hg removal efficiency and removal mechanism of ceramic and activated carbon under different pH and temperature.

2. MATERIALS AND METHODS

2.1. Adsorbent materials

Present study used ceramic and activated carbon as adsorbents to quantify the Hg removal efficiency from aqueous phase in different pH and temperature. Ceramic was procured from EKOAIRANDO Co. Ltd. Kochi, Japan, made by amalgamating clay (69%), silica (30%) and shell powder of shell fish (1%) using specific grinder and mixer equipments. According to the company, the mixture of three ingredients were heated and fired gradually increasing the temperature @ 10°C min$^{-1}$ from 100 to 900°C applying a advance furnace equipment. In the present study, used other material activated carbon was also collected from market produced by Kanto Chemical Co., Inc., Tokyo, Japan.

2.2. SEM-EDS analysis

Morphological and chemical characterization of the adsorbents, ceramic and activated carbon, was carried out by scanning electron microscopy (SEM) using a jeol model equipment coupled with energy dispersive spectroscopy (EDS) facility (JSM-6500F, JEOL) in the Center for Advanced Marine Core Research, Kochi University, Japan.

2.3. Experimental design for adsorption study

Hg adsorption study was conducted in the 54 (200 ml) conical flasks using batch operation mode in the laboratory. All conical flasks were filled with 100 ml water of 100 µgL$^{-1}$ Hg concentration prepared from standard stock solution of mercuric chloride (HgCl$_2$, Cica-Reagent, Kanto Chemical Co., Inc., Tokyo, Japan) and randomly divided into two batches (27 x 2) - first batch was used to study the effects of pH and rest one employed for examining the effects of temperature in the adsorption process of ceramic (CR) and activated carbon (AC). Therefore, each batch again divided into 3 sets (9 x 3) - one used for control (C) received no adsorbent and another two sets provided with CR and AC @ 1.0 g flask$^{-1}$. Further, each set of one batch were subdivided for three pH - 4, 7 and 10 (herein called as C_{pH 4}, C_{pH 7} and C_{pH 10}) maintained by adding the 1 N HCl and 1 N NaOH and each set of another batch was also subdivided into three and kept in incubators maintaining 15, 25 and 35°C temperatures (herein called as C_{T15}, C_{T25} and C_{T35}). Each treatment of the study having three replicates was observed for 153 hours.

Water sample was collected from each treatment at short interval initially and long interval afterwards to determine the mercury concentration using the advanced RA-3 Mercury Analyzer made by Nippon Instruments Corporation (NIC), Japan.

2.4. Hg adsorption efficiency

Hg adsorption efficiency of CR and AC was calculated in different treatments and expressed as per unit mass and per unit time according to following formula:

$$AE = \frac{C_i - C_f}{M (t_f - t_i)}$$

Where, AE is adsorption efficiency; Ci and Cf are the initial and final concentrations (µgL$^{-1}$), respectively; M is the mass (g) of the adsorbents and ti and tf are initial and final time (h).

2.5. Statistical analysis

Obtained data was statistically interpreted to determine the effects of pH and temperature in adsorption mechanism using one-way ANOVA. In case of significant difference, the ANOVA was followed by a LSD (least significance difference) test. All statistical tests were performed at 5% probability level using statistical package EASE and MSTAT.

3. RESULTS

3.1. Characterization of adsorbent

SEM images of used adsorbents, CR and AC are shown in the Figure-1. This figure reveals the different aspects of morphological information, megascopic and microscopic texture of the adsorbents in three magnifying
stages (25x, 400x and 5000x). Megascopic images (25x and 400x) gives the shape and size of the adsorbents, where a wide range of shapes and sizes was found for individual particles of both adsorbents, whereas microscopic images (5000x) clearly showed the elaborated surface structure of the employed adsorbents; it was also observed that surface of AC is highly uneven and porous than that of the CR (Figures-1a and b).

Chemical composition was obtained by EDS analysis of the CR and AC (Figures-1a400x and b400x). The EDS data also exhibited that CR is composed of Na₂O, MgO, Al₂O₃, SiO₂, K₂O, CaO and FeO excluding C, where SiO₂ is the major constituent (73.65%) followed by CaO (11.6 %) and Na₂O (7.86%) and rest of the elements are present in very little quantity (Table-1). In AC, the major constituting element is C (98.46%) whereas remaining constituents (Na₂O, Al₂O₃, K₂O, CaO and FeO) are present in very negligible percentage (Table-1). Mapping of the different constituting elements of CR and AC was also analyzed by the EDS shown in Figures 2a and b.

![Figure-1. SEM macro and micrographs of ceramic (a) and activated carbon (b) used in the experiments.](image)

<table>
<thead>
<tr>
<th>Adsorbents</th>
<th>Chemical composition (wt. %)</th>
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<tbody>
<tr>
<td></td>
<td>Na₂O</td>
</tr>
<tr>
<td>Ceramic</td>
<td>7.86</td>
</tr>
<tr>
<td>Activated carbon</td>
<td>0.49</td>
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</table>
3.2. Hg adsorption

Irrespective of treatment, the Hg adsorption ranged from 47.4 to 99.61 µgL\(^{-1}\) and 51.1 to 100 µgL\(^{-1}\) in the experiment of pH and temperature effect, respectively throughout the period of experimentation. Mean concentration of Hg in water showed a treatment dependent significant different between the CR and AC (ANOVA, p > 0.05). In AC, the total adsorption value was 16 to 52% and 21 to 48% higher over the CR treatment in the experiment of pH and temperature effect, respectively. As time progressed, the concentration pronounced a gradual declining trend in CR and a sharp decreasing trend in AC (Figures-3a and b).
3.3. Effects of pH

There was a significant pH dependent response in the adsorption of Hg in two experiments (ANOVA, p > 0.05). Hg adsorption was maximum in CRpH7 (83.08 µgL⁻¹) and minimum in CRpH4 (47.4 µgL⁻¹) in CR, whereas an increasing trend was observed with decreasing pH in AC and ranged from 96.39 to 99.11 µgL⁻¹ (Figure-3a). CRpH7 showed 40 to 43% higher adsorption value over the CRpH4 and CRpH10, whereas ACpH4 exhibited 0.26 to 3.23% greater adsorption value than that of the ACpH7 and ACpH10.

3.4. Effects of temperature

The concentration of Hg also showed a significant temperature dependent response in CR and AC (ANOVA, p > 0.05). Unlike pH, an increasing adsorption rate of Hg was exhibited with increasing temperature for both CR and AC (Figure-3b). CRT35 adsorbed 32 to 35% higher Hg over the CRT25 and CRT15, whereas ACT35 exhibited 0.13 to 0.84% greater value than that of the ACT25 and ACT15.

3.5. Adsorption efficiency (AE)

Adsorption efficiency (AE) varied from 0.31 to 0.65 µgL⁻¹g⁻¹h⁻¹ and 0.33 to 1.75 µgL⁻¹g⁻¹h⁻¹ in the experiment of pH and temperature effect, respectively (Figures-4a and b). AC exhibited 15 to 52% (experiment of pH effect) and 49 to 70% (experiment of temperature effect) higher AE than that of the CR. Cent percent of AE
was found in AC within 57 h in ACT treatment, whereas CR adsorbed Hg from the water slowly until 153 h.

4. DISCUSSIONS

As total Hg adsorption was varied from 47.4 to 83.08 µg L$^{-1}$ in ceramic, whereas an extremely elevated value of adsorption (96.39 - 100 µg L$^{-1}$) was revealed in activated carbon; furthermore, adsorption efficiency of activated carbon exhibited 15 to 52% (experiment of pH effect) and 49 to 70% (experiment of temperature effect) higher than that of the ceramic. Considering these results, it implies that the activated carbon is a proficient adsorbent than that of the ceramic from the Hg adsorption point of view. Because elaborate surface structure obtained from the SEM study clearly demonstrated that total surface of the activated carbon is highly uneven possessing more porosity resulting in the greater available Hg adsorptive total surface area compared to ceramic due to having very less uneven surface and less porosity (Figures-1a and b). Former proposition is also strongly supported by EDS results (Figures-2a and b). Former proposition is also strongly supported by EDS results (Figures-2a and b).

It is also signified that pH 7 is optimum in ceramic for Hg adsorption which reduced H$^+$ concentration and conferred a congenial environment for minimizing the positive ions competition between proton (H$^+$) and the positively charged Hg(I) ion on the surface of ceramic and increased the Hg adsorption rate than pH 4 in one hand, similarly higher pH (pH 10) increased the another competition of positive metal ions that was also responsible for lower adsorption over pH 7 in other hand. In this respect, it may be concluded that ion exchange mechanism also responsible to reduce the Hg concentration in water along with adsorption in ceramic. Chen and Wang put forwarded that pH increases or the concentration of protons is reduced; this results in a production of surface metal-adsorbent complex or higher removal of metal ions [34].

In activated carbon, maximum adsorption was found in pH 4 because it may be optimum to reduce HgCl$_2$ into Hg (I) by the surface functional groups than the remaining pH. From the above points of view and chemical composition of activated carbon clearly concluded that the adsorption is the main mechanism for Hg removal from aqueous phase. The adsorption of HgCl$_2$ on activated carbons in the liquid phase may take place by two mechanisms, i.e. adsorption of the HgCl$_2$ specie and/or reduction to Hg (I) by the surface functional groups [28]. In contrary, highest temperature (35°C) of the medium facilities the adsorbents to remove higher amount of Hg from water phase in both ceramic and activated carbon. Therefore, it may be concluded that surface group activity of adsorbents, ionization and movements of Hg ions increases with increasing temperature that leads to the higher rate of Hg adsorption. Salim et al. suggested that adsorption of cadmium was found to be dependent on contact time, temperatures, initial metal concentrations, adsorbent size and doses and also proposed that pH 7.5 in the optimum for arsenic adsorption of ceramic [26,27].

5. CONCLUSIONS

On account of the above discussion derived from the critical appraisal of results of present experiment, the following conclusions may be drawn:

- Though Hg adsorption of activated carbon is higher compared to ceramic but ceramic is also an alternative low cost, natural, ecofriendly and promising adsorbent with slow adsorption rate.
- PH and temperature have significant influence in the Hg adsorption mechanism of ceramic and activate carbon. PH 7 is the optimum for Hg adsorption in ceramic, whereas increasing and decreasing pH levels from pH 7 govern the reduced Hg adsorption. In activated carbon, the lower pH (pH 4) is favourable for higher rate of Hg adsorption.
- Increasing temperature enhances the Hg adsorption efficiency in ceramic as well as activated carbon.
- In ceramic, adsorption and ion exchange are the main mechanism whereas only adsorption is the principal mechanism for activated carbon to remove Hg from aqueous phase.
Figure 4. Hg adsorption efficiency (AE) of ceramic and activated carbon in different pH (a) and temperature (b).

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