

Investigating methods and effective parameters in the adsorption of mercury from aqueous solutions

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Abstract:

A serious environmental threat from heavy metal ion pollution, especially mercury, has generated a great deal of attention in recent years. In this paper, we have evaluated the efforts which have been done for controlling the mercury emissions from aqueous solutions. According to the Indian Standard Institution, the tolerance limit for Hg (II) for discharge into inland surface water is 10µg/l and for drinking water is 1µg/l. Mercury (Hg) is one of the heavy metals of concern and has been found in the waste waters coming from manufacturing industry, oil refinery, materials processing and natural sources. Among several types of technology for removing of Hg in water (chemical precipitation, reverse osmosis, ion-exchange, etc.), adsorption is one of most frequently used. It is a complex process involving physical, chemical, and electrical interactions at sorbent surfaces.

Keywords: Mercury; Removal; Adsorption; Aqueous solutions

Introduction

Mercury is one of the priority pollutant listed by USEPA [1]. The World Health Organization (WHO) reported that between 25,000 and 125,000 tons of mercury were released into the environment in 1976 [2]. Mercury (Hg) has been used for millennia in many applications, primarily in artisanal mining and as an electrode in the chlor-alkali industry. It is anthropogenically emitted as a pollutant from coal fired power plants and naturally emitted, primarily from volcanoes [3]. Mercury is well known as one of the most toxic pollutants with serious impact in the food chain due to potential Bioaccumulation. Mercury and its compounds act as dangerous and insidious poisons and can be adsorbed through the gastrointestinal tract and also through the skin and lungs [4]. After adsorption, mercury circulates in the blood and is stored in the liver, kidneys, brain, spleen and bone which can lead to several health problems such as paralysis, serious intestinal and urinary complications, disfunction of the central nervous system and, in more severe cases of intoxication, death. But mercury is still used worldwide in applications such as barometers, thermometers, pumps, lamps and in many others. Industries mainly responsible for the dispersion of mercury are the chlor-alkali, paint, oil refining, rubber processing and fertilizer [4]. According to the Indian Standard Institution, the tolerance limit for Hg (II) for discharge into inland surface water is 10µg/l and for drinking water is 1µg/l [1]. Among the many methods available for the removal

of trace metal from water namely chemical precipitation, ion exchange, coagulation, solvent extraction and membrane processes, adsorption has been shown to be an economically feasible alternative. Activated carbon is one of the most popular adsorbents for removal of mercury from aqueous solution.

Materials

Many different materials have been used as adsorbents for mercury removal. One of those is acrylic textile fibre and commercial sample of Kynol that Nabais et al. [4] used it for the preparation of two activated carbon fibres. Inbaraj and Sulochana [1] applied the fruit shell of Indian almond (*Terminalia catappa*) to make carbonaceous adsorbents. Also, rubber from the tyre wastes is used by Vizuete et al. [2] for the preparation of adsorbents. In this way, other carbonaceous raw materials that can be used for preparing activated carbon for mercury removal are walnut shell, coconut shell, eggplant skin, pine, oak, and olive woods, etc. Some researchers used other adsorbents such as microorganisms [5], Fuller's earth (FE) [6], fly ash produced from coal combustion in power plant [7], antibiotic waste [8], and furfural [9]. Fly ash was used in water treatment to remove mercury and also to immobilize mercury mobile forms in silts and soils. Stabilization and solidification (S/S) of mercury-containing solid wastes is also made by the combination of activated carbon and Portland cement [10].

Effect of pH

Zhang et al. [11] are reported that in the pH range of 1–4.1, decreasing pH value would decrease the amount of Hg(II) photo-reduced. They have achieved higher Hg (II) removal by increasing the pH value as it shown in Figure 1.

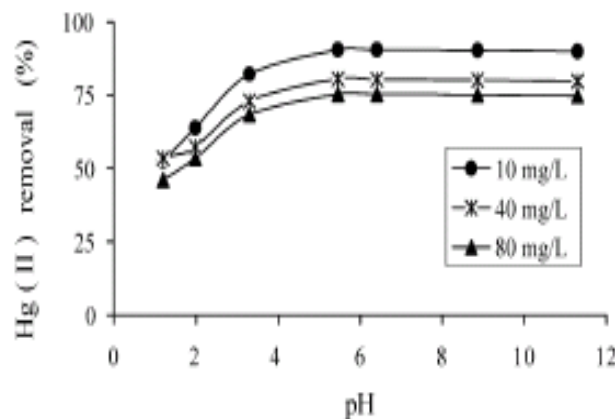


Fig. 1. Effect of pH on Hg(II) removal with different initial Hg concentration by sewage sludge carbons [11].

Rio and Delebarre [7] have reported that the percentage of Hg (II) removal increased with the increase of pH value by using different adsorbents according to the results shown in Table 1. Ruiz [5] has used microorganisms and found that an intermediate pH value between 4.5 and 6.0 could substantially increase mercury removal. This effect was more

significant when the mercury concentration was low (1 and 5 mg.l⁻¹). It is expected that the adsorption of metals decrease at low pH values because of competition between cations and protons for binding with sites. The results presented in Table 2 suggest that these two processes occurred in the mercury–bacteria-pH systems studied, with maximum biosorption at pH between 4.5 and 6. Inbaraj and Sulochana [1] have also found that the pH of the solution plays a vital role in any adsorption process. The removal of Hg (II) increased with increase in pH and reached a shoulder-like maximum at pH of 6.0 followed by a sharp increase in removal reaching close to 100% over the pH range of 7.0–10.0. They have used a carbonaceous sorbent derived from the Indian almond shell. Yardim et al. [9] studied the effect of pH of the solution on the extent of adsorption. They have adjusted the pH by the addition of hydrochloric acid. The adsorption percentage increased in the pH range from 2 to 5 and stayed almost constant for pH higher than 4 as shown in Figure 2.

Table 1. Effect of pH on removing mercury by different adsorbents [7].

Type of adsorbents (Fly ashes)	pH of adsorption experiments	Hg ⁺² removal (%)
Silico-aluminous	3	42.1
	4	43.4
	5	52.7
Sulfo-calcic	3	70.2
	4	78.6
	5	81.2

Table 2. Effect of pH on Hg (II) biosorption at 25°C and initial Hg concentration of 5 (mgL⁻¹) [5].

pH	Removal mercury(%)
3	31.4±11.6
4.5	68.3±14.6
6	88.1±18.2
7.5	15.9±9.7
9	12.9±9.7

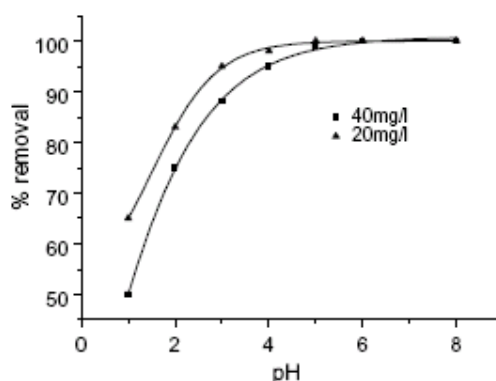


Fig. 2. Effect of pH on Hg(II) removal with different mercury concentration: ▲ 20 mg/l, ■ 40 mg/l [9].

Some authors indicated that surface charge is an important factor for the metal adsorption. The surface charge is very much dependent on the pH of the solution. Budinova et al. [8] showed that the antibiotic activated carbon is effective for the quantitative removal of Hg (II) over the pH range of 5.0–7.0. They also indicated that adsorption of mercury will be increased by increasing pH as can be seen in Figure 3.

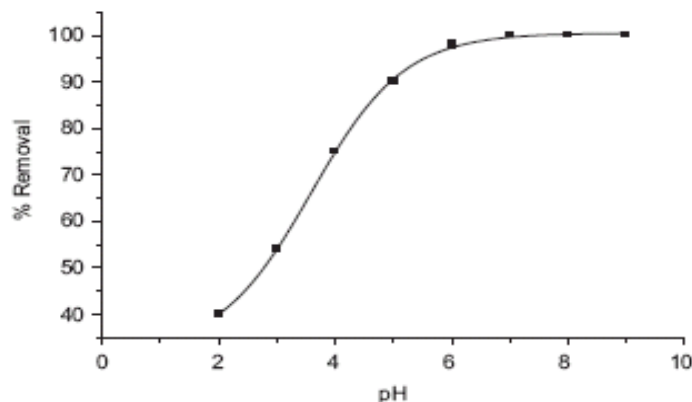


Fig. 3. Effect of pH on Hg(II) removal at Hg(II) concentration of 40 mg/l [8].

Effect of initial Hg (II) concentrations

Zhang et al. [11] studied mercury adsorption with sewage sludge carbon and showed that the Hg removal increased almost linearly with the enhancement of Hg (II) concentration (Figure 4).

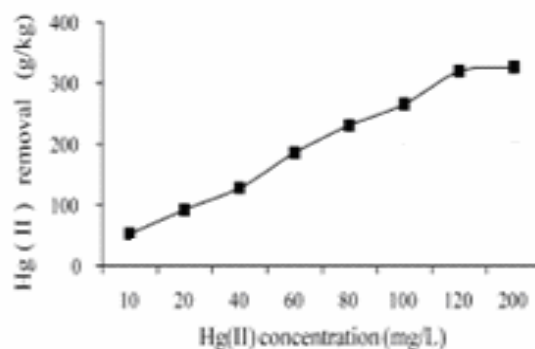


Fig. 4. The effect of initial Hg (II) Concentrations on its removal by sewage sludge carbon [11].

Inbaraj and Sulochana [1] found that the adsorption capacity increased from 21.67 to 85.32 mg/g while initial Hg (II) concentration increase from 5 to 60 mg/l. Similar results have been obtained from the study of Yardim et al. [9] that can be seen in Figure 5.

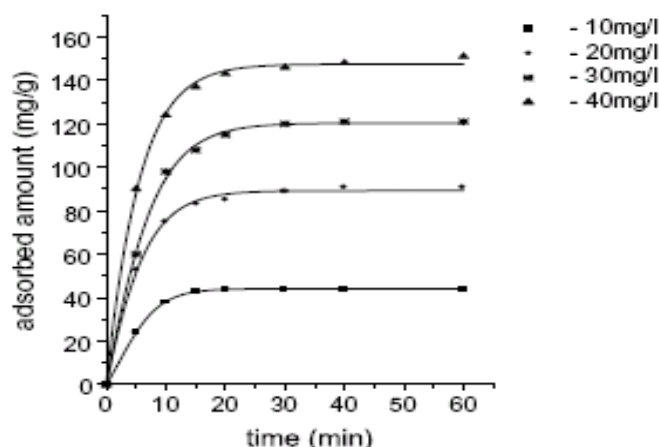


Fig. 5. Effect of initial Hg (II) concentration on its adsorption at pH=5.5 [9].

Applying microorganisms for removing mercury is found to be an effective technology for the treatment of industrial waste waters and may become an effective tool for the remediation of man-impacted coastal ecosystems with this metal. Nonviable biomass of an estuarine *Bacillus* sp. was employed for adsorbing Hg (II) ions from aqueous solutions at six different concentrations [5]. It has found that with increasing the initial Hg (II) concentrations, adsorption will be increased according to the graphs shown in Figure 6.

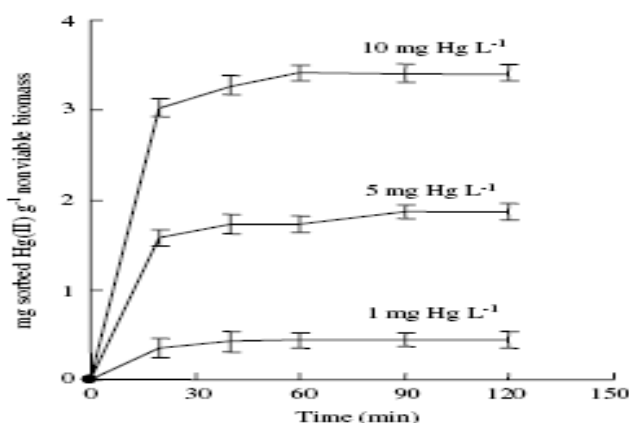


Fig. 6. Effect of initial Hg(II) concentration on its adsorption at pH=6 [5].

Effect of impregnation

Vizuite et al. [2] have reported that the adsorption process of mercury is faster when the material is heated or treated with the H_2SO_4 , HNO_3 or mixture of 1:3 $\text{H}_2\text{SO}_4/\text{HNO}_3$ solutions. They used rubber of the tyre wastes to prepare carbonaceous adsorbents and maximum adsorption of mercury was 211 mg g^{-1} in that case. Nabais et al. [4] have used commercial acrylic textile fiber and sample of kynol for preparing carbonaceous adsorbents and modified them by reaction with powdered sulfur and H_2S gas in order to increase the sulfur content of the adsorbents for the removal of mercury from aqueous

solution. The sulfur introduced ranged from 1 to 6 wt% depending on the two methods used (method A: sulfur introduction with solid S and method B: sulfur introduction with H₂S gas).

It can be concluded that the principal factor for mercury uptake is the sulfur functional groups present in the adsorbent and the chemical interactions between them. These groups were formed by the sulfurizing technique and the best method was found to be H₂S in the gas phase as the samples had the highest mercury uptake values, despite the low sulfur amount introduced. Utilizing powdered sulfur as sulfurizing method produced samples that could totally remove the mercury species presented in the stack of a fluidized bed using fossil fuels. In another case, when the carbonaceous adsorbents prepared from sewage sludge was impregnated with methanol, it was found that methanol addition into the adsorption system greatly enhanced the mercury adsorption capacity of the SS carbon as seen in Figure 7 [11].

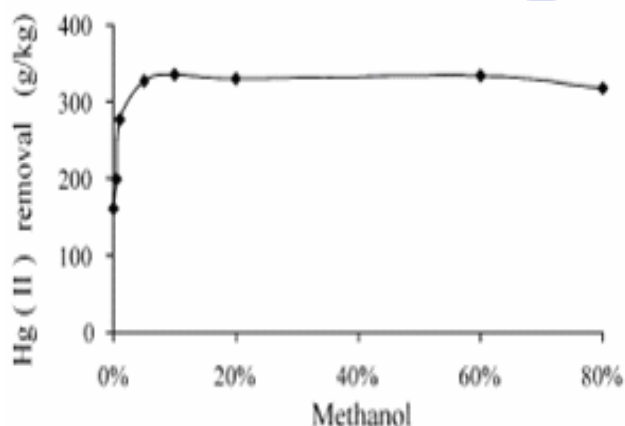


Fig. 7. Effect of methanol addition on the removal of Hg(II) by SS carbon [11].

In the study of Budinova et al. [8] porous carbon was prepared from waste antibiotic material by a chemical activation method using K₂CO₃ as an activating reagent. The adsorption capacities of activated carbons towards iodine (mg/g) increased slightly with the enhancement amount of K₂CO₃ in the mixture from 0.5 to 1. The results for the samples with K₂CO₃:antibiotic weight ratios of 1:1 and 3:1 revealed that, in the experimental conditions used, the development of porosity in the sample is almost independent of the K₂CO₃ content. Since the use of the smallest amount of the activating agent permits to achieve practically the same textural characteristics of the materials where the highest amount of K₂CO₃ was used, the sample 1:1 was selected for further detailed investigations. In the case in which a carbonaceous sorbent derived from the fruit shell of Indian almond by sulfuric acid treatment was used for the removal of mercury (II) from aqueous solution [1], it has been found that by impregnating of the adsorbents, their surface area would be decreased. One should know that this parameter is very important in adsorption, because by impregnating adsorption will be increased.

Effect of carbonization temperature

Vizuet et al. [2] found that the adsorption capacity of tyre rubber towards mercury is greatly enhanced when it is heated at 400 or 900 °C. In the study of Budinova et al. [8] the effect of calcination temperature on the iodine adsorption capacity of the antibiotic carbons was clear. There was a correlation between the adsorption capacity towards iodine and the BET surface area for the adsorbents with a surface area around 1000m²/g. As it seen in Figure 8, the iodine adsorption capacity of carbons increase continually from 490 to 1170 mg/g with the activation temperature between 600 and 900°C, and then conversely decrease to 980 mg/g at 950°C.

It is obvious that the increase in temperature promotes a continuous development of the porosity. This indicates that, K₂CO₃ functions as an activating reagent at a temperature above 600°C. Reduction of adsorption capacity over 900°C may be due to the fact that K₂CO₃ evaporates above this temperature. At temperature above 900°C, further enhancement in temperature probably induces combination of micropores, resulting in the increase in meso- and macropores and corresponding decrease in micropore volume and specific surface area [8]. In another case, where the carbonaceous adsorbents were prepared from the shell of *Terminalia catappa*, sorption capacity increased with temperature enhancement and the thermodynamic parameters of ΔH° , ΔS° and ΔG° indicated that the Hg (II) sorption was endothermic and spontaneous with increased randomness at the solid–solution interface.

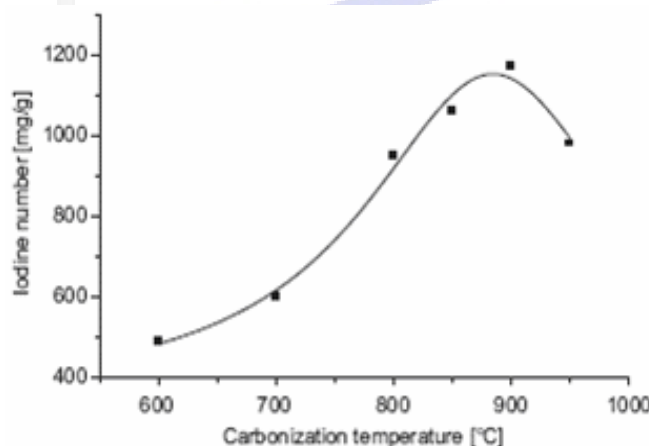


Fig. 8. Influence of carbonization temperature on mercury removal with activated carbon from antibiotic waste [8].

Effect of porosity structure

The adsorption process of mercury is faster provided that the adsorbent is a non-porous solid, its mesopore volume is high or its pore size distribution in the macropore region is wide. But, usually the adsorption capacity is larger for the adsorbents with higher developments of the microporosity. This result has been obtained from the research done on the adsorption of mercury using carbonaceous adsorbents prepared from rubber of tyre wastes [2]. The surface properties strongly depend on the preparation conditions. The

antibiotic carbon adsorbent, derived by chemical activation, had high specific surface area and predominantly microporous structure [8].

Conclusions

The results of several investigations on the adsorption of mercury by carbonaceous materials from aqueous solutions reveal that the best absorbent is activated carbon with agricultural base. Employing activated carbons, adsorption will be increased by increasing initial Hg (II) concentration, pH of the solution, contact time and surface area of the absorbent. With physical activation, carbonization temperature in the adsorbent preparation step, and with chemical activation, types of chemicals used in the impregnation step are the most influencing parameters on the adsorption of mercury. Another important factor is the structure of porosity. In this regard, micropores have significant role in the adsorption capacity and meso- and macropores influence the adsorption kinetics. Finally, all the information collected from the literature are summarized in Table 3 for comparison.

Table 3. Summary of the results about absorbents and the best condition for mercury adsorption

Type	Base	Impregnant	Model	Surface area (m ² /g)	Capacity or mercury removal	Porosity or avg. particle size	pH	Temp. (°C)
C-S & C-N	Rubber from tyre wastes	H ₂ SO ₄ , HNO ₃ or H ₂ SO ₄ /HNO ₃	Freundlich	2.3 & 2.0	211 mg g ⁻¹	Microporosity	3.8	400 or 900
Fuller's earth (FE)	Fuller's earth (LobaChemie, India)	-	Freundlich	120-140	99.8%	10 μm	6.7±0.2	30
Activated carbon (AC)	merck	-	Freundlich	1250	96.1%	104 μm	6.7±0.2	30
KACFH2S61h	Commercial acrylic textile fibre & Kyno	powdered sulfur & H ₂ S gas	-	1259	-	-	6	400
Ss activated carbon	Sewage sludge	ZnCl ₂	Freundlich	555	98%	-	5-12	650
Silicoaluminous fly ashes	Silico-aluminous fly ashes	-	-	12	52.7%	20 μm.	5	30
Sulfo-calcic fly ashes	Sulfo-calcic fly ashes	-	-	12	81.2%	20 μm.	5	30
Activated carbon	Antibiotic waste	K ₂ CO ₃	Langmuir	1260	129 mg/g	Microporosity	5.5	Room temp.
F-400 [12]	Activated carbon	-	Freundlich	1050	-	-	8.8-9.5	Room temp.
CB II [12]	Activated carbon	Sulfur	Freundlich	1150	-	-	8.8-9.5	Room temp.
Mersorb [12]	Activated carbon	Sulfur	Freundlich	1000	-	-	8.8-9.5	Room temp.
GT73 [12]	Ion-exchange resin	Thiol and minor sulfonic acid groups	Freundlich	55	-	-	8.8-9.5	Room temp.
Carbonaceous sorbent (tcc)	Shell of Indian almond (<i>Terminalia catappa</i>)	Sulfuric acid	Langmuir & Redlich-Peterson	13	94.43 mg/g	180-210 μm	7-10	32-60
Activated carbon	Furfural	Sulfuric acid		1100	174 mg/g	0.2 mm	5.5	20

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