Impregnation of Cupper into Kanuma Volcanic Ash Soil to Improve Mercury Sorption Capacity

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Abstract—The present study attempted to improve the Mercury (Hg) sorption capacity of kanuma volcanic ash soil (KVAS) by impregnating the cupper (Cu). Impregnation was executed by 1 and 5% Cu powder and sorption characterization of optimum Hg removing Cu impregnated KVAS was performed under different operational conditions, contact time, solution pH, sorbent dosage and Hg concentration using the batch operation studies. The 1% Cu impregnated KVAS pronounced optimum improvement (79%) in removing Hg from water compare to control. The present investigation determined the equilibrium state of maximum Hg adsorption at 6 h contact period. The adsorption revealed a pH dependent response and pH 3.5 showed maximum sorption capacity of Hg. Freundlich isotherm model is well fitted with the experimental data than that of Langmuir isotherm. It can be concluded that the Cu impregnation improves the Hg sorption capacity of KVAS and 1% Cu impregnated KVAS could be employed as cost-effective adsorbent media for treating Hg contaminated water.

Keywords—Cupper, impregnation, isotherm, kanuma volcanic ash soil, mercury, sorption

I. INTRODUCTION

MERCURY (Hg) is one of the most persistent and hazardous metals in the environment [1]. High toxicity, volatility and potential bioaccumulation properties of Hg are responsible for posing serious human and environmental health risks. Harmful toxic effects of Hg and its derivatives lead to develop various disorders in organ systems of humans [2]–[5]. The U.S. Environmental Protection Agency estimated 630,000 newborns in America are at risk of unsafe levels of Hg exposure [6].

Generally, natural, anthropogenic and re-emitted Hg is basic sources of contamination in the environment [7]. It can be released into the aquatic environment from natural processes such as, volcanic activity and weathering rocks, as well as from industries such as, coal burning, electronic, paper, pharmaceutical industries [8], [9] chlor-alkali, paint, pulp and paper, oil refinery, electrical, rubber processing, and fertilizer industries [10], [11]. About 2000 tonnes/annum Hg is emitted by anthropogenic sources, of which about 30% are from coal-fired power plants [12].

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To control the persistent hazardous problems of Hg contamination in the aquatic environment, several removal techniques, employed include chemical or electrochemical precipitation [13], coagulation [14], electrodialysis [15], ultra filtration [16], ion exchange [17], biologic [18], and adsorption [19]. Adsorption is one of the simple and cost effective techniques. Recently, varieties of materials have been tested as alternative low-cost sorbents, activated carbon [20], [21], minerals and soils [22], [23], zeolites and clay/soil based ceramic [24]–[28] to adsorb various toxic metals and metalloids. Study also suggested that soil or clay derived ceramics are an alternative adsorbent media to remove mercury from water [19], [29]. The present study used Kanuma volcanic ash soil (herein named as KVAS) has also been characterized as a good low-cost Hg removing agent by [29]. From this point of view, the improvement of Hg sorption capacity of existing sorbent media is also important aspect to reduce the treatment cost of contaminated water. Therefore, the aim of present study was to impregnate cupper into KVAS for the improvement of Hg adsorption capacity from aqueous phase. Influence of different factors concerning the sorption process of the impregnated material was also characterized in this investigation.

II. MATERIALS AND METHODS

A. Impregnation of Cupper

Cupper (Cu, 99.5%; Kanto Chemical Co. Inc., Tokyo, Japan) was impregnated into KVAS in the present study. Cupper powder was added in 10 ml distilled water @ 1 and 5% and 5 g KVAS was mixed properly to each solution to make homogenous slurry. Only 5 g KVAS was mixed with distilled water for using as control received no Cu powder. Slurries were then oven dried at 100°C for overnight. The Cu impregnated KVAS was used for sorption experiments.

B. Hg Sorption Experiment

To find out the effect of different percentages of Cu in sorption capacity of KVAS, nine capped glass bottles (0.1 L) were filled with 0.05 L Hg (HgCl$_2$; Cica-Reagent, Kanto Chemical Co. Inc., Tokyo, Japan) solution (0.4 mg/L) and randomly divided into three groups having three replicates each (3 x 3). One group employed for control received control KVAS @ 1 g/L (K) and remaining two groups provided with 1 and 5% Cu impregnated KVAS (K+1%Cu and K+5%Cu) @ 1 g/L. Bottles were shaken at 200 excursion/min by a mechanical shaker for sufficient contact period 24 h at 25°C. Samples were collected to determine the Hg^{2+} removal

capacity by calculating the mercury removal percentage (MRP) following the equation (1):

$$MRP = \frac{C_0 - C_e}{C_0} \times 100 \qquad (1)$$

Where, C_0 and C_e are the initial and final concentrations (mg/L), respectively. Optimum Hg^{2+} removing Cu impregnated KVAS was used for determining the effect of process parameters in sorption process.

C. Influence of Process Variables

Hg^{2+} sorption of selected Cu impregnated KVAS was performed in capped glass bottles (0.1 L) using known weight of sorbent, volume of water (0.05 L) and concentration of Hg following the batch operation mode within temperature controlled mechanical shaker at 25°C. The effect of contact periods was determined maintaining the initial concentration 0.4 mg/L and sorbent dose 1 g/L. The experiment was carried out in 5 different pH values 3.5, 6.21, 7.57, 9.9 and 10.8 to determine the specific pH required for optimum Hg^{2+} sorption. The initial concentrations, 0.1, 0.2, 0.3, 0.4, 0.5 and 0.6 mg/L were maintained to examine the effects of initial Hg^{2+} concentration, whereas the sorbent dosages, 0.4, 0.8, 1.2, 1.6, 2 and 2.4 g/L were provided to ascertain the effect of sorbent dosages in Hg removal process. The mean value of at least two studies maintaining identical conditions was considered for data analysis.

The Hg^{2+} sorption onto the Cu impregnated KVAS at the equilibrium, q_e (mg/g) was calculated by following equation (2) of mass balance relationship:

$$q_e = \frac{(C_0 - C_e)\, V}{M} \qquad (2)$$

Where, C_0 (mg/L) and C_e (mg/L) are initial and equilibrium water phase concentration of Hg, respectively, V (L) is the volume of Hg solution and M (g) is the mass of Cu impregnated KVAS.

D. Hg Analysis

The collected water samples were 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.

III. RESULTS AND DISCUSSION

A. Hg Sorption Experiment

Values of MRP were 24.6, 79 and 94% in K, K+1%Cu and K+5%Cu, respectively (Fig. 1). MRP of K+1%Cu and K+5%Cu were 221 and 282% higher compare to K, respectively. Data revealed that MRP of K+5%Cu is only 1.19 times greater than that of the K+1%Cu, whereas percentage impregnation of Cu in K+5%Cu was five times higher over K+1%Cu. Results clearly demonstrated that though Hg^{2+} removal capacity was increased with increasing the percentage

impregnation of Cu, but it was not proportionate with increasing percentage of Cu impregnation. The probable reasons might be the hindering the process of Hg binding onto the functional surface area in K+5%Cu which resulting in the lower rate of Hg binding in K+5%Cu. Therefore, from the environmental and cost-effective viewpoints, it can be suggested that impregnation of 1% Cu powder in the KVAS would be appropriate for removing optimum Hg from water phase. Due to this reason, further Hg sorption studies was carried out with 1% Cu powder impregnated KVAS (K+1%Cu).
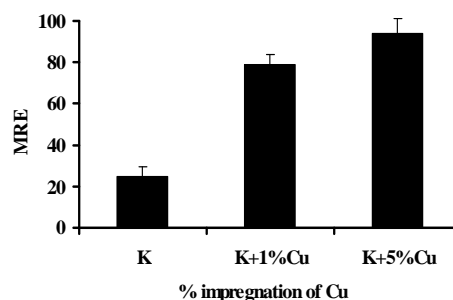

Fig. 1 Removal percentage of Hg^{2+} in Cu impregnated KVAS and control KVAS

B. Influence of Process Variables

1. Contact Time (T)

The influence of contact time in Hg^{2+} removal process of K+1%Cu was shown in Fig. 2. A sharp Hg^{2+} sorption trend was found at 3 h period which followed by slow rate of sorption thereafter and equilibrium state was achieved at 6 h. From the present experimental condition, 6 h could be considered as equilibrium contact time.

2. Initial pH

Fig. 3 showed the influence of pH on the Hg^{2+} sorption process of K+1%Cu. The Hg^{2+} sorption was lowest at pH 7.57, whereas it showed an increasing trend with increasing and decreasing level of pH of water. The maximum sorption was observed at pH 3.5 in the present experiment. Results clearly revealed that the pH of solution plays a role in Hg^{2+} sorption mechanism of K+1%Cu.
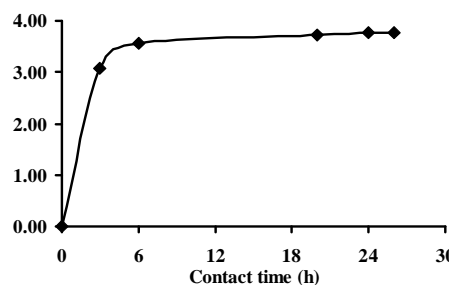

Fig. 2 Influence of contact time in the Hg^{2+} sorption of K+1%Cu (initial concentration 0.4 mg/L, dosage 1 g/L and pH 6.5)

Though pH 3.5 (0.37 mg/g) showed higher (8 – 27%) sorption capacity than that of the remaining pH, but pH ~6.5 could be considered as effective condition of water medium to remove substantial amount of Hg^{2+} (0.34 mg/g) from the view point of environmental perspective. Therefore, this pH was used for other experiments.
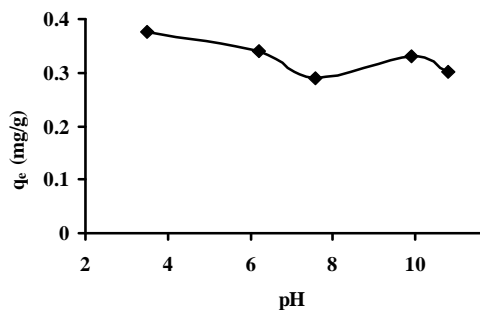

Fig. 3 Influence of initial pH on the Hg^{2+} sorption onto K+1%Cu (initial concentration 0.5 mg/L, dosage 1 g/L and contact time 6 h)

3. Initial Hg Concentration (C_0)

The effect of initial Hg^{2+} concentration in the sorption of used sorbent media was shown in Fig. 4. The sorption was gradually increased with increasing initial concentration of Hg^{2+} by per gram of employed sorbent. The maximum Hg^{2+} sorption of highest initial concentration (0.595 mg/L) was higher (14.5 – 471%) compare to remaining initial concentrations. Hg^{2+} saturation rate on the binding sites of functional groups of sorbent was greater in the higher concentrations by means of increasing electrostatic interactions which resulting in the increasing rate of sorption.

4. Adsorbent Dosage (M)

The influence of sorbent dosages was depicted in Fig. 5. Total Hg^{2+} sorption of K+1%Cu adsorbent media increased with increasing the dosages, whereas a declining trend was observed in the sorption amount for per gram of sorbent.
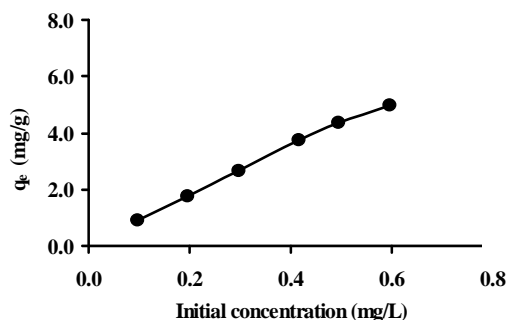

Fig. 4 Influence of initial concentration on the Hg^{2+} sorption onto K+1%Cu (dosage 1 g/L, contact time 6 h and pH 6.5)

The maximum sorption rate (1.36 mg/g) in lowest dose (0.4 g/l) was 100, 189, 277, 388 and 466% higher than that of 0.8, 1.2, 1.6, 2 and 2.4 g/l dosages, respectively. The decreasing of sorption rate with the increasing sorbent doses may results from the electrostatic interactions, interference between binding sites, and reduced mixing for higher densities at

higher doses of adsorbent [30], [31]. This is supported by the metal removal results of sequential adsorbent treatment using solid adsorbents (such as sand, silica, coal and alumina) proposed by Yabe and de Oliveira [32].
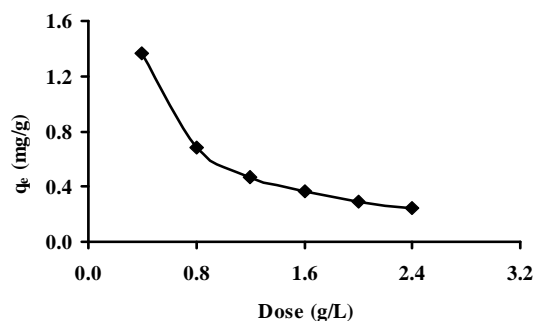

Fig. 5 Influence of sorbent dosages on the Hg^{2+} sorption of K+1%Cu (initial concentration 0.5 mg/L, contact time 6 h and pH 6.5)

C. Sorption Isotherms

The equilibrium data of sorption studies are commonly known as sorption isotherm. It depicts the relationship between the solid phase concentration and liquid phase concentration of sorbate. This relationship under different operational conditions of the batch experiments helps to determine the effectiveness of adsorbent which is most important for applying in the practical fields [33], [34]. Generally, the Langmuir and the Freundlich equations are commonly used for isotherm models. In the present study, the Langmuir and the Freundlich models were considered to ascertain the Hg^{2+} sorption capacity of K+1%Cu. The used Langmuir and Freundlich equations are described in following equation 3 and 4, respectively:

$$q_e = \frac{K_L q_m C_e}{1 + K_L C_e} \qquad (3)$$

Where,
K_L = Constant related to free energy of adsorption
C_e (mg/g) = Equilibrium concentration in solution
q_m (mg/g) = Adsorption capacity corresponding to the complete monolayer coverage

$$q_e = K_F C_e^{1/n} \qquad (4)$$

Where,
K_F (L/mg) = Freundlich constant
C_e (mg/g) = Equilibrium liquid phase concentration
$1/n$ = Heterogeneity factor

The equilibrium curve of Hg^{2+} sorption and calculated fittings parameters of K+1%Cu were presented in Fig. 6 and Table 1, respectively. In the present study, calculated R^2 values of Langmuir (0.836) and Freundlich (0.948) signified that the Freundlich isotherm is well fitted with the

experimental data compare to the Langmuir isotherm. Besides, a high K_F and n values of the Freundlich isotherm equation are the indicators of high adsorption throughout the concentration range. K_F and n values of the present study are also favourably higher which indicating the good Hg^{2+} adsorption characteristic of K+1%Cu. Oliveira and Montanher proposed that n value ranging between 1 to 10 signified good adsorption [35].

D. Sorption Mechanism onto K+1%Cu

Generally, both physical and chemical adsorptions are responsible to remove Hg from water solution. It is known that when Freundlich constant 1/n value is greater than unity, the adsorption bond becomes weak, i.e., probably physical sorption. 1/n value of present study is smaller than unity (Table I); therefore, it favours the chemisorptions rather than physical sorption. Moreover, it can be explained like that sorption mechanism of Hg^{2+} onto the K+1%Cu is largely influenced by the chemical interaction between surface functional group of K+1%Cu sorbent and Hg^{2+} which forms a ion complex resulting in the chemisorptions of Hg^{2+}. The mineral constituents of clay/soil serve as surface functional groups for forming ion complex with Hg onto soil. Clay minerals have a well-known structural adsorption, rheological and thermal properties [36], [37].
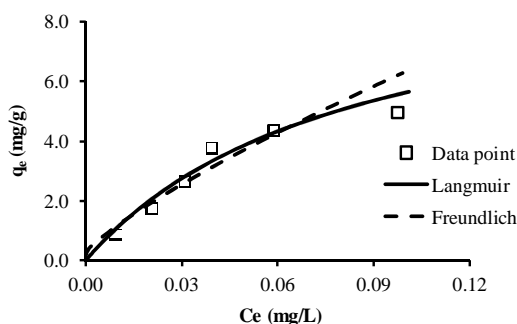

Fig. 6 Equilibrium curve of K+1%Cu for the sorption of Hg^{2+}

E. Practical Application and Management of Sorbent

Present study explored Hg sorption capacity of K+1%Cu adsorbent material that could be developed from naturally available KVAS by following simple method of impregnation described here. No higher technological and infrastructural facilities are required to develop such adsorbent media. From these viewpoints, it is obvious the present study used Hg removing materials would be low-cost adsorbent media compare to few other available low-cost adsorbents.

Practical application is the major aspects for any adsorbent media. A suggestive small scale application device comprising an adsorption chamber with continuous agitating system is a simple, feasible and affordably convenient approach (Fig. 7) for applying in the practical field especially in case of small scale industries to remove metals. Before discharging into the environment, contaminated effluents can be treated using the adsorbent by such simple devise. Besides, utilization of such Hg adsorbing media in the wastewater treating artificial wetland system as a bed would be another possible effective application method. Application of clay based ceramic as a vesicle with plant in the constructed wetland treatment system is a new approach for wastewater reclamation [29], [38]. From the environmental points of view, the proper management of metal loaded spent adsorbent should be important aspect to avoid the further hazardous problems. Hg can be desorbed from the spent adsorbent by EDTA which may be a simple and low-cost separating method though it was not considered in the present study. After separation, the Hg free sorbent could be recycled to lower the treatment cost of the contaminated water. Finally, the EDTA and metal complexes can easily be separated as a solid EDTA and metal salts with the help of sulfuric or hydrochloric acid. Apart from that, only acid extraction process of Hg would be a safe method if desorption process is not effective.
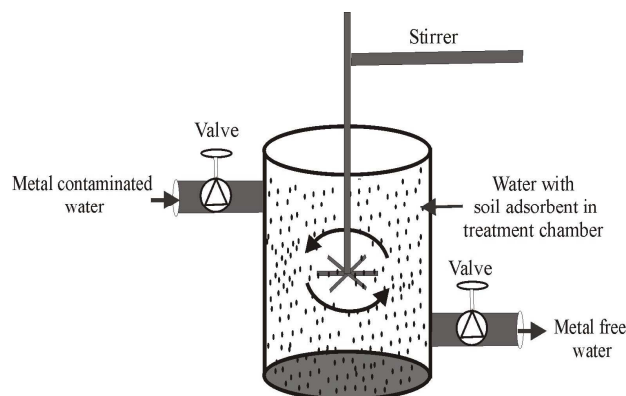

Fig. 7 A simple suggestive device for applying the developed sorbent

IV. CONCLUSIONS

In summary, it can be concluded that Cu powder is an effective improving agent in Hg^{2+} sorption process of KVAS. Lower percentage (1%) of Cu impregnation is comparatively cost-effective and environmentally sound to improve (79%) Hg^{2+} sorption capacity of KVAS. The batch operation studies revealed that Hg^{2+} adsorption properties of K+1%Cu is remarkably influenced by various factors studied herein. The present investigation determined the equilibrium state of maximum Hg adsorption at 6 h contact period and pH 3.5.

TABLE I
PARAMETERS OF LANGMUIR AND FREUNDLICH ISOTHERMS IN REMOVING Hg^{2+} FROM WATER

Sorbent	Langmuir			Freundlich		
	K_L (L/mg)	q_m (mg/g)	R^2	1/n	K_F	R^2
K+1%Cu	12.25	10.20	0.836	0.784	37.84	0.948

Obtained results also demonstrated adsorption capacity increased with increasing initial concentration of Hg, whereas a reverse response of adsorption capacity was pronounced in dosages when the other influencing parameters remained constant. The Freundlich isotherm model is well fitted with the experimental data compare to the Langmuir isotherm. The Freundlich constant 1/n value is also suggested the chemical sorption mechanism of the studied sorbent. Therefore, from the viewpoints of economic feasibility, availability and simple preparation method, 1% Cu impregnated KVAS could be employed as cost-effective sorbent media for treating Hg contaminated water.

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