REMOVAL OF HG(II) FROM AQUEOUS SOLUTION BY ADSORPTION USING CHEMICAL MODIFIED SOYBEAN HULLS AS AN ADSORBENT

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ABSTRACT

Adsorption of mercury(II) on chemically modified soybean hulls (CMSH) has been investigated as *a function* of solution pH, adsorbent dose, initial concentration and treatment time in *batch reactors*. The adsorbent modification was adopted to boost metal ion adsorption. Primarily soybean hulls were excreted with 0.2 N NaOH and then with 0.5 M citric acid. The optimized parameters are found to be pH: 4.5, adsorbent dose: 10 g/l, initial Hg(II) concentration: 20 mg/l and treatment time: 100 min. At these optimum conditions 96% removal of Hg(II) is recorded. The maximum adsorption capacity of Hg(II) is found to be7.46 mg/g. Freundlich isotherm suitably fitted to equilibrium data. Adsorption kinetic facts are satisfactorily represented by the pseudo-second order kinetic model. The results of experimental study showed that CMSH an outstanding adsorbent to remove Hg(II) from aqueous solution.

KEY WORD : Adsorption, Mercury(II), Chemically modified soybean hulls, Isotherm, Kinetics

INTRODUCTION

Mercury is the one of the most toxic heavy metals of particular concern in the treatment of wastewater due to its lethal effect to humans (Low *et al.*, 2000). Contamination owing to mercury is caused by several industries such as petrochemicals, mining's, paint, varnish, and fertilizers (Patterson, 1985). Mercury(II) and it's compounds are snowballing toxins and even in tiny quantities are unsafe to human being health (Cyr *et al.*, 2002). The major effects of mercury poisoning marked as neurological and renal disturbances as it can effortlessly enter in the blood-brain fence and have an effect on the brain. High amount of Hg(II) cause damage of pulmonary function and kidney.

Several methods have been employed such as precipitation, sedimentation, membrane processes, biological processes, ion exchange, electro-deposition, chemical reduction and adsorption. All these methods have their advantages and disadvantages in the application, in which adsorption is an effectual sanitization and parting method used in industry, particularly in water and wastewater handling (Al-Asheh *et al.*, 2000). The effective adsorbents reported for the elimination of Hg(II) are Acetobacterxylinum Cellulose (Rezaee *et al.*, 2005), coal fly ash (Sen and De, 1987), eggplant hull (Ahmadpour *et al.*, 2016),activated carbon prepared from agro waste (Rajeshwarisivaraj *et al.*, 2001), chitosan (Reddy and Lee, 2013) and waste citrus fruit peels (Sahety *et al.*, 2015). A lots of works reported on the development of adsorbents for the removal of Hg(II) (Ngah and Hanafiah, 2008).

The aims of the present study are 1) to develop inexpensive and effective adsorbent such as chemically modified soybean hulls (CMSH) for the removal of Hg(II); 2) to optimize the process parameters such as pH, adsorbent dose, treatment time and initial concentration; 3) to determine the kinetics parameter; 4) to determine the applicability of isotherm.

MATERIALS AND METHODS

Preparation of Chemically Modifed Soybean Hulls (CMSH)

In the present study soybean hull was washed and rinsed with deionized water and then sun dried. After freshening, hulls were pulverized and passed through screen of 20 mesh size. A powder soybean hulls treated with 0.1N NaOH. The slurry was enthused at 300 rpm for 1hour and rinsed with distilled water. The damp hulls were added to 200 ml of deionized water and rotate at 300 rpm for 45 minutes to remove excess NaOH. This process was frequently repeated three times to make sure complete removal of NaOH. The soybean hulls were mixed together with 0.5M citric acid in a proportion of 1.0g of soybean hulls to 8.0 ml citric acid. The citric acid treated soybean hulls slurry was dehydrated *over night* at 50 ºC. This modified soybean hulls *was then cleaned* by deionized water and then filtered. Lastly, the modified soybean hulls were dehydrated overnight at 50 ºC.

Adsorbate and Chemicals

The standard stock solution was made from mercury(II) chloride ($HgCl_2$). The known concentration of Hg(II) solution was made from dilution of stock solution. Solution pH was maintained by using 0.2N HCl or NaOH. All chemicals used in the study were of analytical grade.

Batch Adsorption Experimentation

Batch studies were performed for the removal of Hg(II) by using chemically modified soybean hulls. Each experiment was carried out using 50 ml solution of desired concentration of Hg(II) in 250 mL flask in an orbital shaker incubator at shaking speed of 300 rpm. Prior to experiment, a predetermined amount of adsorbent was added to the flask. At the end of experiments, solution was filtered throughout Whatman filter paper no 1 and then the filtered solution was used to analyze by Atomic Absorption Spectrophotometer (AAS) for residual Hg(II) content.

The proportion adsorption was determined as follows:

$$\% \text{ removal} = \frac{(C_i - C_o) \times 100}{C_i} \qquad .. (1)$$

Where, C_i and C_o are the initial and final concentration of Hg(II) ion.

The uptake of Hg(II) ions from aqueous solution was calculated by eq. 2.

$$q_e = \frac{(C_i - C_e) \times V}{W} \qquad .. (2)$$

Where, q is equilibrium quantity of Hg(II) ion adsorbed per unit mass of adsorbent (mg/g), v is volume of liquid, C_i is preliminary concentration of Hg(II) metal ion in the aqueous phase (mg/l), C_e is final equilibrium concentration of metal ion in the aqueous phase (mg/l), and w is mass of adsorbent in g.

RESULTS AND DISCUSSION

Effect of pH

Solution pH plays *a* significant role for adsorption process. Batch experiments were performed in the pH range of 2.0 to 9.0, while all others parameters were kept constant to get the optimum pH for adsorption process. Fig. 1 shows that the adsorption of Hg(II) is found minimum (75.2%) at higher pH (9.0)and maximum (96%) at the pH value of 4.5. High removal of Hg(II) implies that the CMSH has high affinity towards it. The most favorable pH for removal is found to be at pH value of 4.5, this is due to the high affinity as well as increase in *the carboxyl group* implanted on the hulls by reaction with citric acid.
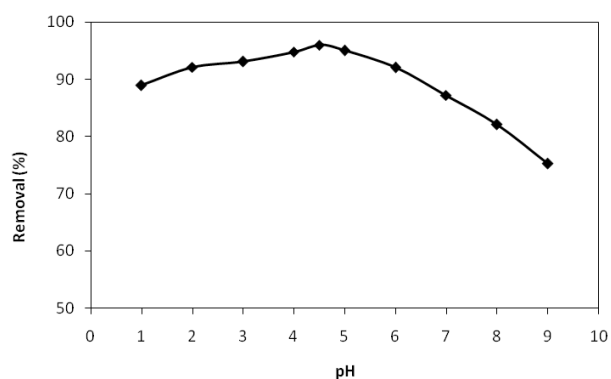

Fig. 1. Effect of pH on adsorption of Hg(II) (initial concentration: 20 mg/l, treatment time: 100 min., adsorbent dose: 10 g/l)

Effect of Adsorbent Dose

The effect of adsorbent dose on removal of Hg(II)is illustrated in Fig 2. It is revealed from Fig. 2 that the percent removal of Hg(II) increases from 57.2% to 96% by increasing the dose of the CMSH from 1 g/l to 11 g/l, respectively. As the dose increases, at *a fix concentration* of Hg(II), more surface area as well as active site were available for adsorption thus the removal increases. The equilibrium was achieved at

10 g/l adsorbent dose. However, after 10 g/l since the majority of the Hg(II) were adsorbed, the driving force (concentration gradient) to bring the Hg(II) ions from the bulk of the solution to the adsorbent surface decreases. Accordingly, increase in adsorbent dose does not increase the percentage removal above 10 g/l of adsorbent dose.

Effect of Treatment Time

Fig. 3 illustrates the effect of treatment time on adsorption of Hg(II) onto CMSH. For 20 mg/l initial concentration nearly 60% of total Hg(II) uptake achieved in first 10 minutes and then increases gradually to 96 % at 100 min and finally attained equilibrium value. *At* the start of adsorption, *a more active site* was available at fix *concentration, hence* high removal (96%) achieved. As the time passes free site of adsorbent and concentration driving force both reduces which result in less removal. *For* further experiment an equilibrium time of 100 minutes was chosen as the most favorable time.
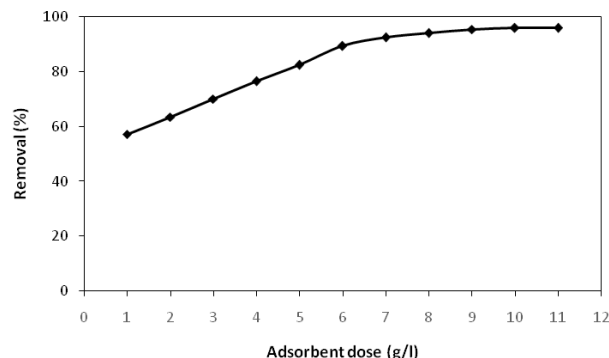

Fig. 2. Effect of Adsorbent dose on removal of Hg(II) (pH: 4.5, initial concentration: 20 mg/l, treatment time: 100 min.)

Effect of Initial Concentration

The experimental results of adsorption of Hg(II) by CMSH at various initial concentrations 20, 40, 60, 80, and 100 mg/l for fixed dose 10 g/l of adsorbent at pH 4.5 is shown in Fig. 4. It is found that with the augment in initial Hg(II) concentration, the Hg(II) removal decreases, while the adsorption capacity increases and found maximum at 100 mg/l. Maximum percentage removal (96%) achieved at 20 mg/l initial concentration. *In* lower *Hg(II)* concentration, the number of CMSH adsorbent surface active sites is sufficiently high and accommodates abundance of Hg(II) ions. An augment in the Hg(II) concentration, less proportion of surface active sites of CMSH to Hg(II) ions available, thus, an insufficient accommodation of

Hg(II) ions results in the decrease of removal efficiency. When the initial concentration of Hg(II) increases percent adsorption decreases, whereas the amount of Hg(II) adsorbed per unit mass of CMSH increases. The equilibrium adsorption is augmented from 1.52 to 5.15 mg/g as the Hg(II) concentration increased from 20 to 100 mg/l.
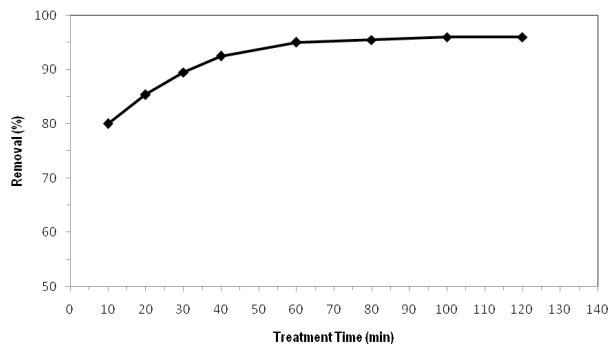

Fig. 3. Effect of treatment time on removal of Hg(II) (pH: 4.5, initial concentration: 20 mg/l, adsorbent dose: 10 g/l)

Adsorption Isotherm Model Studies

Adsorption isotherm indicates the circulation of adsorbate molecules among solid and liquid phase when system is in equilibrium. For the design purpose adsorption model with isotherm data are essential.

Langmuir isotherm model (Langmuir, 1916) is largely implemented to monolayer adsorption on uniform and vigorously standardized surfaces. The Freundlich isotherm model (Freundlich, 1906) is extensively in use to conclude the adsorbed amount of absorbent surfaces with non-uniform energy division. The mathematical equations of Langmuir and Freundlich isotherm models are articulated by equation no. 3 & 4, respectively:

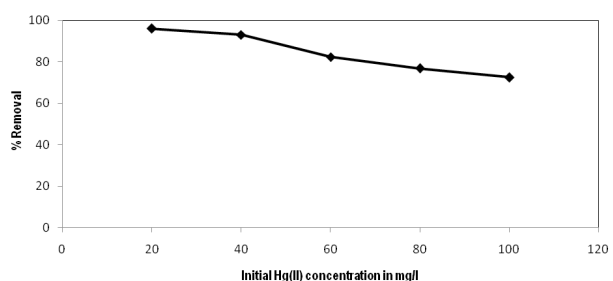$$\frac{C_e}{q_e} = \frac{1}{q_{max} K_L} + \frac{C_e}{q_{max}} \qquad .. (3)$$

Fig. 4. Effect of initial Hg(II) concentration on removal of Hg(II) (pH: 4.5, adsorbent dose: 10 g/l, treatment time: 100 min.)

$$logq_e = logK_f + \frac{1}{n}logC_e \qquad \text{.. (4)}$$

Where, q_{max} (mg/g) is the maximum amount of dye adsorbed at equilibrium, K_L is the Langmuir isotherm constant, n is a heterogeneity factor and K_f is the Freundlich isotherm constant.

Graph between C_e/q_e Vs C_e, $logq_e$ Vs $logC_e$ were plotted. The Langmuir isotherm model and Freundlich isotherm model on CMSH are illustrate in Fig. 5 and Fig. 6, respectively. The values of q_{max}, K_L, K_f and n were calculated by use of the slopes and intercepts of the graphs (Fig. 5 and Fig, 6) and provided in Table 1.
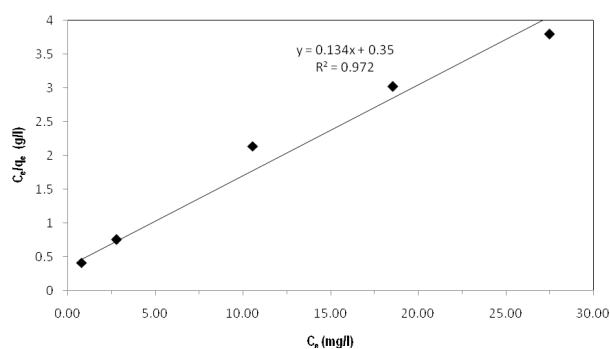

Fig. 5. Langmuir isothermal model graph for removal of Hg(II) on CMSH
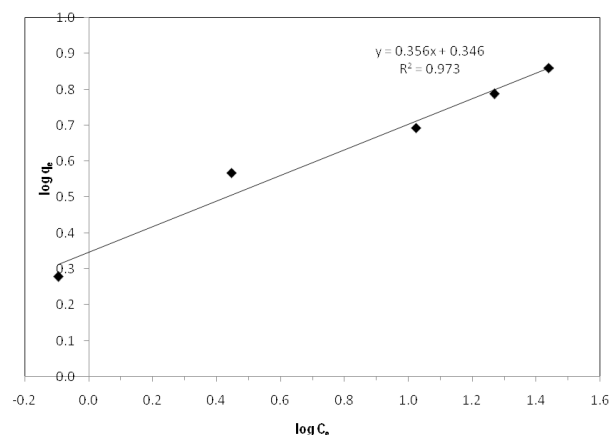

Fig. 6. Freundlich isothermal model graph for removal of Hg(II) on CMSH

For Langmuir model, Hg(II) adsorption onto CMSH monolayer maximum adsorption capacity is found to be 7.46 mg/g. The value for Langmuir constant is found to be 0.383 for Hg(II) at R^2 of 0.972. Hall *et al.* (1966) narrated a dimensionless equilibrium parameter to be precise separation factor (R_L), in order to disclose the vital feature of the Langmuir isotherm involving R_L with Langmuir constant band the initial concentration of the

Table 1. Langmuir isotherm model and Freundlich isotherm model constants for adsorption of Hg(II) onto CMSH.

Langmuir			Freundlich		
q_{max}	K_L	R^2	K_f	n	R^2
7.46	0.383	0.972	2.218	2.808	0.973

adsorbate solution, C_o i.e. $R_L = 1/(1+bC_o)$. The R_L is found to be 0.1155 thus R_L falls in between zero and one, which signifies highly favorable adsorption and applicability of the Langmuir isotherm also.

Fig. 6. Shows the logarithmic graph of the Freundlich isotherm for the Hg(II). The adsorption activities of the dyes undertaken could be described well by Freundlich isotherm model with high values of correlation coefficient (R^2: 0.973). When n>1 indicates a approving adsorption situation (Treybal, 1998). According to Kadirvelu and Namasivayam (2000), the value of n amongst 1 and 10 represents an advantageous adsorption procedure. Heterogeneity factor 1/n is related to the intensity of adsorption. In this study 1/n is found to be 0.356, which is observed to be less than 1 and describes a favorable nature of adsorption onto WHRP. Based on the R^2 value, Freundlich isotherm suitable represents the equilibrium data of Hg(II) adsorption process.

Adsorption Kinetics Models Fitting

For adsorption study both rate and time are essential to appreciate the adsorption kinetic and interaction of Hg(II) on CMSH. Hence, two kinetic models pseudo-first-order (PFO) and pseudo-second-order (PSO) were used to designate the kinetic data of Hg(II) adsorbed onto CMSH. The numerical equations for pseudo-first and pseudo-second-order kinetics models were articulated by equation 5 & 6, respectively.

$$ln(q_e - q_t) = lnq_e - K_1t \qquad \text{.. (5)}$$

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \qquad \text{.. (6)}$$

Where, q_e (mg/g) and q_t (mg/g) are adsorption capacity at equilibrium and time t, respectively. Whereas, k_1 (min⁻¹) and k_2 (g mg⁻¹min⁻¹) are the rate constant of PFO and PSO, respectively.

Table 2 represents the kinetic parameters for Hg(II) adsorption on CMSH. From Table 2, it is evident that the pseudo-second-order model gives better t to the experimental data for Hg(II) adsorption on CMSH with R^2 values of 0.999.

Table 2. Adsorption rate constant and coefficient of correlation associated with the pseudo first and pseudo- second-order kinetic model.

	C_o(mg/l)	q_e (mg/g)	q_{cal} (mg/g)	k	R^2
Pseudo I[st] order kinetic model	20	1.92	0.561	0.050	0.987
Pseudo IInd order kinetic model	20	1.92	1.94	0.236	0.999

Therefore, it may be conclude that Hg(II)adsorption on CMSH follows a chemisorption/ion exchange mechanism.

CONCLUSION

The study showed the effectiveness of chemically modified soybean hulls (CMSH) for removing Hg(II) from wastewater using adsorption techniques. CMSH natural adsorbent is found outstanding adsorbent for removal of Hg(II). The kinetic study data fitted well with the pseudo-second-order kinetics model rather than pseudo-first-order kinetics model. Adsorption isotherm data are well fitted in Langmuir and Freundlich isotherm both. The obtained adsorbent shows a high removal (96%) of Hg(II) at optimum conditions. Chemisorption/ion exchange mechanism is found responsible for high removal of Hg(II). Moreover, the CMSH adsorbent provides an natural and feasible method for a removal of Hg(II). In addition to that, the results obtained from the experimental research would be useful in the design of an Hg(II) treatment process for industrial application.

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