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تحت عنوان

Mercury Adsorption on a Carbon Sorbent Derived from Walnut Shell

در دوازدهمین کنگره ملی مهندسی شیمی ایران موجب امتنان و غنای علمی هرچه بیشتر این همایش ملی گردید. بدین وسیله از طرف برگزار کنندگان و شرکت کنندگان حاضر در کنگره از فعالیت و تلاش علمی جنابعالی و سایر همکاران تقدیر و تشکر نموده و موفقیت روز افزون حضرتعالی را در عرصه های مختلف علمی، پژوهشی و صنعتی از درگاه احدیت مسئلت داریم.

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MERCURY ADSORPTION ON A CARBON SORBENT DERIVED FROM WALNUT SHELL

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Abstract. A carbonaceous sorbent derived from an Iranian walnut shell (WS) were prepared by chemical activation method using $ZnCl_2$ as an activating reagent. WS may be used in water treatment to remove mercury (Hg^{++}) from water. The adsorption of mercury ion (Hg^{++}) were performed from aqueous solutions at 302 K. Adsorption studies of Hg (II) were carried out by varying several conditions such as: treatment time, metal ion concentration, adsorbent amount, pH and solution temperature. It was also determined that Hg (II) adsorption follows both Langmuir and Freundlich isotherms. It was shown that Hg (II) uptake decreases with increasing pH of the solution. The monolayer sorption capacity was obtained as 151.5 mg/g.

Keywords: Adsorption, Mercury, Kinetic, Sorbent, Walnut shell.

1. Introduction

Mercury is one of the priority pollutant listed by USEPA as it can easily pass the blood-brain barrier and affect the fetal brain. High concentration of Hg(II) causes impairment of pulmonary function and kidney, chest pain and dyspnea [1,2]. According to the Indian Standard Institution (ISI), the tolerance limit for Hg(II) for discharge into inland surface waters is 10μg/L [3] and for drinking water is 1 μg/L [4]. Consequently, removal of mercury in water and wastewater assumes importance. Although the flux of mercury into the aquatic system has declined in recent years, there is still a lack of an effective, cheap means for the treatment of mercury containing wastewaters. Activated carbon is one of the most popular adsorbents for the removal of mercury from aqueous solution [5–6] although other materials have been used including onion skin [7], waste rubber [8], coconut husk [9], and fertilizer waste slurry [10]. In view to combine efficiency and cost effectiveness several non-conventional cheap materials like peanut hull [11], jackfruit peel [12], coir pith [13] flax shive [14] and sago waste [15] have been tried as carbonaceous precursors and applied for the removal of mercury.

In recent years, adsorption techniques have been widely investigated for the removal of heavy metals from wastewaters. There are two fundamental methods for the preparation of popular adsorbents i.e. activated carbons: physical and chemical activation. The physical activation method involves carbonization of raw material followed by activation at high temperature in carbon dioxide, steam or water vapor atmosphere [16-18]. Chemical activation which is a well-known method for the preparation of activated carbon, involves one step heat treatment at lower temperature than physical activation in the presence of some chemical agents. This method has been the objective of numerous studies within the last few years as it presents several advantages compared to the so-called physical activation. In this paper we have used chemical activation method for the preparation of activated carbons from local walnut shell.

2. Materials and methods

Fruit shell of walnut, collected from a local source, was dried and ground into small pieces. The powdered samples were impregnated with $ZnCl_2$ (136.28 g/mol, 98%) concentrated solution in a weight ratio of 1:0.5 (shell:$ZnCl_2$) and the resulting black product was dried in an oven at 120°C for at least 5 hrs. The impregnated sample was placed on a ceramic boat and then inserted to a tubular furnace. The sample was heated to the carbonization temperature under N_2 flow at the rate of $15^{o}C/min$. After carbonization, the sample was cooled down under N_2 flow. The carbonized sample was washed several times sequentially with hot water, and finally with cold distilled water to remove any residual chemicals. The activated carbon product was then dried at $130^{o}C$. The adsorbent particle size distribution was obtained and the mean diameter was about 0.088 mm. All the chemical and reagents used were of analytical reagent grade obtained from Merck.

3. Adsorption studies

The adsorption of Hg(II) from aqueous solution by activated carbon derived from walnut shell was studied. The adsorbate containing solution was prepared by dissolving necessary amount of $HgCl_2$ in distilled water. The solution was diluted to obtain standard solutions containing 9.7-107 mg/L of Hg(II). Batch adsorption studies were carried out with 0.05g sorbent and 50ml of Hg solution with the desired concentration at pH solution of 5 in conical flasks. The flasks containing adsorbent and adsorbate were agitated for predetermined time intervals at room temperature on a mechanical shaker with 720rpm. At the end of agitation the suspensions were filtered by the aid of microporous filter paper. The amount of the Hg(II) ion in the final volume of 25 ml was determine spectrophotometrically on Specord UV–VIS (Varian, spectra-110-220/880 Australia Pty. Ltd.).

4. Results and discussion

4.1. Effect of pH

The uptake of Hg (II) as a function of hydrogen ion concentration was determined in the pH range of 2-11. At pH values below 2, hydrogen ions are likely competing with the mercuric ions and adsorption of mercury was decreased by increasing pH. The results at two different initial concentrations are presented in Fig. 1. The maximum adsorption was observed at pH 2. In general the results indicated that the adsorption is highly pH dependent. Similar results have been reported in previous studies [10,19,21].

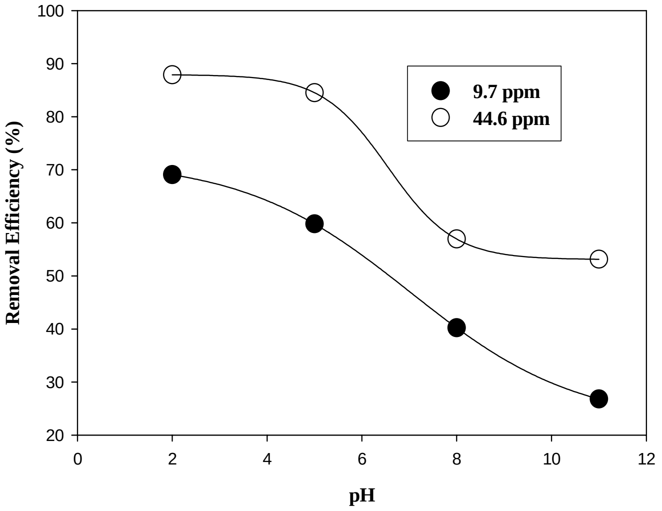

Fig. 1. Effect of pH on the adsorption of Hg (II) (time=15 min, temperature=$29^{o}C$)

4.2. Effect of temperature

In general the adsorption phenomena is exothermic, so by increasing temperature of solution, uptake of Hg(II) should be decreased. But in liquid phase, diffusion is the control step of the process, therefore by increasing temperature uptake of Hg(II) would be increased. This can be observed in Fig. 2.

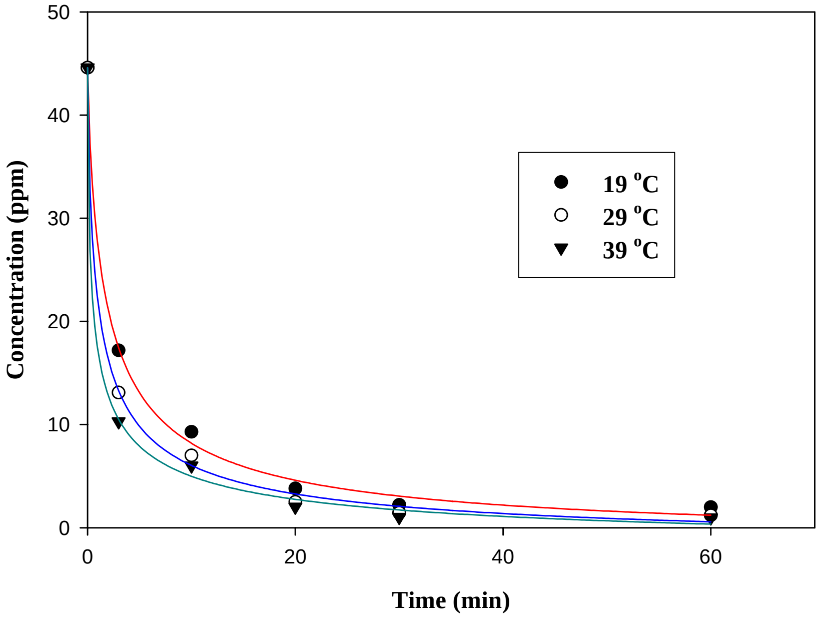

Fig. 2. Effect of temperature of Hg solution

4.3. Effect of initial concentration

Usually in studies of mercury adsorption, the Hg(II) removal increased almost linearly with the enhancement of Hg(II) concentration. Many researchers have observed similar results. For example, Zhang et al. [22] studied mercury adsorption with sewage sludge carbon and showed that the Hg removal increased linearly with the enhancement of Hg(II) concentration. Inbaraj and Sulochana [23] found that the adsorption capacity increased from 21.67 to 85.32 mg/g while initial Hg(II) concentration increased from 5 to 60 mg/L. Similar results have also been obtained from the study of Yardim et al. [24]. Our findings shown in Fig. 3 are another confirmation for the above subject. In this case, several solutions with initial concentrations of 9.7, 20.8, 44.6, and 107 ppm were prepared and for each solution the fixed amount of 0.05g adsorbent was used. Also, the temperature of solutions was maintained at 29^{o}C and pH of initial solutions was set to 5. In similar experiments for obtaining the isotherms, 0.02g absorbent was used for 60 min time at 29^{o}C and pH=5.

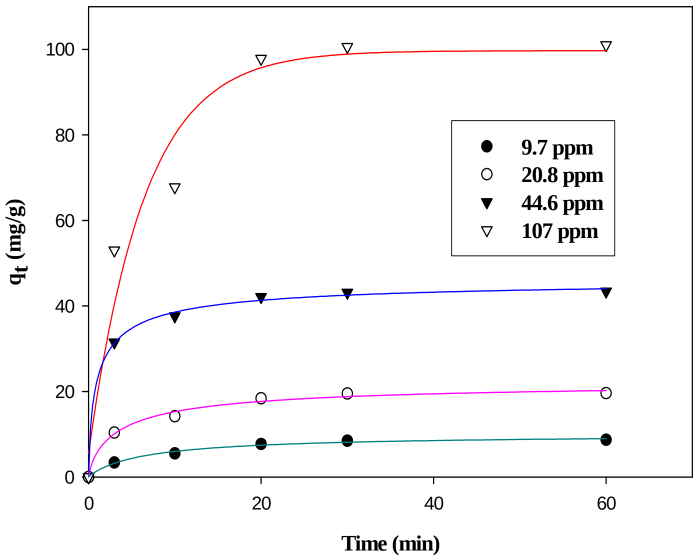

Fig.3. Effect of initial concentration of Hg solution

4.4. Adsorption Isotherms

Adsorption isotherm of mercury that was examined with Hg(II) concentration ranged from 9.7 to 107 mg/L is presented in Fig. 4. The amount of mercury adsorption is calculated by:

$$q_e = \frac{(C_o - C_e)V}{W} \tag{1}$$

Where q_e (mg/g) is the amount of ion adsorption by the adsorbent phase at equilibrium, C_0 and C_e are the initial and equilibrium concentrations of mercury ion (mg/L) in the solution, V is the volume of solution (L), and W is the weight of adsorbent (g) in the mixture.
The experimental data on equilibrium studies for the adsorption of Hg(II) on walnut shell were also tested to fit the various 2-parameter adsorption isotherm models.

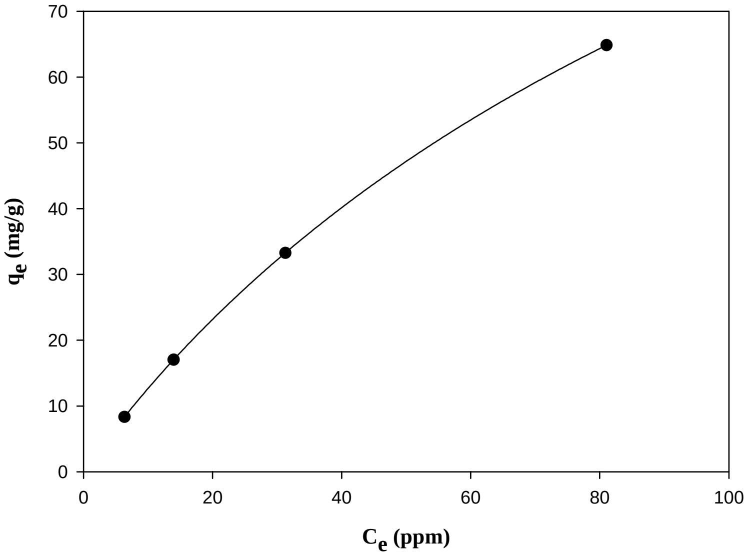

Fig.4. Adsorption isotherm of mercury on WS

4.4.1. Freundlich model

The Langmuir and Freundlich equations are commonly used for describing adsorption equilibrium for water and wastewater treatment applications. Freundlich model often gives a better fit particularly for adsorption from liquids and can be expressed as [25]:

$$q_e = K_f C_e^{\frac{1}{n}} \qquad (2)$$

Where K_f and n are Freundlich constant related to adsorption capacity and adsorption intensity. The plot for the adsorption of Hg(II) on WS are shown in Fig. 5. It gives a good fit to the experimental data with the correlation coefficient of R^2 = 0.99651. Usually, for a good adsorbent $0.2<1/n<0.8$. A smaller value of $1/n$ indicates better adsorption and formation of relatively strong bond between the adsorbate and adsorbent.

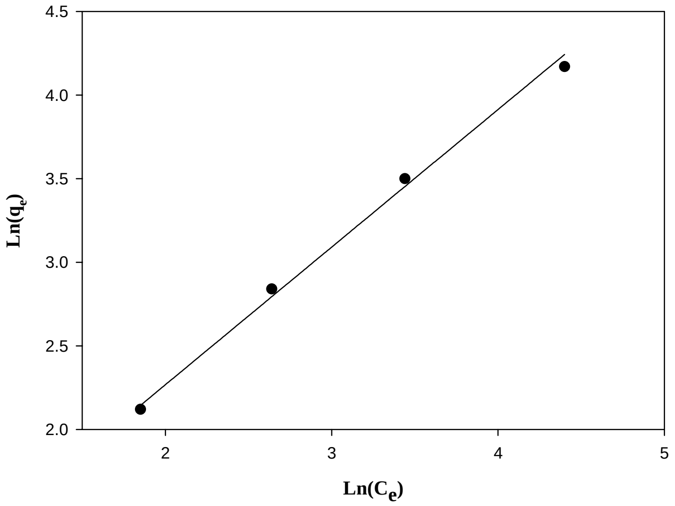

Fig.5. Freundlich plot of Hg (II) at 29°C

4.4.2. Langmuir model

The Langmuir adsorption isotherm is given by the following equation [26]:

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

In the model, q_m (mg/g) is the amount of adsorption corresponding to complete monolayer coverage, i.e. the maximum adsorption capacity and b (L/mg) is the Langmuir constant related to the energy or net enthalpy of adsorption. When C_e/q_e is plotted against C_e, a straight line with the slope of $1/bq_m$ is obtained (Fig. 6), which indicate that the adsorption of mercury follows the Langmuir isotherm.

A host of research workers have applied this model to interpret their sorption data [27,28]. In the present work, we find that the plot gives a fairly good fit to the experimental data with R^2 =0.99812. The Freundlich and Langmuir constants were obtained from the plots and their values are given in Table 1 for comparison. It is seen that the Langmuir model fitted the results slightly better than the Freundlich model.

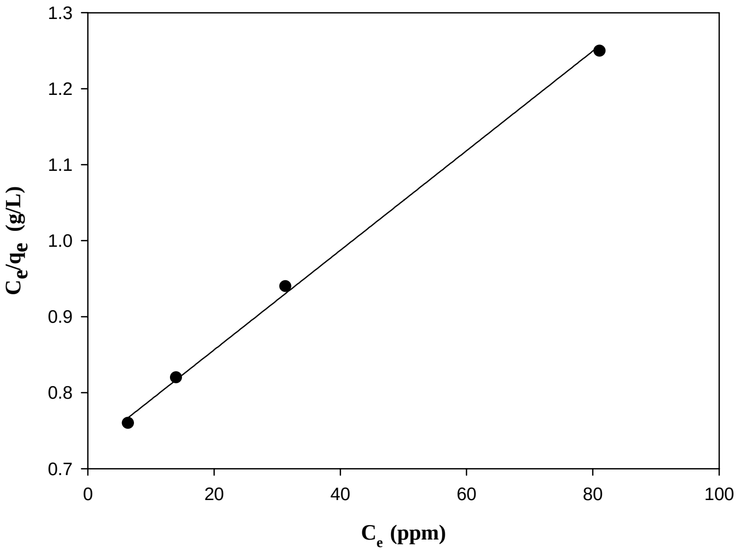

Fig. 6. Langmuir plot of Hg (II) at 29°C

Table 1. Fitted isotherm models for the adsorption of Hg(II) on WS.

Model	Linearized equation	Parameters	R^2
Freundlich	$Ln(q_e) = Ln(K_f) + \frac{1}{n} Ln(C_e)$	K_f=1.8623 1/n=0.8229	0.99651
Langmuir	$\frac{C_e}{q_e} = \frac{1}{q_m b} + \frac{1}{q_m} C_e$	q_m=151.5 b=0.0091025	0.99812

4.5. Kinetic studies

The rate constant for surface adsorption of the Hg(II) ion on WS is also studied under the light of the pseudo-first-order rate expression of Lagergren model and the pseudo-second order kinetic rate expression of Ho and McKay [29]. The integrated form of the Lagergren equation is given by:

$$Ln(q_e - q_t) = Ln(q_e) - \frac{K_1}{2.303} t \tag{4}$$

Where q_t (mg/g) is the amount of adsorbed metal ion on the adsorbent at time t, q_e is the equilibrium sorption uptake, and K_1 (min^{-1}) is the rate constant of first-order adsorption. q_e is extrapolated from the experimental data at time t = infinity. A straight line of $ln(q_e - q_t)$ versus t suggests the applicability of this kinetic model. q_e and K_1 can be determined from the intercept and slope of the plot, respectively.

The pseudo second-order kinetic rate expression in the integrated form is:

$$q_t = \frac{t}{(1/K_2 q_e^2) + (t/q_e)} \tag{5}$$

where K_1 and K_2 are the first order and second order rate constants (min^{-1}).

The values of different parameters determined from pseudo-second-order and pseudo-first-order kinetic model for mercury ions with their corresponding correlation coefficients are presented in Table 2. The fitted curves of the models along with the experimental data are illustrated in Figs. 6 and 7 for comparison. The experiments were performed at three different temperatures and with the initial mercury concentration of 44.6 ppm.

Table 2. Parameters of the kinetic models for adsorption of Hg(II) on WS.

Kinetic model	Fitted parameters (min^{-1})	R^2	Temp. (^oC)
Pseudo first order	$K_1 = 0.3788$	0.95159	19
Pseudo first order	$K_1 = 0.3461$	0.98926	29
Pseudo first order	$K_1 = 0.3630$	0.90550	39
Pseudo second order	$K_2 = 0.0121$	0.99785	19
Pseudo second order	$K_2 = 0.0182$	0.99845	29
Pseudo second order	$K_2 = 0.0265$	0.99837	39

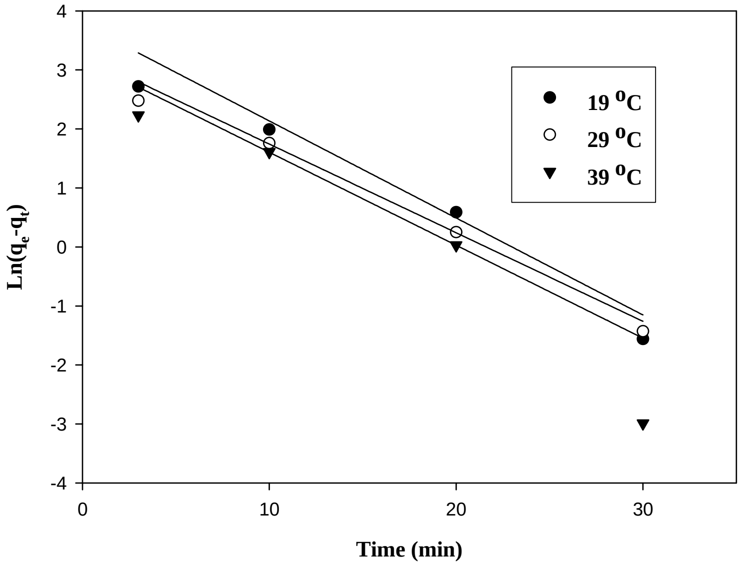

Fig. 6. Lagergren plots for the adsorption of Hg (II) at 19, 29, 39°C, first order model.

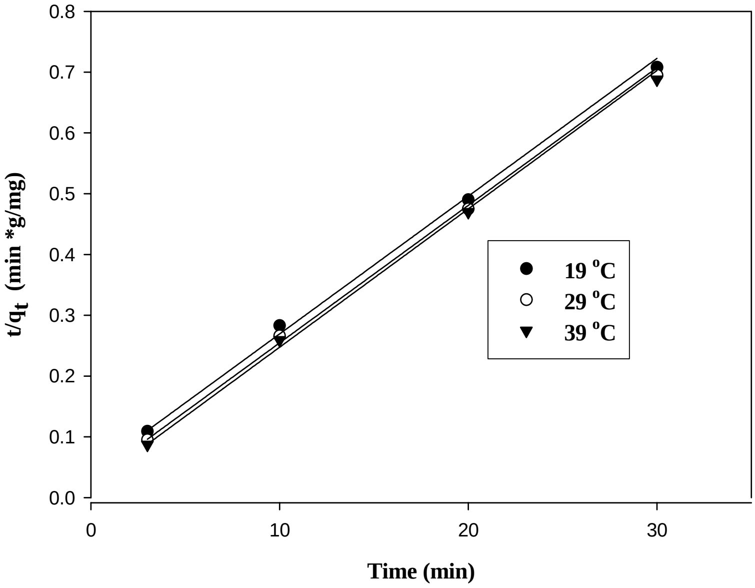

Fig. 7. Lagergren plots for the adsorption of Hg (II) at 19, 29, 39 °C, second order model.

The correlation coefficients for the second-order kinetic model are very close to 1, therefore this model will be better to explain the kinetics of adsorption in the present case. The monolayer adsorption capacity of Hg(II) on WS is calculated as 151.51 mg/g at pH 5.0 and room temperature of 29°C. For the comparison cases, the monolayer adsorption capacity of mercury by using several other adsorbents is presented in Table 3. It is seen from the table that our adsorbent (WS) has a high capacity for Hg(II) removal from the aqueous solutions compared to the other adsorbents.

Table 3. Monolayer adsorption capacity of mercury for various adsorbents.

Adsorbent type	q_m (mg/g)	Ref.
Acrylic textile fibre Kynol fiber	290-710	[30]
Furfural	174	[24]
Activated carbon (coirpith)	154	[13]
Walnut shell (WS)	**151.51**	*
Activated carbon (antibiotic waste)	129	[31]
PHC-peanut hull carbon	110	[11]
Coal adsorbents (Some)	105	[32]
Activated carbon (Indian almond)	94.43	[23]
Coal adsorbents (Mengen)	92	[32]
Activated carbon	69.44	[33]
Coal adsorbents (Seyitomer)	56	[32]
Sago waste carbon	55.6	[15]
Coal adsorbents (Bolluca)	37	[32]
Carbon aerogel	34.96	[34]
Commercial activated carbon	12.38	[11]
Sulfo-calcic ashes	4.9	[35]
Waste rubber	4	[8]
Silico-aluminous ashes	3.2	[35]
Fuller's earth	1.145	[33]
Granular activated carbon	0.8	[7]
Activated carbon (fertilizer waste)	3.62×10^{-3}	[21]

* Adsorbent used in the present study.

5. Conclusion

The present study has revealed the feasibility of using a WS sorbent derived from an agriculture waste for the removal of mercury from aqueous solutions. The adsorption was well described by pseudo-second-order kinetic and Langmuir isotherm models. The adsorption capacity of the WS was 151.51 mg/g at pH 5.0 for the particles of 0.088 mm size. The WS is a local cheap adsorbent which is available in most areas in the country.

References

[1] Berglund F. and Bertin M., Chemical Fallout, Thomas Publishers, Springfield, 1969.

[2] Krishnamoorthi C.R. and Vishwanathan P., Toxic Metal in the Indian Environment, Tata McGraw Hill Publishing Co. Ltd., New Delhi, 1991.

[3] "Tolerance limits for industrial effluents", Indian Standards Institution, IS, 1981, 2490.

[4] "Drinking water specifications", Indian Standards Institution, IS, 1991, 10500.

[5] Huang C.P., “Chemical interactions between inorganic and activated carbon”, Carbon Adsorption Handbook, Ann Arbor Science, Ann Arbor, MI, 1978, 281– 329.

[6] Koshima H. and Onishi H., “Collection of mercury from artificial sea-water with activated carbon”, Talanta 27, 1980, 795–799.

[7] Ma X., Subramanian K.S., Chakrabarti C.L., Guo R., Cheng J., Lu Y. and Pickering W.F., “Removal of trace mercury(II) from drinking water: sorption by granular activated carbon”, J. Environ. Sci. Health, 27, 1992, 1389–1404.

[8] Knocke W.R. and Hemphill L.H., ”Mercury(II) sorption by waste rubber”, Water Res. 15, 1981, 275–282.

[9] Sreedhar M.K., Madhukumar A. and Anirudhan T.S., “Evaluation of an adsorbent prepared by treating coconut husk with polysulphide for the removal of mercury from wastewater”, Indian J. Eng. Mater. Sci., 6, 1999, 279–285.

[10] Srivastava S.K., Tyagi R. and Pant N., “Adsorption of heavy metal ions on carbonaceous material developed from the waste slurry generated in local fertilizer plants”, Water Res., 23, 1989, 1161–1165.

[11] Namasivayam C. and Periasamy K., “Bicarbonate-treated peanut hull carbon for mercury(II) removal from aqueous solution”, Water Res., 27, 1993, 1163–1168.

[12] Inbaraj B.S. and Sulochana N., “Utilisation of an agricultural waste, jack fruit peel for the removal of Hg(II) from aqueous solution, in: R.L. Mersky (Ed.)”, Proceeding of 17th International Conference on Solid Waste Technology and Management, Philadelphia, 2001, 802–811.

[13] Namasivayam C. and Kadirvelu K., “Uptake of mercury(II) from wastewater by activated carbon from an unwanted agricultural solid by-product coirpith”, Carbon, 37, 1999, 79–84.

[14] Cox M., El-Shafey E.I., Pichugin A.A. and Appleton Q., “Removal of mercury(II) from aqueous solution on a carbonaceous sorbent prepared from flax shive”, J. Chem. Technol. Biotechnol., 75, 2000, 427– 435.

[15] Kadivelu K., Kavipriya M., Karthika C., Vennilamani N. and Pattabhi S., “Mercury(II) adsorption by activated carbon made from sago waste”, Carbon, 42, 2004, 745–752.

[16] Minkova V., Budinova T., Petrov N., Razvigorova M. and Goranova M., “Preparation and characterization of activated carbons obtained from carbonaceous materials”, Acta Montana IRSM AS CR, Praha, Series BNO 112, 1999, 25–32.

[17] Savova D., Apak E., Ekinci E., Yardim F., Petrov N., Budinova T., Razvigorova M. and Minkova V., “Biomass conversion to carbon adsorbents and gas”, Biomass and Bioenergy, 21, 2001, 133–142.

[18] Gonzales M.T., Rodriguez-Reinoso F., Garcia A.N. and Marcilla A., “CO_2 activation of carbonized under different experimental conditions”, Carbon, 35, 1997, 159–162.

[19] Sen K. and De A.K., “Adsorption of mercury (II) by cool fly ash”, Water Res., 21, 1987, 885–888.

[20] Srivastava K., Tyagi R. and Pant N., “Adsorption of heavy metal ions on carbonaceous material developed from the waste slurry generated in local fertilizer plants”, Water Res., 23, 1989, 1161–1165.

[21] Mohan D., Gupta V.K., Srivastava S.K. and Chander S., “Kinetics of mercury adsorption from wastewater using activated carbon derived from fertilizer waste”, Colloids and Surfaces A: Physicochemical and Engineering Aspects, 177, 2001, 169–181.

[22] Zhang F.S., Nriagu J.O. and Itoh H., “Photocatalytic removal and recovery of mercury from water using TiO_2-modified sewage sludge carbon”, Journal of Photochemistry and Photobiology A: Chemistry, 167, 2004, 223–228.

[23] Inbaraj B.S. and Sulochana N., “Mercury adsorption on a carbon sorbent derived from fruit shell of *Terminalia catappa*”, Journal of Hazardous Materials, B133, 2006, 283–290.

[24] Yardim M.F., Budinova T., Ekinci E., Petrov N., Razvigorova M. and Minkova V., “Removal of mercury (II) from aqueous solution by activated carbon obtained from furfural”, Chemosphere, 52, 2003, 835–841.

[25] Freundlich H.M.F., Adsorption in solution, Z. Phys. Chem., 57, 1906, 384–470.

[26] Langmuir I., “The adsorption of gases on plane surfaces of glass, mica an platinum”, J. Am. Chem. Soc., 40, 1918, 1361–1368.

[27] Abdulkarim M., Abu Al-Rub F.A., “Adsorption of lead ions from aqueous solution onto activated carbon and chemically-modified activated carbon prepared from date pits”, Ads. Sci. Technol., 22, 2004, 119–134.

[28] Wu F.C., Tseng R.L. and Juang R.S., “Role of pH in metal adsorption from aqueous solutions containing chelating agents on chitosan”, Ind. Eng. Chem. Res., 38, 1999, 270–275.

[29] Ho Y.S., “Citation review of Lagergren Kinetic rate equation on adsorption reactions”, Scientometrics, 59, 2004, 171-177.

[30] Nabais J.V., Carrott P.J.M., Ribeiro Carrott M.M.L., Belchior M., Boavida D., Diall T. and Gulyurtlu I., “Mercury removal from aqueous solution and flue gas by adsorption on activated carbon fibres”, Applied Surface Science, 252, 2006, 6046–6052.

[31] Budinova T., Petrov N., Parrab J. and Baloutzovc V., “Use of an activated carbon from antibiotic waste for the removal of Hg(II) from aqueous solution”, Journal of Environmental Management, 2007.

[32] Ekinci E., Budinova T., Yardim F., Petrov N., Razvigorova M. and Minkova V., “Removal of mercury ion from aqueous solution by activated carbons obtained from biomass and coals”, Fuel Processing Technology, 77–78, 2002, 437– 443.

[33] Oubagaranadin J.U.K., Sathyamurthy N. and Murthy Z.V.P., “Evaluation of Fuller’s earth for the adsorption of mercury from aqueous solution: A comparative study with activated carbon”, Journal of Hazardous Materials, 142, 2007, 165–174.

[34] Kadirvelu K., Goel J. and Rajagopal C., ”Sorption of lead, mercury and cadmium ions in multi-component system using carbon aerogel as adsorbent”, Journal of Hazardous Materials, 2007.

[35] Rio S. and Delebarre A , “Removal of mercury in aqueous solution by fluidized bed plant fly ash”, Fuel, 82, 2003, 153–159.