

Studies on Biosorption of Mercury (II) from Aqueous Solution on Nitric Acid Modified Activated Carbon Prepared from Water Hyacinth

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ABSTRACT

The aim of this study was focused on using dried Water hyacinth stems and leaves (DS, DL) and nitric acid modified activated carbon stems and leaves (MACS, MACL) as effective adsorbents for removal of Hg(II) from aqueous solutions. Adsorption experiments were performed in batch technique to study the effect of various operating parameters, pH of the solution (1 to 5.5), initial concentration of lead ions (10 to 500 mg /l), contact time (2 – 250 min), and temperature (298- 323 K), ionic strength, and adsorbent dose. It is clear that the maximum adsorption capacity of mercury at pH 5 and 298K onto MACS, MACL, DL and DS was 102.6, 81.9, 57.59 and 41.70 mg. g⁻¹, respectively. The obtained results revealed that the percentage of mercury removal increased with increased contact time till reach to the equilibrium time (60 min). When the bio sorbent dosage increased from 0.4 to 4 g/L, the percent of mercury removal by DS, DL, MACS and MACL increased from 37.43 % to 79.58 %, from 32.59% to 78.27 %, from 41.49 % to 82.33% and from 28.66 % to 87.17%, respectively. The adsorption capacity of mercury decreased with the increase in ionic strength. The equilibrium data were fitted well with the linear form of Langmuir model. Adsorption kinetic data followed a pseudo-second-order model. Thermodynamic parameters, involving ΔH° , ΔG° , and ΔS° for the adsorption process of mercury from aqueous solution onto dried water hyacinth and modified activated carbon indicated that adsorption was endothermic and spontaneous process. Desorption were also investigated using HCl as desorbing agent. The results revealed that the percent recovery of Hg (II) increased from 53 % to about 88 % with increase of HCl from 0.3 to 0.8 M and then remained constant.

Key words: Water hyacinth, Nitric acid, Adsorption, Modified activated carbon, Desorption, Mercury

INTRODUCTION

Mercury, as one of the known toxic metals, can be found in wastewaters of some industries, including chloralkali, battery, pulp paper, oil refining, electrical, rubber processing, and fertilizer industries (Horvat et al, 1996). A unique characteristic of mercury is its extensive adsorption into biological tissues and slow elimination from them. Mercury can be adsorbed

in the body through gastrointestinal tract, skin, and lungs. As a heavy metal, mercury circulates in the blood and accumulates in some vital organs such as liver, kidneys, brain, spleen, and bone after adsorption in body. This may lead to serious health problems including pulmonary and kidney malfunctions, damages to chromosomes, adverse effects on central nervous system, and in severe cases, death.

Consequently, removal of mercury ions from waste waters is a very important issue. For this reason, various technological methods are available, including lime softening, chemical precipitation, coagulation, solvent extraction, reverse osmosis, ion exchange, volatilization, membranefiltration, and activated carbon adsorption. Adsorption is among the most extensively used methods for up-taking metal ions. Recently, numerous approaches have been studied for the development of cheaper and effective adsorbents. Many low cost adsorbents, including natural materials, bio sorbents, and waste materials from agriculture and industry, have been proposed by several workers such as orange peel, and Apricot stones (Demirbas et al, 2008). These materials could be used as adsorbents for the removal of Hg(II) from solution (Attia et al, 2008). Water hyacinth (WH) is aquatic plant belongs to the family Pontederiaceae, order Liliiflorae (Monocotyledoneae). The WH propagates both by seed germination and by vegetative means where by mature plants produce rosettes of leaves and fibrous roots at each node of the growing stem. A single plant can produce approximately 65,000 offspring during a single season. Water hyacinth can cause a variety of problems when its rapid mat-like proliferation covers areas of fresh water.

The aim of this study was to deal with the rapidly expanding carpets of water hyacinth. The idea was to prepare activated carbon from the pyrolysis of water hyacinth and evaluate the potentiality of DS, DL, MACS, and MACL for the removal Hg (II) from aqueous solution. The effects of initial Hg(II) concentration, contact time, solution pH, adsorbent dosage, and temperature on Hg (II) adsorption were evaluated. The adsorption kinetics, isotherms and temperature dependent performance, were investigated.

EXPERIMENTAL

Materials and reagents

Stock solution of mercury

Containing 1mg mercury cm^{-3} was prepared by dissolving 1.3535g of HgCl_2 in distilled water acidified with HCl and this solution is completed up to the mark of 1L measuring flask. Mercury solutions of lower concentrations were prepared by further dilution with 0.001M HCl.

PAR solution

PAR (2-pyridylazoresorcinol) solution 0.1% (w/v) prepared by dissolving 0.1g of solid substance in least amount of distilled water then transfers to 100ml measuring flask and complete to the mark using distilled water.

Spectro photo metric determination of Hg^{2+}

Add 1ml of PAR (0.1g /100ml) + 10ml of borate buffer pH= 9 + X ml of metal in 25 ml measuring flask then complete to the mark with distilled water to obtain a final concentration of (0.5,1,2,3, 4,5ppm) and shake well. Measure the absorbance of the solutions at wave length = 522nm and construct the standard calibration curve. The

absorbance of unknown sample was measured at the same wave length and the concentration was determined from the standard calibration curve.

Preparation of Adsorbents

The modified activated carbon stems (MACS) and leaves (MACL) were prepared from water hyacinth collected from Canal extended from river Nile in Mansoura, Egypt according to the following steps as shown in Fig.1.

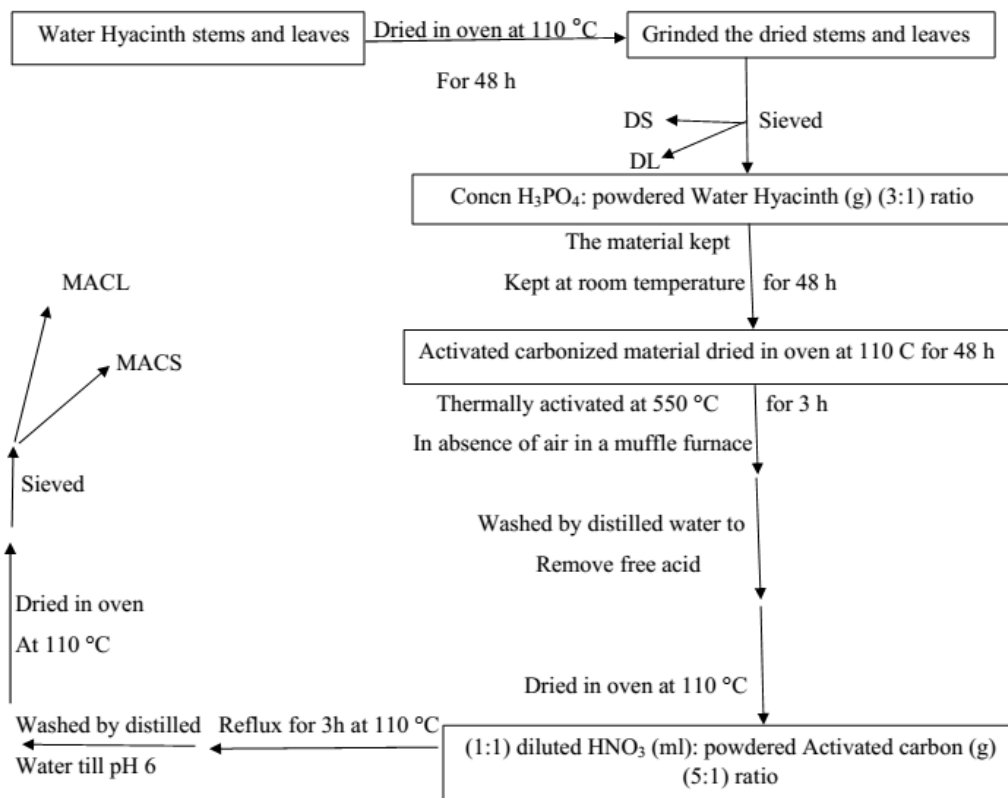


Figure 1: Schematic diagram of water hyacinth biomass-derived modified activated carbon.

Batch adsorption experiments

Batch sorption experiments were done by shaking 0.025 g of each adsorbent DS, DL, MACS, and MACL with 25 ml aqueous solution of Hg(II) in 250 ml-Erlenmeyer flasks placed in a temperature controlled shaking water bath at different concentrations (between 10 and 500 mg/L), pHs (between 1 and 5.5), ionic strength (between 0.05 and 0.5 mol /L NaCl), temperatures (between 25 and 50 °C) and sorbent doses (between 0.01 and 0.1 g) at a constant shaking rate of 125 rpm. The amounts of Hg (II) removed by sorbents q_e and percent extracted %E can be calculated using the following equations:

$$\text{Extraction \%} = \frac{(C_0 - C_e)}{C_0} \times 100 \quad (1)$$

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (2)$$

Where q_e is the amount of dye adsorbed (mg/g). C_0 and C_e are the initial and equilibrium liquid-phase concentrations of Hg (II) (mg/g), respectively. V is the volume of the solution (L), and m is the weight of the sorbent used (g).

For kinetic studies, 100 ml of 250 ppm of Hg (II) solution of known amount of adsorbent (0.1 g) were taken in a 100 ml Stoppard bottle and agitated at 150 rpm. Samples were withdrawn at different time intervals (2-300 min), and analyzed for remaining Hg (II) concentration. The amount of Hg (II) removed by adsorbent at time t , q_t can be calculated by using equation (2).

Desorption Studies

Batch experiments were conducted to evaluate desorption of Hg (II) from DS, DL, MACS, and MACL using HCl as desorption chemical solution. Initially, 25 ml of 250 ppm mercury solution were added into 100 ml a conical flask containing 25 mg of DS, DL, MACS, and MACL. After about 7 h of rotation, the residual Hg (II) concentration in the supernatant was determined. The bio sorbent was filtered and washed three times with distilled water. Subsequently, 25 ml of xMHCl desorption solution were introduced and the system bio-sorbent eluting agent was rotated for 7 h. Finally, the desorbed Hg (II) concentration in the aqueous phase was determined.

RESULT AND DISCUSSION

Effect of nitric acid treatment on the surface area, porous structure, and surface functional groups.

Table 1. shows the Surface area of dried water hyacinth(stems, leaves) and modified activated carbon (stems, leaves) were determined from the application of BET equation to the adsorption-desorption isotherm of N_2 at 77K (Minczewskietel, 1982). It clears that the surface area of dried stems and leaves are relatively small (57.46, 71.83) while modified activated carbon samples with nitric acid have a larger surface area t , reaching the surface area for MACS to 381.22 and for MACL to 365.22. The function of nitric acid is the destruction of the cellulosic structure, enhancing thermal degradation, creation of porous carbonization product.

Examination of the surface nature morphology and porosity of different adsorbents using scanning electron microscope. Fig.2. reveals that the adsorbents MACS and MACL at magnification of 1000x are more porous than DS and DL at magnification 1500x.

FTIR spectra is used to prove the chemical composition and acidic groups on the surface. Oxidation with concentrated nitric acid creates new carboxylic groups. This is indicated by the appearance of a sharp absorption peak at $1608-1713\text{ cm}^{-1}$ for MACL and MACS are due to stretching vibration of carboxyl groups on the edges of layer plane (Macías-García et al, 2006) as shown in fig.3.

Table 1: Characteristics of the dried Water hyacinth (stems and leaves), activated carbon and modified activated carbon (stems and leaves).

	DS	DL	MACS	MACL
Surface Area (m^2/g)	57.46	71.83	381.22	365.22
Total pore volume (cc/g)	0.01	0.03	0.43	0.29

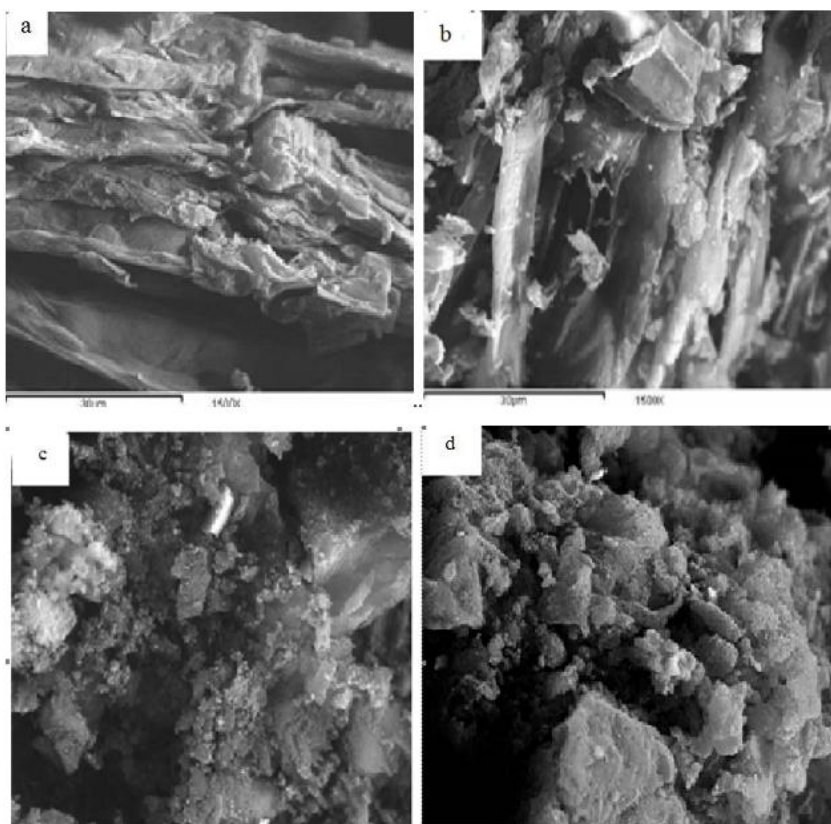


Figure 2: SEM photographs of (a) DS, (b) DL, (c) MACS, (d) MACL.

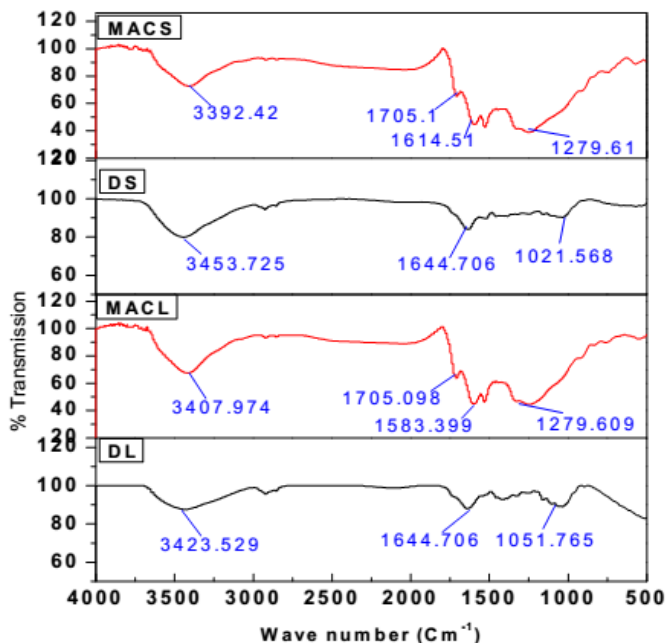


Figure 3: FTIR spectrum of dried Water hyacinth (stems and leaves), and nitric acid modified activated carbon

Adsorption parameters

Effect of pH on Hg^{2+} adsorption

To study the influence of pH of solution on mercury sorption by DS, DL, MACS, and MACL, pH was varied from 1 to 5.5 as shown in Fig.4. The experiments were conducted with an initial metal concentration of 50 mg/L and the biomass concentration of 1 g/L at 25 °C. When the pH increases from pH=1 to pH=5, The amount of Hg^{2+} adsorbed at equilibrium (q_e) increase from 13.74 to 38.2 mg/g, from 12.7 to 43.46 mg/g, from 7.96 to 44.76 mg/g and from 10.2 to 43.06 mg/g for DS, DL, MACL and MACS, respectively. The highest bio-sorption efficiency was observed at pH of 5. In fact, pH dependency of the adsorption of aqueous mercury can be described by at least two mechanisms.

1. *The first mechanism* is the effect of pH on dissociation of acidic and basic surface functional groups as well as the effect on mercury species. It is reported that the most dominant mercury species at $\text{pH} < 3$ and $\text{pH} > 5$ are Hg^{2+} and $\text{Hg}(\text{OH})_2$, respectively (Shin & Bae, 2009). In the presence of chloride and pH range between 4 and 6, HgCl_2 , $\text{Hg}(\text{OH})^+$, $\text{Hg}(\text{Cl})_2$, $\text{Hg}(\text{Cl})^+$, can slightly from these cationic complexes in aqueous solutions. At different solution pH values, surface charge of activated carbon can be changed due to the protonation or hydroxylation of surface functional groups. Hence, different mercury species with different charges can bind to adsorption sites on the activated carbon at each different pH of the solution. Especially at low pH values, surface of activated carbon is positively charged which has adverse effect on the adsorption of mercury cations such as Hg^{2+} , $\text{Hg}(\text{Cl})^+$ and $\text{Hg}(\text{OH})^+$ (Carrottetel, 1998).

2. *The second mechanism* is the competition of mercury species and protons for being bound on the adsorption sites of activated carbon at low pH amounts (Sahooetel, 1992). In fact, at very low pH amounts, concentration of H^+ is high enough to compete with mercury species for being adsorbed in the activated carbon. As pH increases, the negative charge density on the adsorbent surface increases due to deprotonation of active sites thus the approach of positively charged ions is promoted

At pH values ($\text{pH} > 5$), the solubility of mercury decreases due to extensive hydrolysis (the percentage of HgClOH and $\text{Hg}(\text{OH})_2$ species increases) so to avoid precipitation of $\text{Hg}(\text{II})$ ions, all the following experiments were conducted at $\text{pH} = 5.0$.

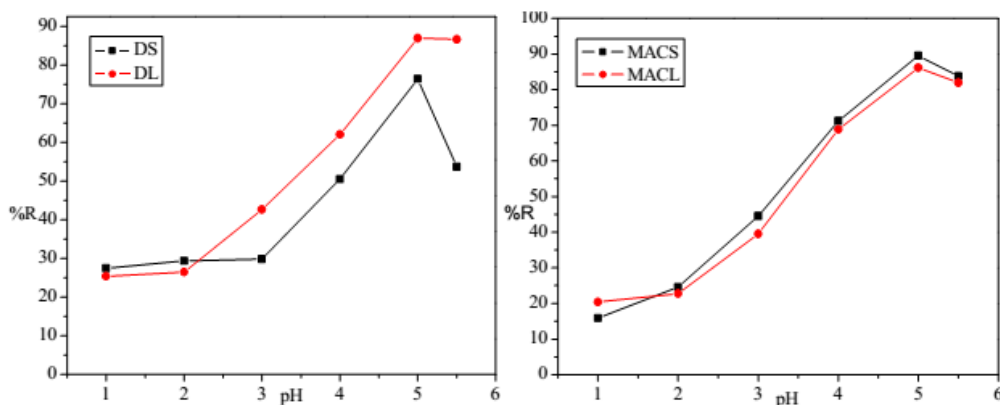


Figure 4: Effect of the pH values on adsorption capacity of Hg^{2+} by DS, DL, MACS and MACL (Conditions: $C_o = 50 \text{ mg/l}$, $T = 25^\circ\text{C}$; adsorbent dose = 0.025 g/25 ml).

Effect of initial concentration on the uptake of Hg²⁺

The effect of initial Hg (II) concentration on the equilibrium uptake capacity is shown in Fig. 5. From the figure, it is evident that, when the initial concentration of Hg (II) increases from 10 to 500 mg/l at 25 °C, The amount of Hg(II) adsorbed at equilibrium (q_e) increase from 7.96 to 41.7 mg/g, from 9.6 to 57.59 mg/g, from 9.95 to 102.6 mg/g, and from 9.95 to 81.9 mg/g for DS, DL, MACS and MACL, respectively. Apparently, the initial Hg (II) concentration plays an important role in affecting the capacity of Hg (II) to adsorb onto different adsorbents. The amount of the Hg(II) adsorbed onto DS, DL, MACS, and MACL increases with an increase in the initial Hg(II) concentration at a constant amount of adsorbent. This may be attributed to the fact that, the higher the Hg (II) concentration is, the stronger the driving force of the concentration gradient thus the higher the adsorption capacity. The C_0 provides the necessary driving force to overcome the resistances to the mass transfer of Hg (II) between the aqueous and the solid phases. The increase in C_0 also enhances the interaction between Hg (II) and MACS, MACL, DS, and DL adsorbents. Therefore, an increase in C_0 of Hg (II) enhances the adsorption uptake of the Hg(II).

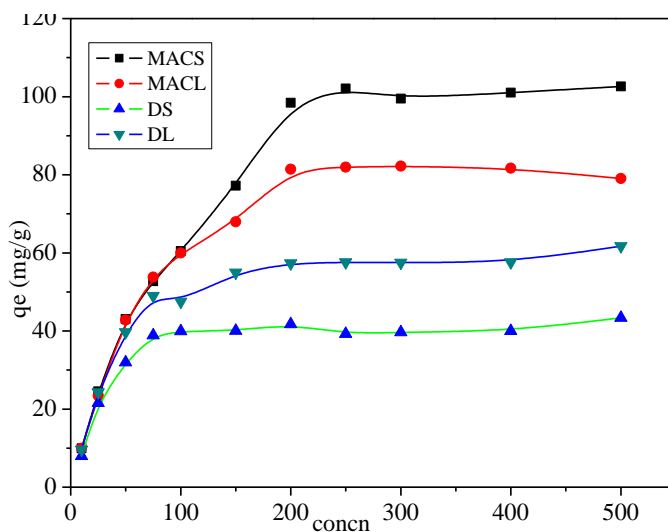


Figure 5: Effect of initial metal concentration on the removal of Hg²⁺ by DL, DS, MACL and MACS. (Conditions: $C_0 = 5-500$ mg/l, $T=25^\circ\text{C}$; adsorbent dose = 0.025 g/25 ml).

Effect of temperature on adsorption

To study the influence of the temperature on mercury adsorption by DS, DL, MACS, and MACL adsorbents, temperature was varied from 25°C to 50 °C as shown in Fig. 6. The experiments were conducted within an initial concentration range (50-500 mg/l) and biomass concentration of 1 g/l pH 5.0. Table 23.shows that When the temperature increased from 25 °C to 50 °C, the maximum adsorption capacities of Hg²⁺ removed by DS, DL, MACL and MACS are found to be increased from 41.7 to 83.7 mg/g, from 57.59 to 104 mg/g, from 81.9 to 132.4 mg/g and from 102.6 to 135 mg/g, respectively. In fact, the temperature has two main effects on the adsorption processes of the porous adsorbents. It can affect the diffusion rate of the sorbate within the pores as a result of decreasing solution viscosity and the number of the sorption sites generated because of breaking of some internal bonds near the edge of active surface sites of sorbent, which benefits for improving the adsorption capacity of the adsorbents (Boudrahemetel, 2009).

The results indicate that the adsorption reaction of Hg(II) ions adsorbed by DS, DL, MACS, and MACL adsorbents increase with an increase in temperature, which indicate the process to be endothermic. The increase in mercury removal with an increase in temperature may be due to the increased chemical interactions between mercury ions and the functional groups on the surface of the activated carbon surface, which indicates the process to be chemisorption. In other words, increasing temperature can increase the diffusion rate of Hg(II) ions and the number of the sorption sites and thus enhance the adsorption ability of prepared activated carbon.

If notice to the obtained results, it is obvious that the adsorption of the Mercury increases in the order of $\text{MACS} > \text{MACL} > \text{DS} > \text{DL}$ under all conditions studied such as concentration, temperature and pH. This behavior is attributed to the increase in the surface area of adsorbent and increase in the number of active sites (functional groups) on the surface of adsorbents.

Table 2: Effect of temperature on maximum adsorption capacities of Hg^{2+} by DS, DL, MACS and MACL

Samples	$Q_e(\text{mg g}^{-1})$		
	25 °C	40°C	50°C
DS	41.7	55.5	83.7
DL	57.59	84.8	104
MACS	102.6	125.13	135
MACL	81.9	113.08	132.4

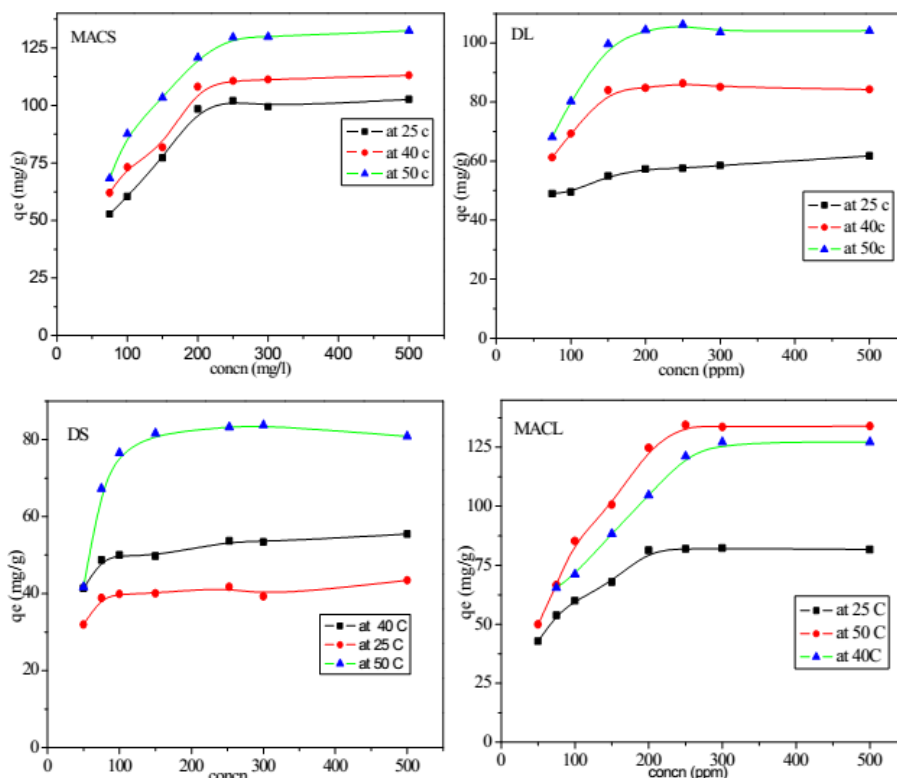


Figure 6: Effect of temperature on adsorption capacity of Hg^{2+} by DS, DL, MACS and MACL. (Conditions: $C_0 = 50\text{--}500$ ppm; adsorbent dose = 0.025 g/25 ml; $\text{pH}=5$).

Effect of ionic strength

Fig.7. presents the effect of ionic strength on the uptake of Hg^{2+} ions. It was observed that the adsorption capacity decreased with the increase in ionic strength. As the concentration of NaCl ions increased from 0.05 to 0.5 M, the removal efficiency (%E) of Mercury decreased from 62.04 % to 42.4 %, from 78.7 % to 42.4 %, from 93.9 % to 34.5 % and from % 91.9 to 30.04% for DS, DL, MACS and MACL, respectively. This may be attributed to competition between cations (Na^+ ions) and Hg (II) for the active sites on the adsorbent surface. As well as, increasing chloride ion concentration considerably decrease the adsorption of mercury by adsorbents due to the formation of more stable Hg-Cl complexes which are poorly adsorbed.

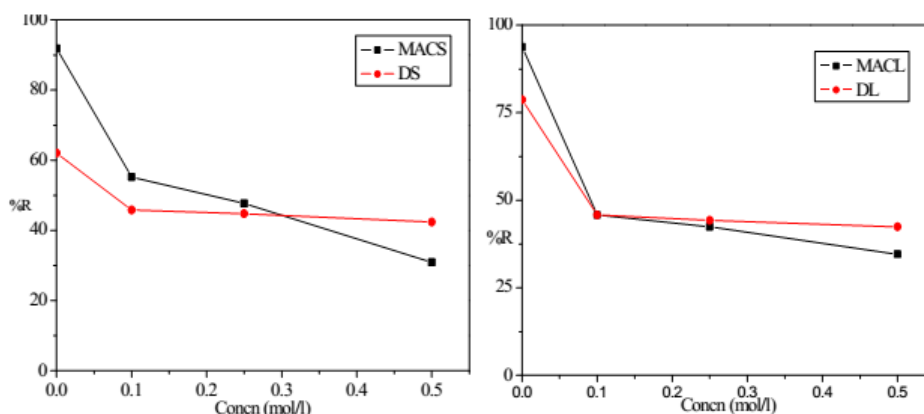


Figure 7: Effect of ionic strength on the removal of Hg^{2+} by DS, DL, MACS and MACL. (Conditions: $T=25^\circ\text{C}$; adsorbent dose = 0.025 g/25 ml; $C_o = 50 \text{ mg/l}$; time = 7 h).

Effect of contact time

The relationship between contact time and Hg (II) sorption onto DS, DL, MACS, and MACL at initial Hg (II) concentration of 250 ppm is shown in Fig.8. The results revealed that the uptake of sorbate species is fast at the initial stages of the contact period and a large fraction of the total amount of metal was removed within a few minutes more than 67 %, 56%, 63%, and 84.4% of the adsorption capacities of corresponding adsorbents for Hg (II) occurred within 5 min for MACL, DL, MACS, and DS, respectively. Thereafter, it becomes slower near the equilibrium and the maximum removal of Hg (II) occurred within 45-60 min at which the rate of sorption is found to be nearly constant. This is obvious by the fact that a large number of vacant surface sites are available for sorption during the initial stage, and after a lapse of time, the remaining vacant surface sites are difficult to be occupied due to repulsive forces between the solute ions on the solid and the bulk phases. After 1h, the uptake was almost constant such that it could be considered the equilibrium time of the Hg (II) adsorption. To ensure that sufficient contact time was obtained, further adsorption experiments were carried out for 7h.

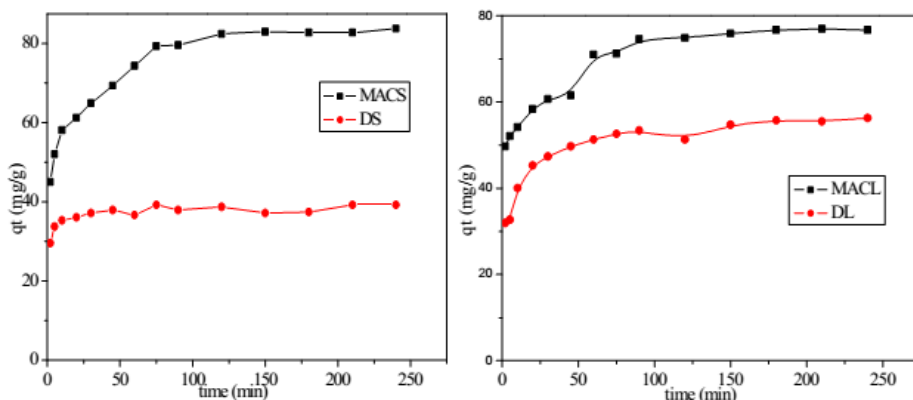


Figure 8: Effect of contact time on adsorption capacity of Hg^{2+} by DS, DL, MACS and MACL. (Conditions: $C_o = 250$ mg/l, $T=25^{\circ}C$; adsorbent dose = 0.1 g/100 ml).

Effect of adsorbent dosage

The effect of bio sorbent dosage on the removal of Hg (II) is shown in Fig.9. As seen in this figure, percentage removal of Hg (II) increase with increase in bio sorbent dosage from 0.4 to 4 g/l., The percent of mercury removal by DS, DL, MACS and MACL increase from 37.43 % to 79.58 %, from 32.59% to 78.27 % , from 41.49 % to 82.33% and from 28.66 % to 87.17%, respectively. There is no significant increase in removal of Hg (II) when bio sorbent dosage increases beyond 4 g/l. This suggests that after a certain bio sorbent dosage, the maximum bio sorption is attained and hence the amount of ions remains constant even with further increase in the surface area of the bio sorbent, which in turn increases the number of binding sites. However, at high sorbent dosages the available metal ions are insufficient to cover all the exchangeable sites on the bio-sorbent, resulting in low metal uptake (Gong et al, 2005). Therefore, the optimum dosage for dried water hyacinth and activated carbon developed from it is 4 g/l but 1 g/l dosage is used for all further experiments.

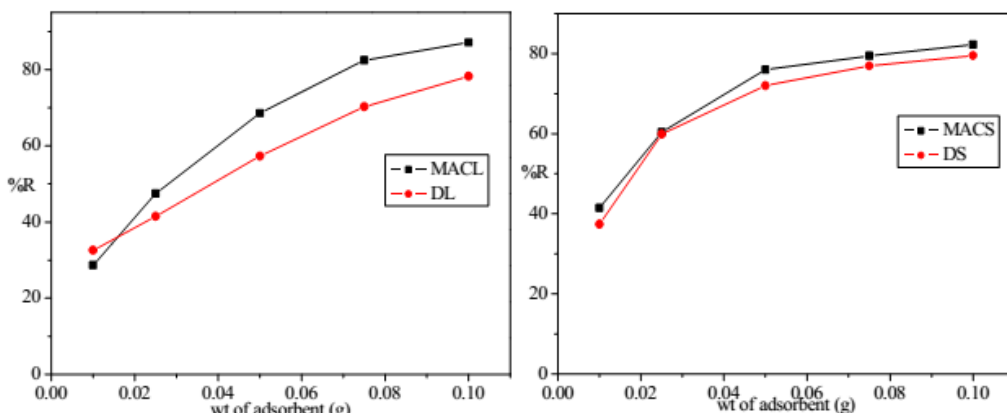


Figure 9: Effect of sorbent dosage on the removal of Hg^{2+} by DS, DL, MACS and MACL. (Conditions: $T=25^{\circ}C$; $C_o = 100$ mg/l, $v=25$ ml; time = 7 h, $pH = 5$)

Adsorption isotherms

The experimental adsorption equilibrium data were analyzed in terms of Langmuir and Freundlich isotherm models which can be expressed:

$$\text{Freundlich isotherm:} \quad \ln q_e = \ln K_f + \frac{1}{n} \ln C_e \quad (3)$$

$$\text{Langmuir isotherm:} \quad \frac{C_e}{q_e} = \frac{1}{Q_b} + \frac{C_e}{Q} \quad (4)$$

Where q_e is the amount adsorbed at equilibrium (mg g^{-1}), C_e is the equilibrium concentration of the Hg (II) (mg L^{-1}), constant b is related to the energy of adsorption (Lmg^{-1}), Q_0 is the Langmuir monolayer adsorption capacity (mg g^{-1}), K_f is roughly an indicator of the adsorption capacity, and $1/n$ is the adsorption intensity. Langmuir and Freundlich isotherms for adsorption of Hg (II) onto DS, DL, MACS and MACL at different initial concentrations are given in Figs. 10, 11, respectively. Tables 24, 25, summarize the Langmuir and Freundlich constants the calculated coefficients. It can be found that the regression coefficient R^2 obtained from Langmuir model is much higher than that from Freundlich model, suggesting that the Langmuir isotherm fits better with the experimental data. The maximum monolayer adsorption capacity (Q_{\max}) of Hg(II) by MACS, MACL, DS and DL at 25°C was calculated to be 105.7, 81.9, 41.1 and 58.5 mg g^{-1} are all the same as the experimental data. The essential characteristics of the Langmuir isotherm can also be expressed in terms of a dimensionless constant separation factor or equilibrium parameters, RL , which is defined as (Pavanetel, 2008)

$$RL = \frac{1}{1 + bC_0} \quad (5)$$

Where b (Lmg^{-1}) is the Langmuir constant and C_0 (mg L^{-1}) is the initial concentration in the liquid phase. The value of RL indicates the shape of the isotherm.

RL value	Type of isotherm
$RL > 1$	Un favorable
$0 < RL < 1$	favorable
$RL = 1$	Linear
$RL = 0$	irreversible

For Hg (II) adsorption on MACS, MACL, DS and DL, RL values obtained are in the range between 0 and 1, thereby confirming that the adsorption is a favorable process.

Table 3: Parameters of langmuir isotherm for adsorption of Hg^{2+} by DS, DL, MACS and MACL.

Adsorbents	Langmuir parameters				
	R^2	b (L/mg)	$Q_{\max, \text{fitted}}$	Q_{exp}	R_L
MACS	0.994	0.0775	105.7	102.6	0.025
MACL	0.997	0.1588	81.9	81.9	0.0124
DS	0.997	0.258	41.1	41.7	0.086
DL	0.997	0.2164	58.5	57.59	0.0181

Table 4: Parameters of Freundlich isotherm for adsorption of Hg^{2+} by DS, DL, MACS and MACL.

Adsorbents	Freundlich parameters		
	R^2	K_f	$1/n$
MACS	0.919	24.95	0.263
MACL	0.948	30.33	0.185
DS	0.0.633	28.05	0.074
DL	0.909	31.32	0.115

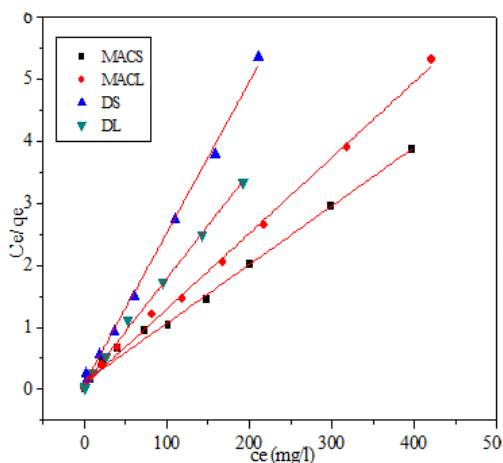


Figure 10: Langmuir plot for the adsorption of Hg^{2+} by DS, DL MACS and MACL

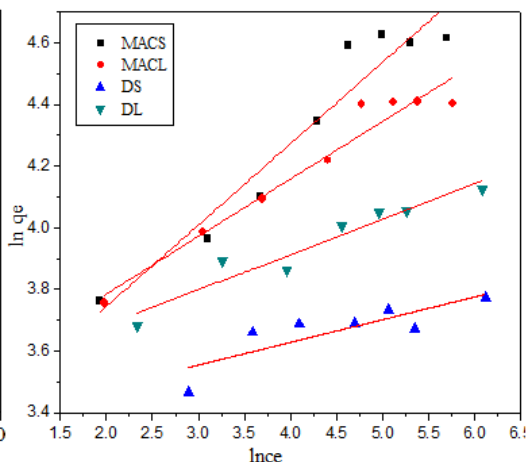


Figure 11: Freundlich plot for adsorption of Hg^{2+} by DS, DL MACS and MACL

Adsorption Kinetics

To study the mechanism of the adsorption process steps, such as the mass transport and chemical reaction processes, kinetic models were used to test the experimental data. The kinetics of Hg (II) adsorption on the modified water hyacinth activated carbon and dried water hyacinth were analyzed using pseudo-first-order, pseudo-second-order, and intra particle diffusion models.

The pseudo-first-order kinetic model is expressed as follow (Webi & Chakravort, 1974):

$$\log(q_e - q_t) = \log q_e - \frac{K_1 t}{2.303} \quad (6)$$

Where q_e and q_t are the amounts of mercury adsorbed ($mg\ g^{-1}$) at equilibrium and at time t (min), respectively, and k_1 the rate constant of adsorption (min^{-1}). Values of k_1 were calculated from the plots of $\ln(q_e - q_t)$ versus t (fig.12) at initial concentration of 250 ppm of mercury. The correlation coefficient values R^2 are low, the experimental q_e values do not agree with the calculated ones, obtained from the linear plots (Table 5). This shows that the adsorption of cadmium on MACS, MACL, DS and DL is not a first-order reaction.

The second-order kinetic model is expressed as:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \quad (7)$$

Where k_2 is the rate constant of second-order adsorption ($g\ mg^{-1}\ min^{-1}$). If the second-order kinetics is applicable, then the plot of t/q_t versus t should show a linear relationship. Values of k_2 and q_e were calculated from the intercept and slope of the plots of t/q_t versus t . The linear plots of t/q_t versus t (Fig. 13) show a good agreement between experimental and calculated q_e values (Table 6). The correlation coefficients for the second-order kinetic model are greater than 0.99 indicating that the adsorption system is probably best described by the pseudo second kinetic model. Moreover, the calculated adsorption capacities determined using pseudo-second-order plots are in good agreement with the experimental values. This fact confirms the earlier hypothesis that the adsorption of mercury by DS, DL, MACS, and MACL is controlled by chemisorption.

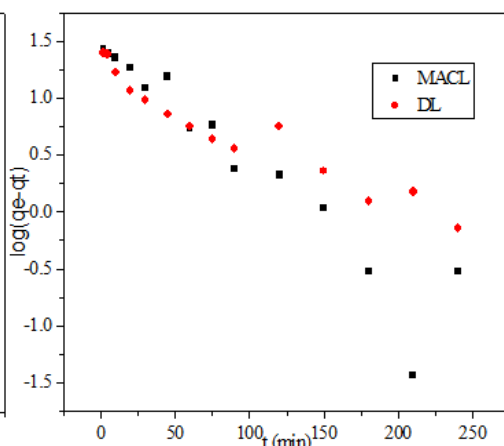
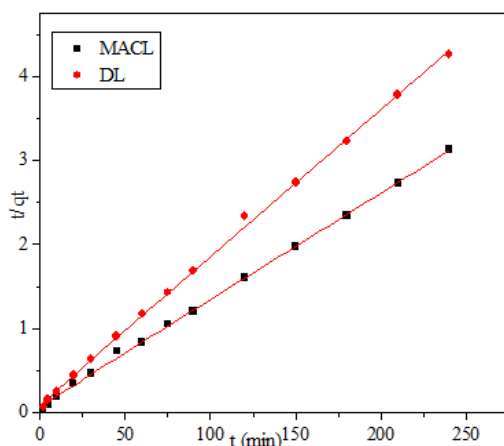
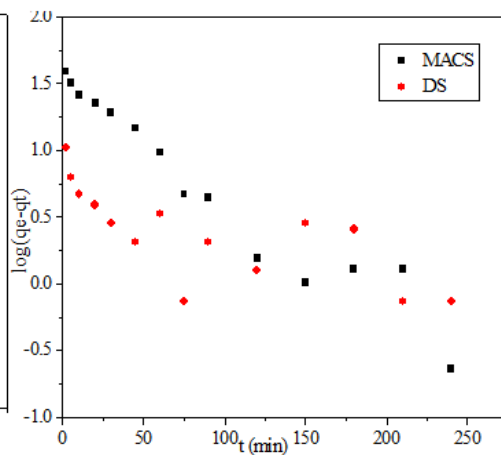
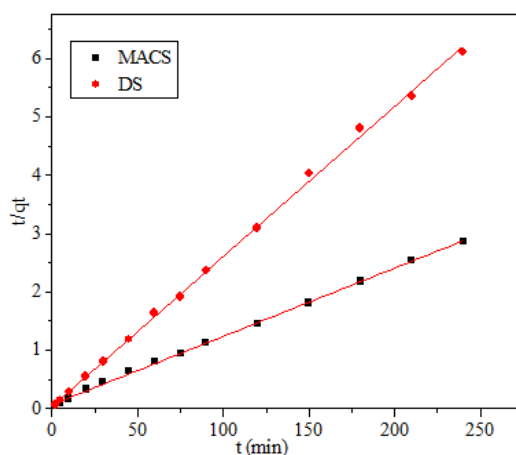


Figure 12: Pseudo-second-order kinetic model for the adsorption of Hg^{2+} by DS, DL, MACS and MACL

Figure 13: Pseudo-first-order model for the adsorption of Hg^{2+} by DS, DL, MACS and MACL

Table 5: Parameters of first order kinetic model for adsorption of 250 ppm Hg^{2+} by DS, DL, MACS and MACL.

Adsorbent Code	Pseudo-first order			
	$q_e \text{ exp. mg.g}^{-1}$	$q_e \text{ cal. mg.g}^{-1}$	$K_1 \text{ (min}^{-1}\text{)}$	R^2
MAC S	84	30.9	0.019	0.9345
MACL	77	29.5	0.024	0.904
DS	40	4.6	0.0075	0.497
D L	57	17.1	0.0133	0.914

Table 6: Parameters of second order kinetic model for adsorption of 250 ppm Hg^{2+} by DS, DL, MACS and MACL

Adsorbent Code	$q_e \text{ exp. mg.g}^{-1}$	$q_e \text{ cal. mg.g}^{-1}$	$K_2 \text{ g.mg}^{-1} \text{ .min}^{-1}$	R^2
MACS	84	85.62	0.0019	0.999
MACL	77	78.55	0.016	0.999
DS	40	38.91	0.0023	0.999
DL	57	56.8	0.0033	0.999

Intra particle diffusion model

The kinetic results were analyzed by the intra-particle diffusion model to elucidate the diffusion mechanism by Weber and Morris equation. The linear form of intra-particle diffusion model was given by (Boyd, 1947):

$$q_t = K_d t^{0.5} + C \quad (8)$$

Where C was the intercept and K_d was the intra-particle diffusion rate constant ($\text{mg g}^{-1} \text{min}^{-0.5}$). According to this model, plot of q_t versus $t^{1/2}$ should be linear if intra-particle diffusion was involved in the adsorption process. If these lines passed through the origin, then intra-particle diffusion was the rate controlling step. When these lines did not pass through the origin, this was indicative of some degree of boundary layer control and this further showed that the intra-particle diffusion was not the only rate-limiting step. The values of K_d were given in Table 7.

In this experiment, the plots did not pass through the origin (fig.14), which indicated the intra particle diffusion was not only the rate controlling step. The boundary layer effect (film diffusion) may control the rate of mass transfer in the time period of the first linear segment; this conclusion could be corroborated by the analysis of data from Boyd's model.

The model of Boyd is expressed as (Reichenberg, 1953):

$$F = 1 - \frac{6}{\pi^2} \exp(1 - B_t) \quad (9)$$

Where

Where F is the fractional attainment of equilibrium, at different times, t , and B_t is a function of F

$$F = \frac{q_t}{q_e} \quad (10)$$

Where q_t and q_e are the metal uptake (mmol g^{-1}) at time t and at equilibrium, respectively.

Eq. (6) can be rearranged to

$$B_t = -0.4977 - \ln(1 - F) \quad (11)$$

From Boyd plot, (Fig.15) it was observed that the plots are linear but do not pass through the origin suggesting that the adsorption process is controlled by film diffusion. However, The Boyd intercept values are greater than 0.5 for all adsorbents indicating that intra-particle diffusion along with film diffusion controls the adsorption of Hg^{2+} on all adsorbents.

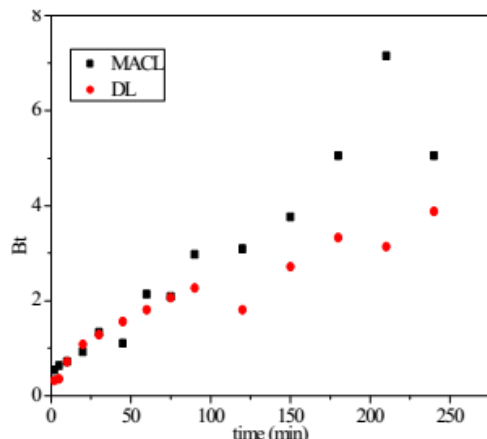
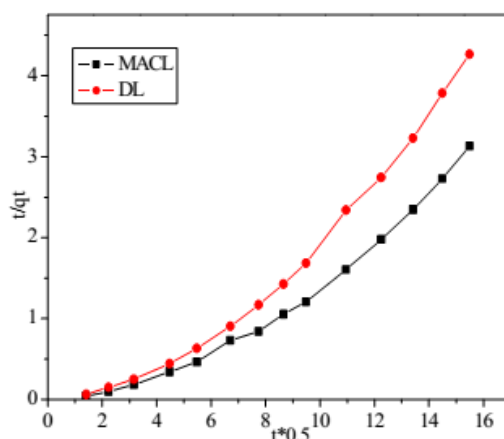
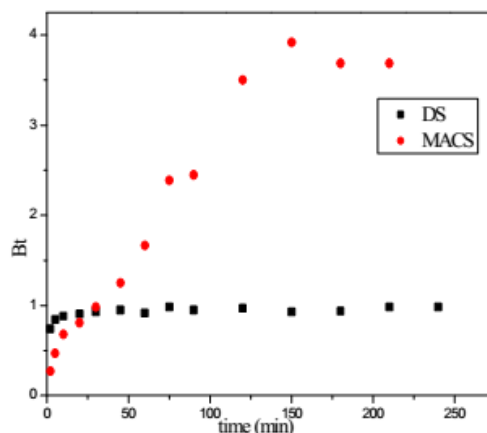
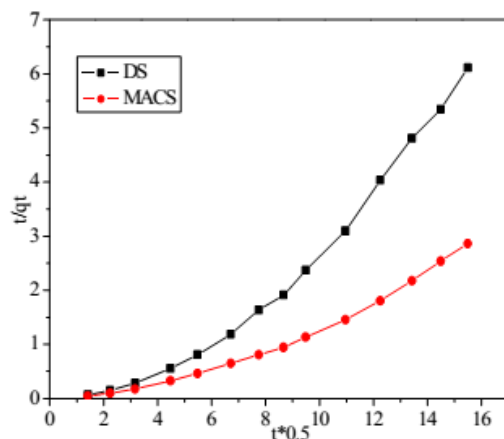


Figure 15: Bt versus t plot for adsorption of Hg^{2+} on DS, DL, MACS and MACL at 250 ppm

Figure 14: Intra-particle diffusion plots for adsorption of Hg^{2+} on DS, DL, and MACL at 250 ppm.

Table 8: Intra-particle diffusion parameters for adsorption of $Hg(II)$ by DS, DL, MACS and MACL at 250 ppm

Intraparticle diffusion model				Boyd model	
Adsorbent code	R^2	K_d	Intercept	Intercept	R^2
MACS	0.953	0.197	-0.53	0.512	0.934
MACL	0.953	0.215	-0.58	0.467	0.904
DS	0.948	0.433	-1.279	0.870	0.360
DL	0.954	0.297	-0.818	0.708	0.914

Evaluation of thermodynamic parameters

The temperature dependence of adsorption is associated with various thermodynamic parameters. To study the thermodynamics of adsorption, adsorption studies were performed at 25, 40, and 50 C. Thermodynamic parameters ΔH° and ΔS° were calculated from the Van't Hoff equation (Dural etel, 2011)]:

$$\ln k_d = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (12)$$

$$K_d = \frac{q_e}{c_e} \times \rho \quad (13)$$

Where K_d is the adsorption coefficient, $\rho=1000$ g/L to make a dimensionless K_d . The plot of $\ln K_d$ versus $1/T$ was found to be linear as illustrated in Fig.16 .The values of ΔS° and ΔH° were calculated from the intercept and slope of linear plot. The standard free energy change, ΔG° , was calculated using the expression (Dural etel, 2011):

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (14)$$

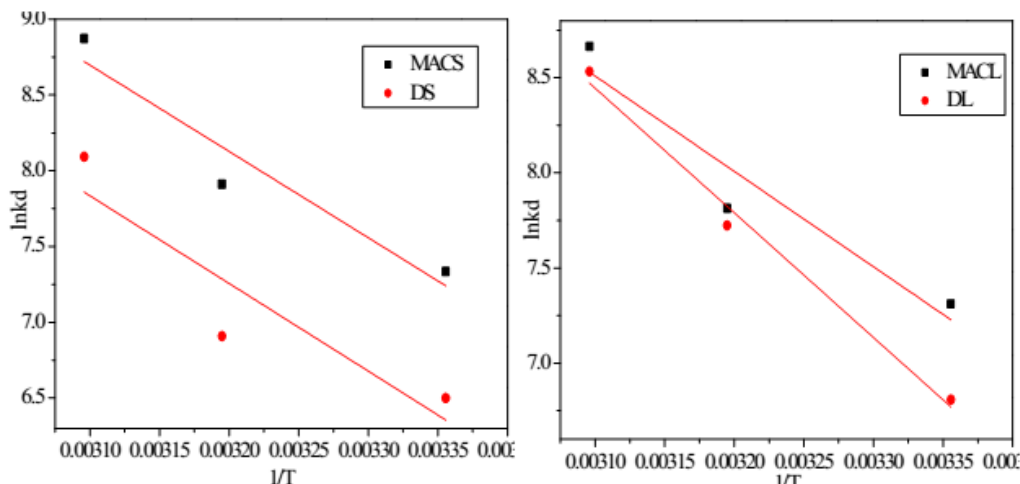


Figure 16: The plots of $\ln K_d$ versus T^{-1} for estimations of thermodynamic parameters of the adsorption process of Hg^{2+} by MACS, MACL, DS and DL. Condition : ($C_o = 100$ ppm, $T= 25 - 50$ °C, $t=5h$, adsorbent dose = 0.025 g/25 ml)

Table 9: Thermodynamic parameters for adsorption of Hg^{2+} by MACS, MACL, DS and DL at different temperatures.

Adsorbents	Mercury concentration (mg/L)	ΔH (kJ/mol)	ΔS (kJ/mol)	ΔG (kJ/mol)		
				298K	313K	323K
MAC S	100	47.35	0.22	-17.94	-21.23	-23.42
MACL	100	41.66	0.199	-17.91	-20.91	-22.91
DS	100	48.11	0.214	-15.75	-18.97	-21.11
DL	100	54.47	0.239	-16.75	-20.34	-22.73

The values of ΔS° , ΔH° , and ΔG° were obtained from the slope and intercept, respectively, of the plot of $\ln K_d$ versus $1/T$, as shown in fig. 16. The thermodynamic values of ΔS° , ΔH° , and ΔG° obtained for the adsorption of Hg (II) on DS, DL, MACS, and MACL are summarized in Table. 9. The enthalpy change is related to the chemical bonding; therefore, the positive value of the enthalpy of adsorption ΔH° obtained in this study confirms the endothermic nature of the adsorption process is likely due to chemisorption and strong interactions between the Hg (II) ions and the functional groups on the surface of the adsorbent. The value of ΔS° is related to the ordering or geometry of the adsorbed ions. The positive value of ΔS° suggests an increase in disorder and randomness at the solid solution interface during the adsorption process. The standard Gibbs free energy change (ΔG°) is the fundamental criterion of spontaneity of an adsorption process. The negative values for ΔG° indicate that the adsorption process is spontaneous and thermodynamically favorable. The high negative values of ΔG° indicate a greater order of

reaction and a stronger driving force the adsorption of Hg (II) on the surface of the modified water hyacinth activated carbon and dried water hyacinth.

Desorption studies

Recovery and regeneration study has become economically and environmentally attractive in recent years. The desorption study is not only helpful for providing scientific evidence of adsorption processes, but also for further application or disposal of the spent carbon. Desorption of adsorbed Hg(II) from spent adsorbent was carried out using different concentration of HCl (0.3-0.8 M) In order to investigate the desorption capacity of DS, DL, MACS and MACL, 0.025 g of different adsorbents were introduced to 25 ml solution of 250 ppm of Hg(II) at pH 5. As the adsorption reaches equilibrium, the metal ion concentration of the solution was measured, Then, the adsorbent loaded with Hg(II) was collected and treated with 25 ml x M HCl to remove the adsorbed Hg(II). Tables 10, 11, 12 revealed that the percent recovery of Hg(II) increased with increase of HCl from 0.3 to 0.8 M and then remained constant. Desorption of Hg(II) by HCl can be attributed to the disruption of coordination with mercury ions. These results indicate that the removal of mercury from water by DS, DL, MACS, and MACL is mainly through affinity adsorption.

Table1: Desorption of mercury using 0.3 M HCl after adsorption of 250 ppm

Adsorbent code	qe adsorbed	qedesorped	%desorption
MACS	80	43.105	53.9
MACL	74	44.634	60.32
DL	52	40.314	77.53
DS	37	24.35	65.8

Table2: Desorption of mercury using 0.6 M HCl after adsorption of 250 ppm

Adsorbent code	qe adsorbed	qedesorped	%desorption
MACS	80	64.92	81.15
MACL	74	53.4	72.2
DL	52	45.54	87.6
DS	37	30.1	81.4

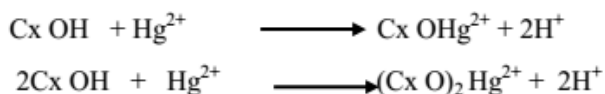
Table3: Desorption of mercury using 0.8 M HCl after adsorption of 250 ppm

Adsorbent code	qe adsorbed	qedesorped	%desorption
MACS	80	64.92	81.15
MACL	74	54.32	73.4
DL	52	45.94	88.351
DS	37	31.54	85.26

Mechanism of adsorption

Finally, it would be of interest to present the mechanisms involved in the mercury removal process by dried water hyacinth and modified water hyacinth activated. In the previous section, it was observed that with progress of mercury adsorption, pH of solution continuously decreases. The increase in H^+ concentration in the adsorption medium can be related to the contribution of oxygen-containing functional groups on the dried water hyacinth and modified water hyacinth activated carbon in metal adsorption. FTIR spectrum also confirmed that COOH, OH and C=O are the main active groups present in activated carbon and water hyacinth. The following reactions between these groups and

mercury ions during the mercury adsorption may be the reason of increasing the concentration of H^+ in the solution:



It is necessary to note that besides ion exchange, physical adsorption in the micro pores of activated carbon has an important part in the adsorption of mercury.

Comparison of the adsorption capacities of sorbents toward Hg (II)

Table 13 lists the comparisons of maximum adsorption capacities of DS, DL, MACS and MACL obtained in this study with various adsorbents previously used for the adsorption of Hg (II). These adsorbents have a higher adsorption capacity than that of the most other adsorbents reported in the literature, suggesting that it may be effective for Hg (II) removal from aqueous solution.

Table4: Comparison of the adsorption capacities of Hg (II) onto various adsorbents

Adsorbents	Adsorption capacities (mg/g)	Ref.
MACS	102.6	This work
MACL	81.9	
DS	41.7	
DL	57.59	
Granular activated carbon	0.8	[5, 30, 31]
Dates nut carbon	1.16	
Waste rubber	4.0	
Commercial activated carbon	12.38	
Eucalyptus camaldulensis bark	33.1	
Carbon aerogel	34.9	
Activated carbon prepared from sugercan bagasse	35.71	
Sago waste carbon	55.60	
Modified palm shell activated carbon	83.33	

CONCLUSION

Based on the results, it is clear that the mercury-removal values achieved with Nitric acid modified water hyacinth activated carbon were higher than those of dried water hyacinth due to the increase in the number of carboxylic groups on the surface of the modified activated carbon. The main advantages of this removal procedure include (i) simplicity, (ii) cost effectiveness, (iii) rapidity, and (iv) a higher removal efficiency of toxic mercury ions. Based upon the experimental results of this study, the following conclusions can be drawn:

- The maximum removal efficiency occurred at pH 5.0.
- The efficiency of mercury removal increased both with increased contact time and initial mercury concentration.
- The results showed that the adsorption increased rapidly till reach to the equilibrium time (60 min).
- The experimental data were fitted well with the linear form of Langmuir model.
- Adsorption kinetics followed a pseudo-second-order model.
- Thermodynamic parameters, including ΔH , ΔG , and ΔS for the adsorption process of mercury from aqueous solution onto dried water hyacinth and modified water hyacinth activated carbon indicated that adsorption was endothermic and spontaneous process.

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