A Comparative Investigation on Removal and Recovery of Cadmium from Aqueous Solution Using Novel Adsorbents Prepared from Water Hyacinth

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Abstract: ***This article sheds light on the preparation of novel activated carbon adsorbents from dried water hyacinth (stems, leaves) and their use as efficient adsorbents for removal of cadmium (II) ions from aqueous solutions. The experimental results revealed that, pH values of solution, contact time, adsorbent dosage, ionic strength, and initial concentration considerably affected the adsorption amount of Cd (II). Based upon the experimental results, maximum adsorption was obtained at pH 5, The amount of Cd^{2+} adsorbed at equilibrium (qe)increases from 9.2 to 40.8 mg/g, from 9.11 to 26.9 mg/g , from 9.8 to 65.5 mg/g and from 9.7 to 58.9 mg/g upon increasing Cd (II) concentration within the range studied (5 - 300 mg/l) for stems (DS), leaves (DL), activated carbon stems (MACS), and activated carbon leaves (MACL), respectively. The kinetic studies were performed based on different kinetic models. The data indicated that the adsorption kinetics of cadmium on all adsorbents followed the pseudo-second order model at different cadmium concentrations. The experimental data fitted with Langmuir isotherm model. Thermodynamic studies revealed that the adsorption process was an endothermic process in nature. The desorption of about 69% of the adsorbed cadmium from carbon was achieved using 0.6 M HC l.***

Keywords: Water hyacinth, Nitric acid, Phosphoric acid, Adsorption, Modified activated carbon, Desorption, Cadmium

1. Introduction

Cadmium is an important metal, which can be used in many fields such as the manufacture of paints, plastic stabilizers, phosphors, Ni−Cd battery materials, electric contacts, fusible alloys and control rods for atomic reactor. However, cadmium and its compounds have been found to be very toxic and long-term exposure to cadmium can cause serious damage to human endocrine system, kidney, and bones [1, 2]. The contamination of Cd in soil, lake and river is still a very serious problem due to the massive mining of zinc-lead [3]. A number of technologies have been developed over the years to remove toxic heavy metals from wastewater [4]. A number of technologies have been developed over the years to remove toxic heavy metals from wastewater. Conventional methods for the removal of heavy metal ions from wastewater include ion-exchange, solvent extraction, dialysis, chemical precipitation, flotation, membrane filtration and electrochemical treatment [5].

All these conventional methods have some advantages and disadvantages such as high consumption of reagent, low efficiency, expensive and generation of secondary pollutants [6]. Hence, it is imperative to identify the appropriate technology to control the Cd^{2+} contamination in the irrigation water ways. One of the effective and time tested treatment techniques for control of water pollution is adsorption. It is known for years that natural raw materials are a possible source of low-cost adsorbents that could bind different heavy metal ions. The main advantages of this technique are the reusability of biomass, cheap, high selectivity for specific metal of interests and short operation time [7].

Water hyacinth (WH) is aquatic plant belongs to the family Pontederiaceae, order Liliiflorae. WH was first introduced to Egypt during the rule of Khedive Tewfik between 1879 – 1892 as an ornamental plant. It was cultivated in ponds of public gardens and thirty years later it had spread too many water bodies in the Nile Delta. After the construction of the Aswan High Dam, the WH problem increased considerably and it is now hard to find a canal, a stream, or a drainage system free of this weed. Water hyacinth can cause a variety of problems when its rapid mat-like proliferation covers areas of fresh water [8, 9]. Some of the common problems are listed such as hindrance to water transport, and rivers causing flooding, micro-habitat for a variety of disease vectors, increased evapotranspiration, problems related to fishing, reduction of biodiversity. Water hyacinth can be used to aid the process of water purification either for drinking water or for liquid effluent from sewage systems. Clean, healthy plants have been incorporated into water clarifiers and help with the removal of small flocks that remain after initial coagulation and flock removal or settling [10]. The result is a significant decrease in turbidity due to the removal off locks and also slight reduction in organic matter in the water.

The main focus of this study was to deal with the rapidly expanding carpets of water hyacinth. The idea is to prepare activated carbon from the pyrolysis of water hyacinth which provide an alternative source of biomass and an alternative income and evaluate the efficiency of dried water hyacinth and the prepared activated carbon for the removal of Cd^{2+} from aqueous solution. The effects of pH, initial Cd^{2+} concentration, temperature, contact time, ionic strength and adsorbent dosage on adsorption capacities were also were investigated. Moreover, kinetic, thermodynamic and equilibrium studies were used to fit experimental data.

2. Experimental

2.1. Materials and reagents

Stock solution of cadmium

Containing 1 mg cadmium Cm^{-3} was prepared by dissolving 1.7911 g of $CdCl_2.H_2O$ in distilled water acidified with HCl and this solution is completed up to the mark of 1 L measuring flask. Mercury solutions of lower concentrations were prepared by further dilution with 0.001 M HCl.

Borate buffer (pH = 10)

Buffer solution (pH 10) prepared by dissolving 25 g sodium tetra-borate, 3.5 g ammonium chloride, and 5.7 g sodium hydroxide in least amount of distilled water, transfer to 1 L measuring flask and complete to the mark using distilled water.

2.2. Preparation of Novel Adsorbents

The carbonaceous material were prepared from water hyacinth using H_3PO_4 as chemical activator then increasing the surface functional groups through oxidation using HNO_3 [11] as shown in fig.1.

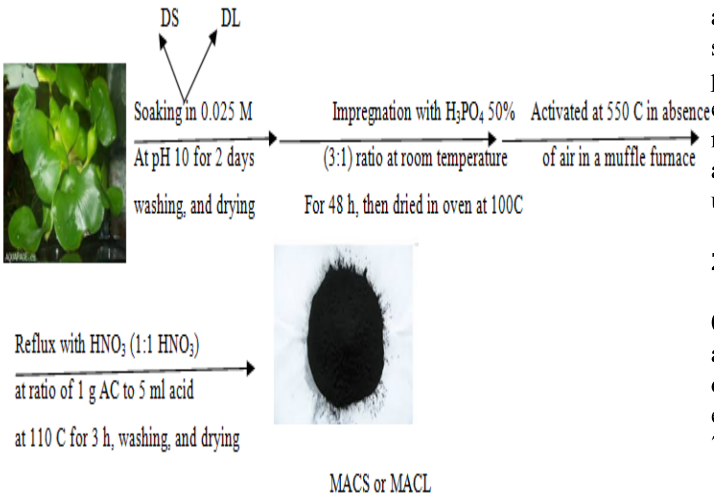


Figure 1: Schematic diagram of dried water hyacinth biomass-derived modified activated carbon.

2.3. Batch equilibrium and kinetic studies

Adsorption experiments were preliminarily carried out by adding a fixed amount of DS, DL, MACS and MACL (0.025g) to a series of 250 ml conical flasks filled with 25 mL aqueous solutions of Cd^{2+} (10 – 300 ppm). The conical flasks were then sealed and placed in shaker and shaken at 150 rpm with a required time at 298 K. The flasks were then removed from the shaker, and the final concentration of Cd^{+2} in the solution was analyzed by measuring the absorption of the respective (2-pyridylazoresorcinol) complex (PAR–Cd) at 491 nm [12]. The amount of Cd^{2+}adsorption at equilibrium qe (mg/g) and percent extraction (%E) was calculated from the following equation:

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

$$qe = \frac{(C_0 - C_e)\ V}{m} \qquad (2)$$

Where C_o and C_e (mg/L) are the liquid phase concentrations of dye at initial and equilibrium, respectively, V (L) the volume of the solution and m (g) is the mass of adsorbent used.

The procedure of kinetic tests was basically identical to those of equilibrium tests. Batch kinetic study carried out at 100 ppm of Cd^{2+} for DS, DL, MACS and MACL, the aqueous samples were taken to preset time intervals and the concentrations of Cd^{2+} were similarly measured. The amount of adsorption at time t, q_t (mg/g), was calculated using Eq.

2.4. Effect of ionic strength and sorbent dosage

To study the effect of ionic strength, 0.025 g sample of DS, DL, MACS and MACL were added to a series of bottles that contains 25 mL of 50 ppm Cd^{2+} solution of different NaCl concentration (between 0.05 and 0.5 mole/l). The flasks were agitated on a shaker at 150 rpm and definite temperatures 298 K for 7 h. After adsorption, the residual concentration of the Cd^{2+} in the solution was determined. The amount of Cd^{2+} adsorbed per unit of sorbent mass calculated by the mass balance equation (2). The effect of sorbent dosage on adsorption rate was investigated using the procedures described above except that different dosages (0.01 – 0.1 g) were used and % E is calculated using equation (1).

2.5. Effect of temperature

0.025 g sample of DS, DL, MACS and MACL was added to each 25 mL volume of Cd^{2+} aqueous solution at different initial concentrations (50 – 300 ppm). The experiments were carried out at 298, 313 and 323 K for 7h.

2.6. Effect of solution pH

Effect of solution pH was investigated at pH range (2 – 6). 0.025 g sample of DS, DL, MACS and MACL was added to each 25 mL volume of Cd^{2+} aqueous solution having an initial concentration of 50 mg/L for a constant adsorption time of 7 h.

2.7. Desorption Studies

For the desorption studies, 25 mg of DS, DL, MACS and MACL was loaded with Cd^{2+} using 25 ml of 100 ppm Cd^{2+} solution at pH=5. Then, the Cd-loaded adsorbent was collected and treated with 25 ml x M HCl to remove the adsorbed Cd^{2+}.

3. Result and Discussion

3.1. Characterization of adsorbents FTIR analysis

Live water hyacinth consists of 94-95%water and WH used contains about used contains about 10 wt% lignin, 42 wt% cellulose ,35 wt% of hemicelluloses , 20 wt% ash and 50-60 g total solid per kilogram [13]. This composition indicates the presence of many hydroxyl (–OH) and other acidic groups that confirmed using FTIR spectra as shown in fig.2. All samples show wide band at about (3373-3442 cm^{-1}) due to O-H stretching mode of hexagonal group and adsorbed water. The peak observed at (1706-1718 cm^{-1}) corresponds to the stretching vibration of C=O bond due to the non-ionic carboxyl groups (– COOH and $–COOCH_3$), and may be assigned to carboxylic or their esters [14]. Asymmetric stretching vibration of ionic carboxylic groups appears at 1600-1636 cm^{-1}.The peak at 1398 cm^{-1}may be assigned to symmetric stretching of –COO [14]. The strong C–O band at 1086 cm^{-1} due to $–OCH_3$ group, also confirms the presence of lignin structure in water hyacinth [14]. It is clear from the FTIR spectra of modified activated carbon that carboxyl groups are present due to oxidation of surface using nitric acid.

3.1.1 Surface area analysis

The nitrogen adsorption isotherm of DS, DL, MACS, and MACL were performed using surface area analyzer (QUANTACHROME- NOVA 2000 Series).Table.1 lists the specific surface area and total pore volume of different adsorbents. It could be noted that the specific surface area and pore volume of MACS and MACL were larger than DS and DL that increased their ability to absorb metal ions.

Table 1: Surface area and total pore volume of the dried Water hyacinth (stems and leaves), activated carbon and modified activated carbon (stems and leaves)

	DS	DL	MACS	MACL
Surface Area	57.46	71.83	381.22	365.22
Total pore	0.01	0.03	0.43	0.29

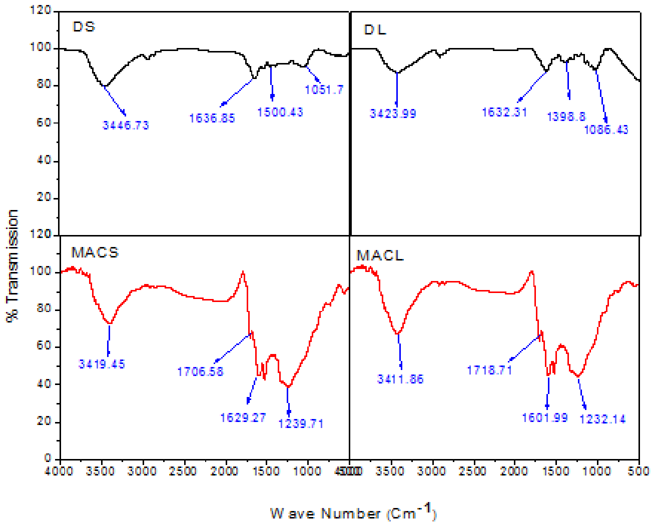


Figure 2: FTIR spectrum of dried Water hyacinth (stems and leaves), and modified activated carbon

3.1.2 SEM analysis

Micrographs of DS, DL, MCS and MCL were obtained using scanning electron microscope (SEM; JEOL, model 6400). Prior to the analysis, the samples were dried at 383K for 4h. A thin layer of gold was coated on the samples for charge dissipation. The SEM analysis of DS, DL, MCS and MCL revealed important information on the surface morphology at magnification of 1500x (Fig. 3). As shown in Fig. 3, all adsorbents have some cavities in its structure capable of up taking metal ions but the porosity of MACS was the highest.

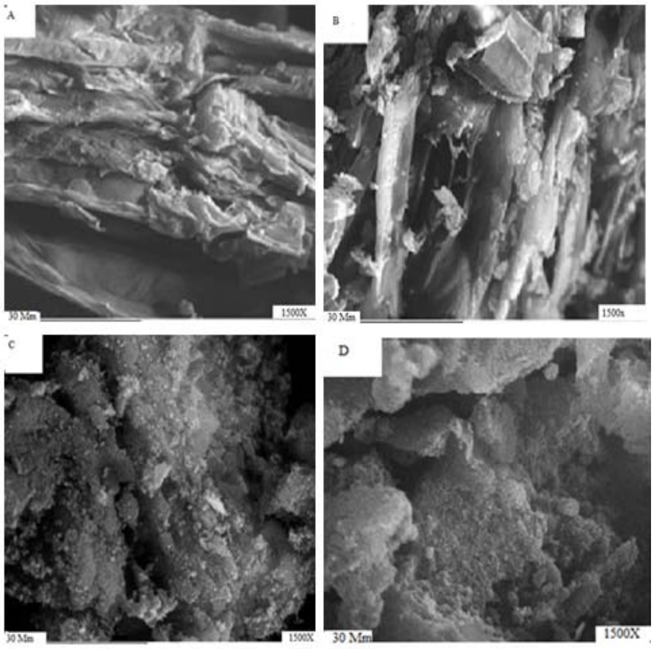


Figure 3: SEM photographs of (a) DS, (b) DL, (c) MACS, (d) MACL

3.2. Adsorption Parameters

3.2.1. Effect of pH on Cd^{2+} adsorption

The effect of the initial pH on the removal of Cd^{2+} by DS, DL, MACS and MACL is shown in Fig.4. The adsorption capacity increases when the pH increases and maximum adsorption of occurs Cd^{2+}at pH 5. However, the uptake capacity does not change significantly from pH 4.5 to 6 and the removal efficiency (%E) is kept practically constant (variations lower than 2.0%). When the pH increases from pH=2 to pH=5, The amount of Cd^{2+} adsorbed at equilibrium (q_e) increase from 8.82 to 36.5 mg/g, from 10.16 to 24.4 mg/g, from 11.58 to 45.7 mg/g and from 8.89 to 47.94 mg/g for DS, DL, MACL and MACS, respectively. DS, DL, MACL and MACS comprised of various functional groups such as hydroxyl and carboxyl groups which are affected by the pH of solutions. Therefore, at various pH values, electrostatic attraction and the ionic properties between Cadmium ions and different adsorbents could play very important roles in the adsorption process.

In the present work, the results show that at low pH values, the removal efficiency of cadmium decrease might be attributed to competition between cadmium which present as free Cd^{2+} ions and hydrogen ions on the adsorption sites of different adsorbents. The hydrogen ion is a strong competitor for adsorption because of its small size. With the increase of solution pH values, the electrical repulsion force became weaker and the cadmium ions may be transported to the surface of the polymer and become attached on the surface. Moreover, more hydrogen ions competed with Cd (II) for adsorption sites, which made the availability of Cd (II) to activated sites difficult to take place; on the other hand, carboxyl groups in the adsorbents existed in the form of –COOH rather than –COO−, which could go against the possibility of Cd (II) adsorbed onto the adsorbents. Similar phenomena were reported by several earlier workers for metal adsorption on different adsorbents [15, 16]. In case of DS and DL, The reduced capacity of adsorption of cadmium beyond pH 5 is probably due to the formation of cadmium complexes with organic components leached from the water hyacinth leaves and stems These complexes have larger sizes than free cadmium ions and thus are weaker competitors for adsorption as well as at pH > 5.5, poorly soluble hydroxide formed $Cd(OH)_2$ [17, 18]. At pH= 5.0, the adsorption capacity of (DS, DL, MACS and MACL) almost reaches the maximum value. To avoid the formation of precipitation in the aqueous solution, the pH of 5 was selected as the initial pH value of Cd (II) solution for subsequent adsorption experiment.

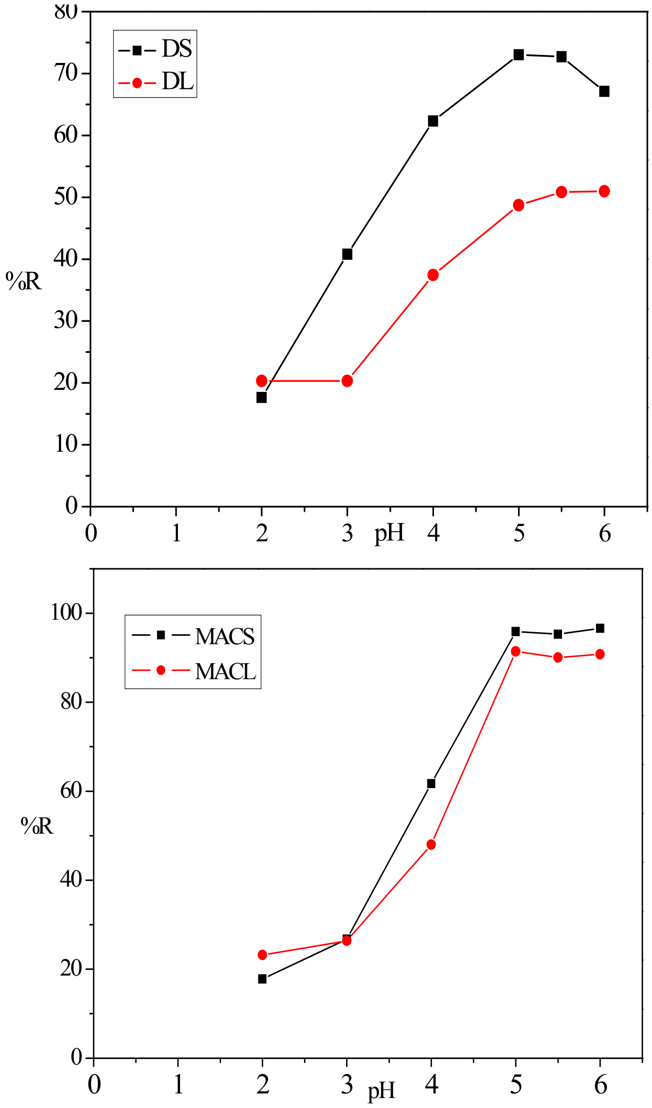


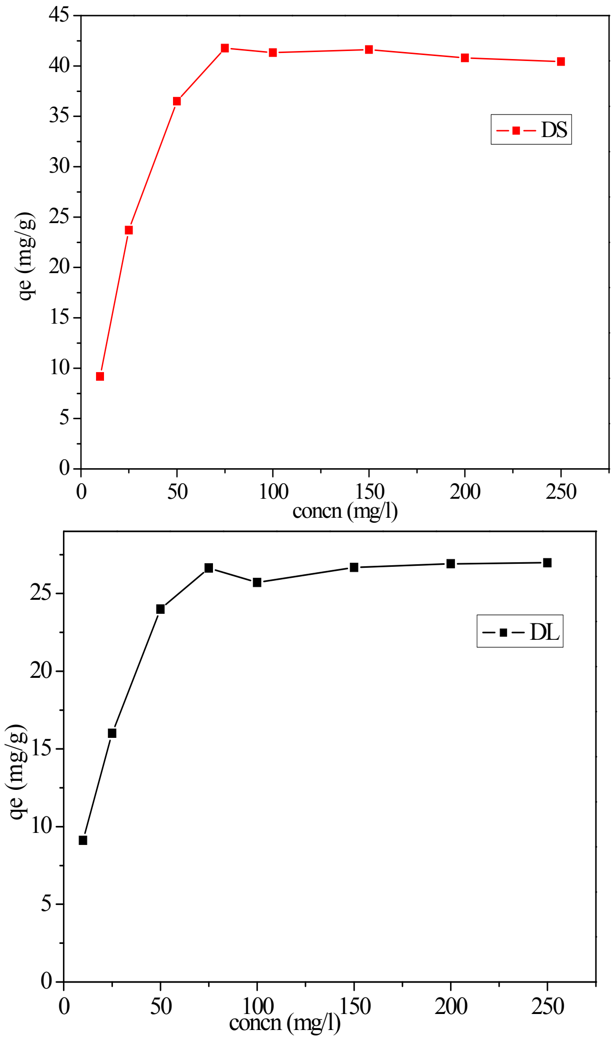
Figure 4: Effect of the pH values on adsorption capacity of Cd^{2+} by DS, DL, MACS and MACL (Conditions: C_o = 50 mg/l, T=25°C; adsorbent dose = 0.025 g/25 ml)

3.2.2. Effect of initial concentration on the removal of Cd^{2+}

The effect of initial concentration on the removal of Cd^{2+} by DS, DL, MACS and MACL were studied at optimum pH =5 and at room temperature, the results were graphed in Fig. 5. It is seen that the equilibrium sorption capacities of the sorbents increase with an increase in initial Cd^{2+} concentration and the adsorption at different concentrations is rapid in the initial stages and gradually decreases with the progress of adsorption until the equilibrium is reached. This is due to, the higher the initial Cd^{2+} concentration, the higher the driving force of the concentration gradient at solid-liquid interface which cause an increase of the amount of Cd^{2+} adsorbed on the adsorbent .When the initial concentration of Cd^{2+} increases from 5 to 300 mg/l at 25 $^{\circ}$C, The amount of Cd^{2+} adsorbed at equilibrium (q_e) increase from 9.2to 40.8mg/g, from 9.11to 26.9 mg/g , from 9.8 to 65.5mg/g and from 9.7 to 58.9 mg/g for DS, DL, MACS and MACL, respectively.

While the removal efficiency of cadmium decrease from 91.78% to 16.2%, from 91.18% to 10.43%, from 97.76% to 21.97% and from 97.3% to 22.69% for DS, DL, MACS and MACL, respectively. This decrease may be attributed to the blockage of water hyacinth (stem, leaves) hydroxyl groups and (modified activated carbon) carboxyl groups confirms their role in sorption of heavy metals. The interactions of metal ions with hydroxyl groups of cellulose of dried plant and carboxyl groups of modified activated carbon have been suggested. These observations, along with the possible assigned functional groups in the FTIR spectra, prove that the carboxyl and hydroxyl groups are principally responsible for the removal of Cd (II) by DS, DL, MACS and MACL, with carboxyl groups being responsible for most of the metal uptake.

As expected, the adsorption efficiency increased with the initial Cd^{2+} concentration. With more Cd^{2+} present in solution, larger fraction of the active sites is involved in the adsorption process. At higher Cd^{2+}concentrations adsorption efficiency reached a plateau indicating saturation of the available binding sites on the adsorbent.



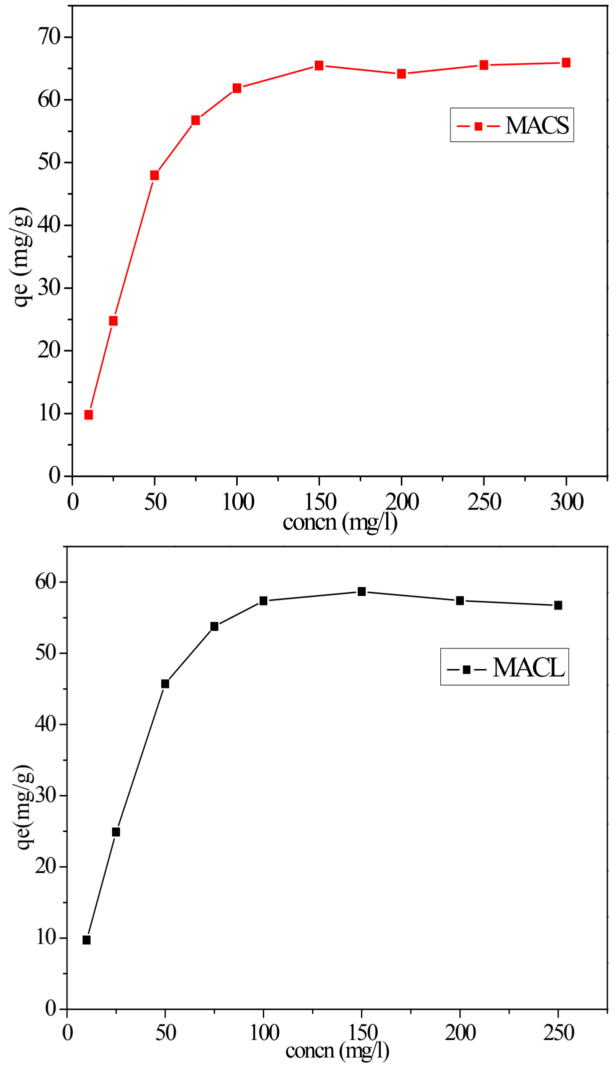


Figure 5: Effect of initial metal concentration on the removal of Cd^{2+} by DL, DS, MACL and MACS. (Conditions: C_o = 5-300 mg/l, T=25°C; adsorbent dose = 0.025 g/25 ml).

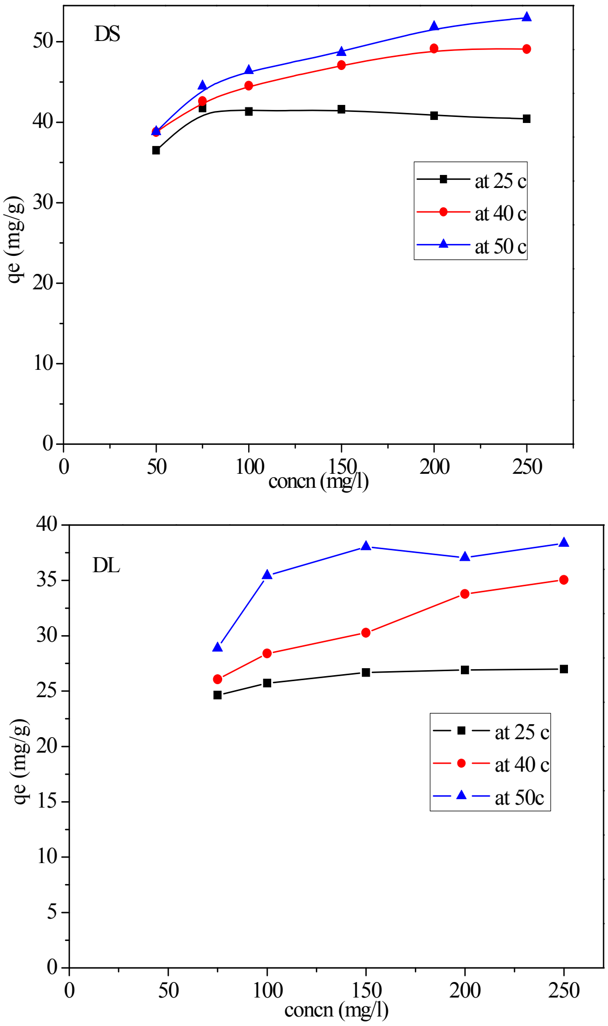
3.2.3 Effect of temperature on adsorption of cadmium

Fig. 6. Shows that the relationship between the temperature and the adsorption capacity of Cd^{+2} by DS, DL, MACS and MACL. Table 2. Shows that when the temperature increased from 25 $^{\circ}$C to 45 $^{\circ}$C, the maximum adsorption capacities of Cd^{2+} removed by DS, DL, MACL and MACS are found to be increased from 40.43 to 52.99 mg/g, from 26.98 to 38.34 mg/g, from 56.7 to 70.77 mg/g and from 65.55 to 73.4 mg/g, respectively. This is attributed to the increase in the kinetic energy of Cd^{2+} with the temperature. Consequently, the rate of diffusion of Cd^{2+} ions across the external boundary layer and in the internal pores in the different adsorbents increases with temperature, and the amount of Cd^{2+} uptake increases may be due to change in size of pores and increase in number of the sorption sites. In other words, the adsorption capacity increases with increase in the temperature of the adsorption process. A physical adsorption is generally understood to be exothermic and the equilibrium adsorption will decrease with increase in the temperature of adsorption process [19]. An increase

of the adsorption capacity with increase in the temperature indicates a significant adsorption being endothermic reaction [20].

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

Samples	Q_e*(mg g^{-1})*		
	25 °C	40 °C	50 °C
DS	40.43	49.1	52.99
DL	26.98	35.05	38.34
MACS	65.55	68.38	73.4
MACL	56.7	66.89	70.77



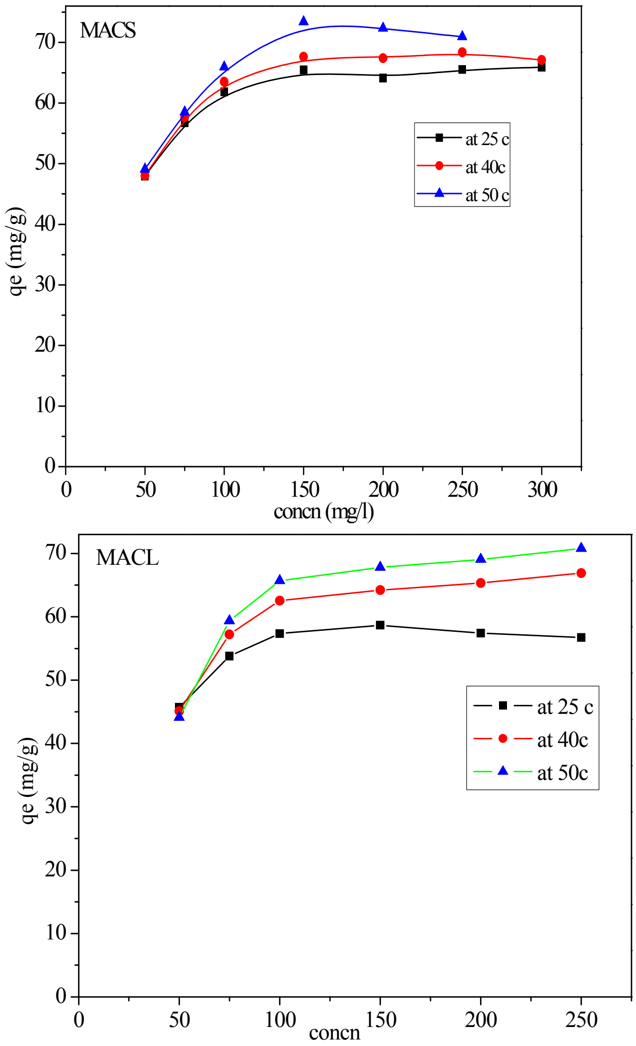


Figure 6: Effect of temperature on adsorption capacity of Cd^{2+} by DS, DL, MACS and MACL. (Conditions: C_o =50-300 ppm; adsorbent dose = 0.025 g/25 ml; pH=5).

3.2.4. Effect of ionic strength

The presences of ions lead to high ionic strength, which may significantly affect the performance of the adsorption process. Fig.7. presents the effect of ionic strength on the uptake of Cd^{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 cadmium decreased from 73.01% to 52.91%, from 56.12% to 46.04%, from 95.9 % to 59.9% and from 91.4% to 64.13% for DS, DL, MACS and MACL, respectively. These results showed ionic strength had an adverse effect on the cadmium ions adsorption, which may be induced by the competition between the cations and the Cd^{+2} ions for the electron rich sites.

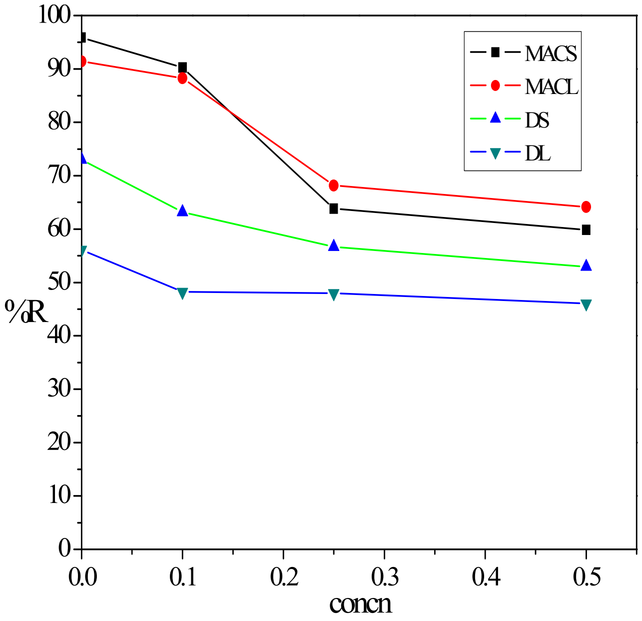


Figure 7: Effect of ionic strength on the removal of Cd+2 by DS, DL, MACS and MACL. (Conditions: T=25 °C; adsorbent dose = 0.025 g/25 ml; C_o = 50 mg/l; time = 5 h).

3.2.5. Effect of contact time

Fig. 8 showed the effect of contact time on the adsorption capacity of DS, DL, MACS, and MACL for Cd^{2+}. It can be observed from Fig.8 that the adsorption process was found to be very rapid initially, and a large fraction of the total amount of metal was removed within a few minutes more than 70 % of the adsorption capacities of corresponding adsorbents for Cd (II) occurred within 5 min for MACL and DL and more than 85% occurred within 5 min for MACS and DS. This means that a large number of vacant adsorption sites on the adsorbent surface were available at this stage as well as The high initial rate of adsorption is due to the high concentration driving force available for mass transfer from the liquid to the adsorbent active sites. Thereafter, it became slower near the adsorption equilibrium and the maximum removal of Cd (II) occurred within 45-60 min. At this time, the amount of metal being adsorbed onto the adsorbent was in a state of dynamic equilibrium with the amount of metal desorbed from the adsorbent. The time required to attain this state of equilibrium was termed the equilibrium time and the amount of metal adsorbed at the equilibrium time reflected the maximum metal adsorption capacity of the adsorbent under these particular conditions so 60 min could be considered as the equilibrium time for the adsorption. To ensure that sufficient contact time was obtained, further adsorption experiments were carried out for 5 h.

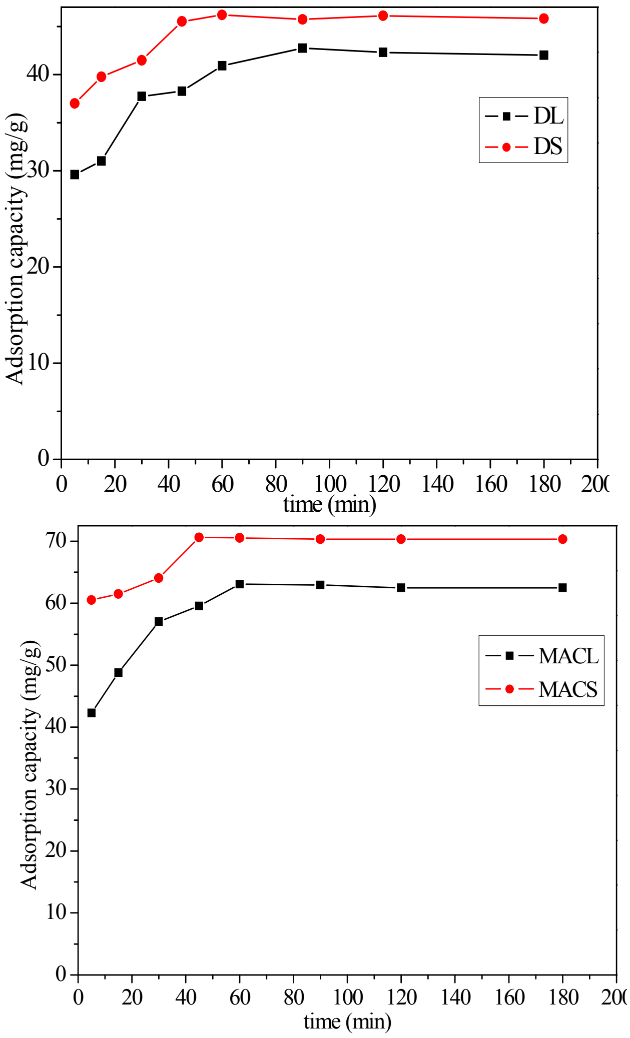


Figure 8: Effect of contact time on adsorption capacity of Cd^{2+} by DS, DL, MACS and MACL. (Conditions: C_o =100 mg/l, T=25 °C; adsorbent dose = 0.1 g/100 ml*)*

3.2.6. Effect of adsorbent dosage

The dependence of removal of Cd^{2+} on dosage of DS, DL, MACS and MACL is shown in Fig. 9 , it could be clearly seen that, an increase in sorbent dose is in favor of Cd^{+2} removal. When the sorbent dose increases from 0.01 to 0.1 g, the percent of cadmium removal by DS, DL, MACS and MACL increase from 57.9 % to 98.7 %, from 49.2% to 91.8 %, from 72.8 % to 99.4% and from 72.4% to 99.01%, respectively. This can be simply attributed to the increased sorbent surface area and availability of more sorption sites [21]. It apparent that by increasing the adsorbent dose, the removal efficiency increased but adsorption density, the amount adsorbed per unit mass, decreased. The decrease in adsorption density with increase in the adsorbent dose is mainly due to the particle interactions such as aggregation resulting from high adsorbent concentration such aggregation would lead to a decrease in the total surface area of adsorbent.

If we notice to the obtained results, it is obvious that the adsorption of the cadmium increases in the order of MACS > MACL > DS > DL under all conditions studied such as concentration, temperature, pH and sorbent dose.

This behavior is attributed to the increase in number of active sites on the surface of adsorbents because of increasing the amount of adsorbents.

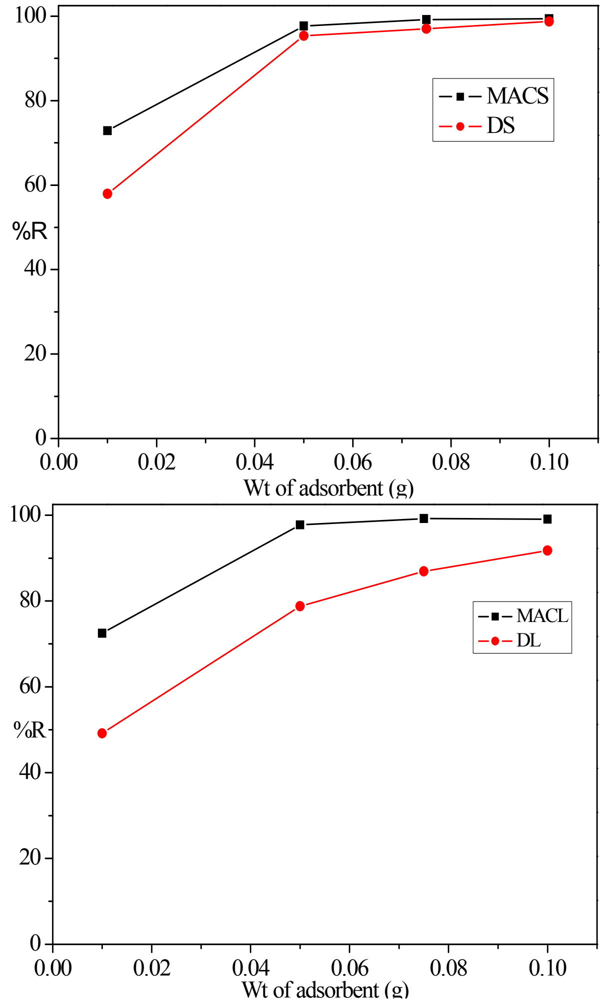


Figure 9: Effect of sorbent dosage on the removal of Cd^{+2} by DS, DL, MACS and MACL. (Conditions: T=25 °C; C_o = 50 mg/l, v=25 ml; time = 5 h, pH = 5)

3.3. Adsorption isotherms

Isotherm studies can describe how the adsorbates interact with adsorbents, affording the most important parameter for designing a desired adsorption system. The Langmuir and Freundlich isotherms for adsorption of Cd (II) onto DS, DL, MACS and MACL at different initial concentrations are given in Figs. 10, 11, respectively. The Langmuir isotherm is often applicable to a homogeneous adsorption surface with all the adsorption sites having equal adsorbate affinity, while the Freundlich isotherm model assumes heterogeneity of adsorption surfaces, which can be expressed as[22, 23]:

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

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

Where q_e is the amount adsorbed at equilibrium (mg g^{-1}), C_e is the equilibrium concentration of the Cd (II) (mg L^{-1}), constant b is related to the energy of adsorption (Lmg^{-1}), Q_o 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.

Tables 3, 4, summarize the Langmuir and Freundlich constants and 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 MACS, MACL, DS and DL at 25 °C was calculated to be 65.5, 58.9, 40.8 and 26.9 mg g^{-1} are all the same as the experimental data. Moreover, the essential feature of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor (R_L) given by the following equation [24]:

$$Rl = \frac{1}{1+bc_e} \qquad (5)$$

Where *b* (Lmg^{-1}) is the Langmuir constant and C_o (mg L^{-1}) is the initial concentration in the liquid phase. The value of R_L indicates the shape of the isotherm to be either unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$) or irreversible ($R_L = 0$). The R_L values between 0 and 1 indicate favorable adsorption. For Cd (II) adsorption on MACS, MACL, DS and DL, R_L values obtained are in the range between 0 and 1, thereby confirming that the adsorption is a favorable process.

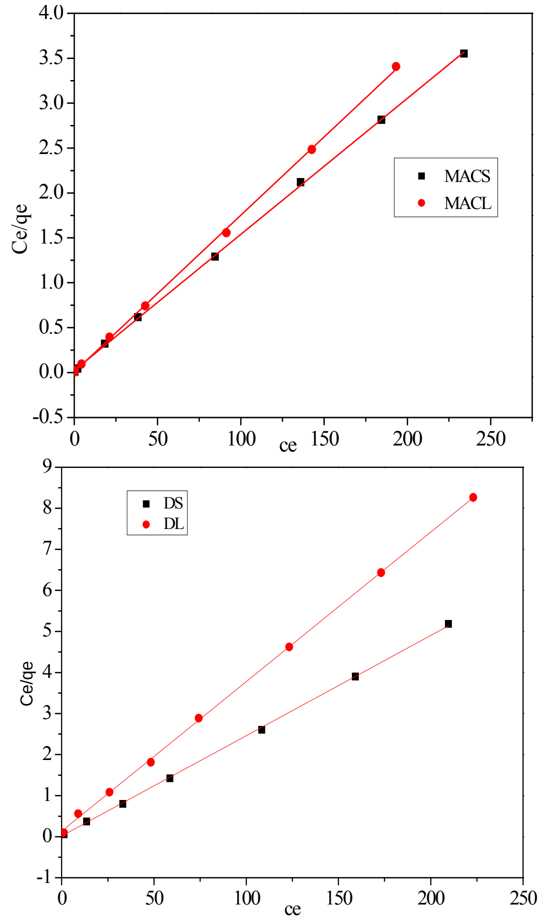


Figure 10: Langmuir plot for the adsorption of Cd^{2+} by DS, DL, MACS and MACL

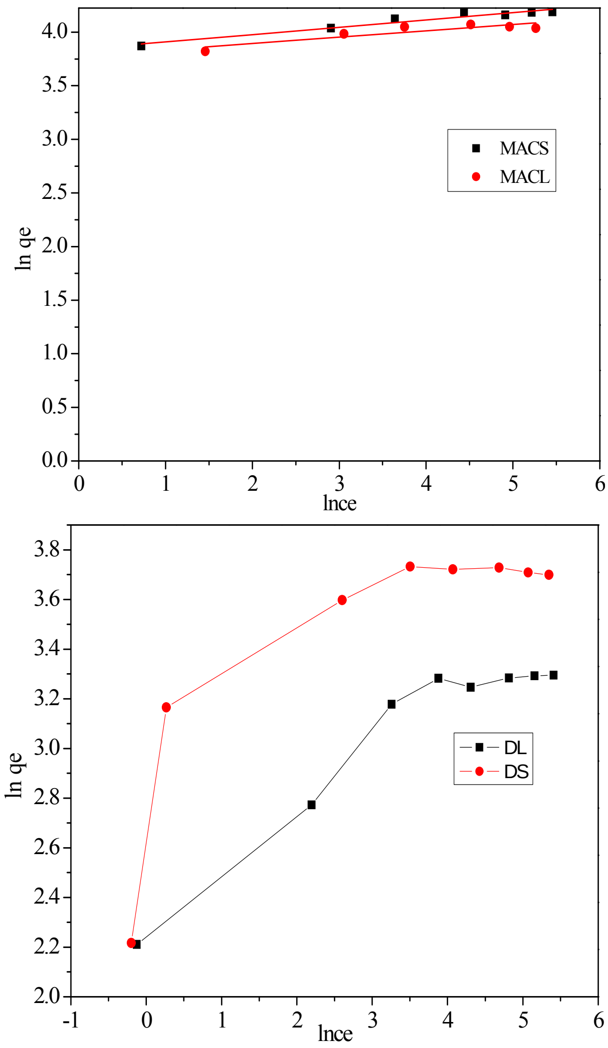


Figure 11: Freundlich plot for adsorption of Cd2+ by DS, DL, MACS and MACL

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

Adsorbents	Langmuir parameters				
	R^2	b (L/mg)	$Q_{max, fitted}$	Q_{exp}	R_L
MACS	0.99	0.61	66.1	65.5	0.0055
MACL	0.99	2.033	57.34	58.9	0.0019
DS	0.99	1.45	40.93	40.8	0.0028
DL	0.99	0.275	27.44	26.9	0.0039

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

	Freundlich parameters		
Adsorbents	R^2	Kf	1/n
MACS	0.93	46.52	0.068
MACL	0.75	43.69	0.0589
MACS	0.21	35.61	0.0298
MACL	0.59	21.28	0.0459

3.4. Adsorption Kinetics

The pseudo-first order equation and the pseudo-second order equation

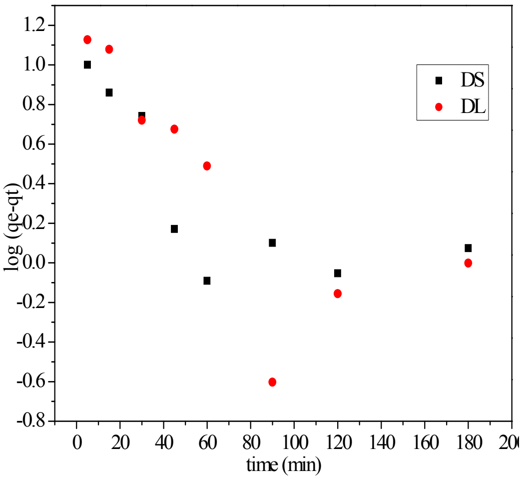
The rate constant of adsorption is determined from the first-order rate expression given by Lagergren and Svenska [25]:

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

Where q_e and q_t are the amounts of cadmium 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 100 ppm of cadmium. The correlation coefficient values R^2 are low, the experimental qe 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 [26]:

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

Where k_2 is the rate constant of second-order adsorption (g mol^{-1} min^{-1}). If the second-order kinetics is applicable, then the plot of t/q_t versus t should show a linear relationship. There is no need to know any parameter beforehand and the equilibrium adsorption capacity, q_e, can be calculated from Eq. (2). Also, it is more likely to predict the behavior over the whole range of adsorption. 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 the applicability of this kinetic equation and the second-order nature of the adsorption process of Cadmium on MACS, MACL, DS and DL adsorbents.



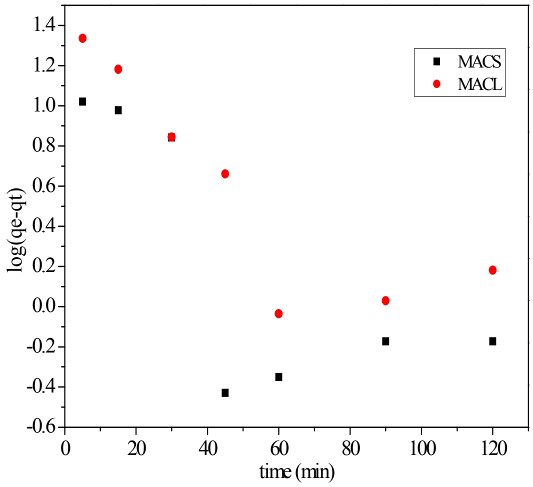


Figure 12: Pseudo-first-order Kinetic model for the adsorption of Cd^{2+} by DS, DL, MACS and MACL.

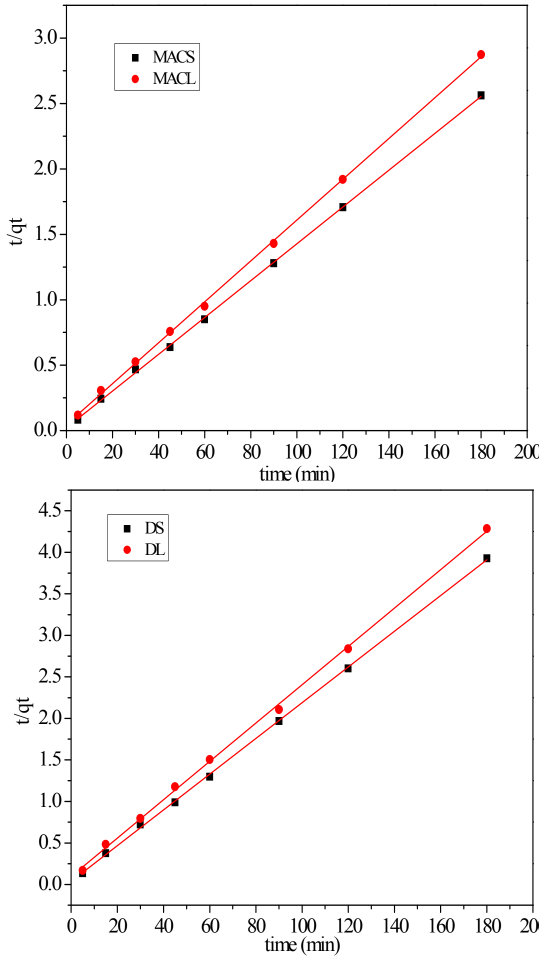


Figure 13: Pseudo-second-order Kinetic model for the adsorption of Cd^{2+} by DS, DL, MACS and MACL.

Table 7: Parameters of first order kinetic model for adsorption of 100 ppm Cd^{+2} by DS, DL, MACS and MACL

Adsorbent Code	*Pseudo-first order*			
	$q_{e\ exp.}$ mg.g^{-1}	*$q_{e\ cal.}$ mg.g^{-1}*	*K_1 (min^{-1})*	*R^2*
MAC S	65.5	7.26	0.0272	0.447
MACL	58.9	15.7	0.0263	0.669
DS	40.8	5.23	0.0124	0.446
D L	26.9	9.185	0.006	0.529

Table 8: Parameters of second order kinetic model for adsorption of 100 ppm Cd^{+2} by DS, DL, MACS and MACL

Adsorbent Code	$q_e$exp. mg.g^{-1}	$q_e$cal. mg.g^{-1}	K^2 g. mol^{-1} .min^{-1}	R^2
MACS	65.5	65.9	0.0098	0.999
MACL	58.9	56.7	0.0052	0.999
DS	40.8	41.7	0.0055	0.999
DL	26.9	26.9	0.037	0.998

3.5. Intra Particle Diffusion Model

Intra-particle model used here referred to the theory proposed by Weber and Morris. The linear form of intra-particle diffusion model was given as [27],

$$q_t = K_d\, t^{0.5} + C \tag{8}$$

Where C was the intercept andK_d was the intra-particle diffusion rate constant (mg g^{-1} $min^{-0.5}$). 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 9.

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. Previous studies reported that more than one step were involved in the intra-particle diffusion process. The initial section indicated the external surface adsorption. The second corresponded to the gradual adsorption. The third indicated the final equilibrium stage where the intra-particle diffusion starts to slow down due to extremely low solute concentrations in the solution. Based on all the explanation, the pseudo-second-order model was the best fit model for the adsorption of Cd (II) onto MACS, MACL, DS and DL.

The boundary layer effect 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 [28]:

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

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

$$F = \frac{q_t}{q_e} \tag{10}$$

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

Eq. (9) can be rearranged to

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

From Boyd plot, (Fig. 15) it was observed that the plots are linear but do not pass though the origin suggesting that the adsorption process is controlled by film diffusion. However it seems that pore diffusion is more important as intercept approaches values close to zero , indicating that external mass transfer is the rate limiting process in the beginning of adsorption and then is the intra-particle diffusion.

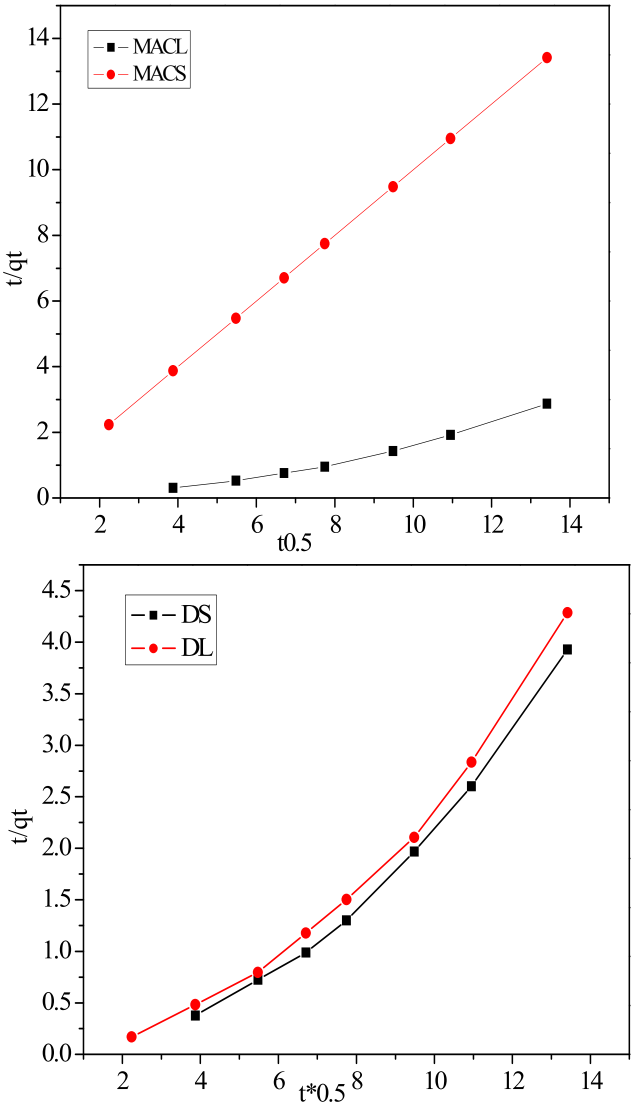


Figure 14: Intra-particle diffusion plots for adsorption of Cd2+on DS, DL, MACS and MACL at 100 ppm

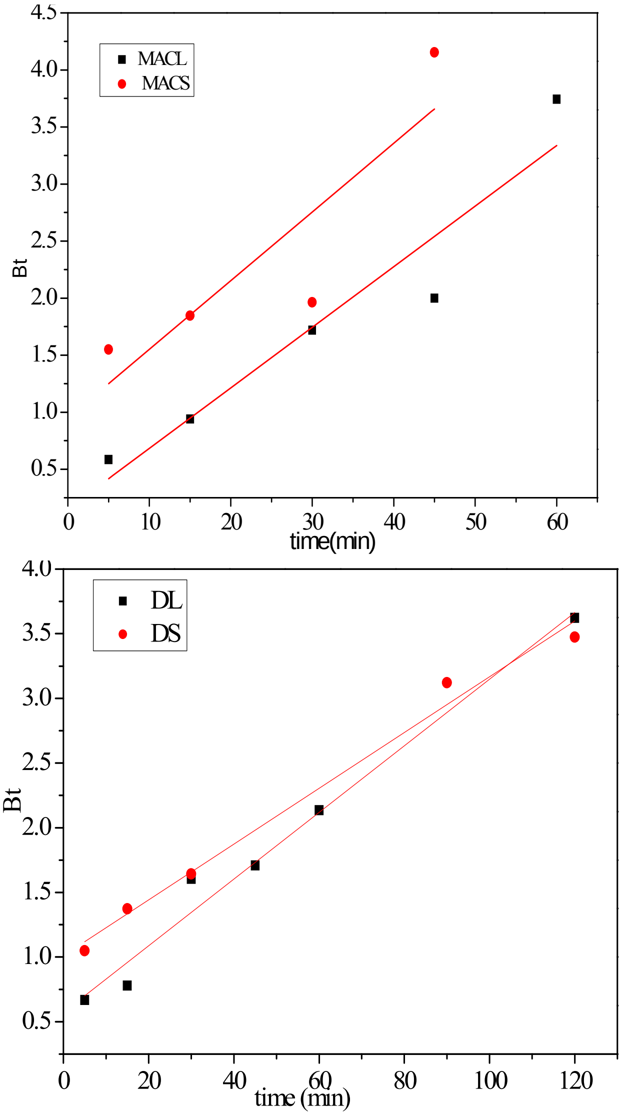


Figure 15: Bt versus t plot for adsorption of Cd2+on DS, DL, MACS and MACL at 100 ppm

Table 9: Intra-particle diffusion parameters for adsorption of Cd (II) by DS, DL, MACS and MACL at 100 ppm

Intraparticle diffusion model				Boyd model	
Adsorbent	R^2	Kd	Intercept	Intercept	R^2
MACS	1	1	0	0.95	0.663
MACL	0.958	0.269	-0.961	0.15	0.893
DS	0.961	0.37	-1.353	1.01	0.986
DL	0.944	0.35	-1.02	0.572	0.978

3.6. Evaluation of thermodynamic parameters

Thermodynamic parameters were calculated from the variation of the thermodynamic distribution coefficient, k_d with change in temperature. The standard free energy change, ΔG°, was calculated using the expression [29]:

$$\Delta G° = \Delta H° - T\Delta S° \qquad (12)$$

The value of $\Delta H°$ and $\Delta S°$ were calculated from the Van'tHoff equation [29]:

$$\ln k_d = \frac{\Delta S°}{R} - \frac{\Delta H°}{RT} \qquad (13)$$

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.

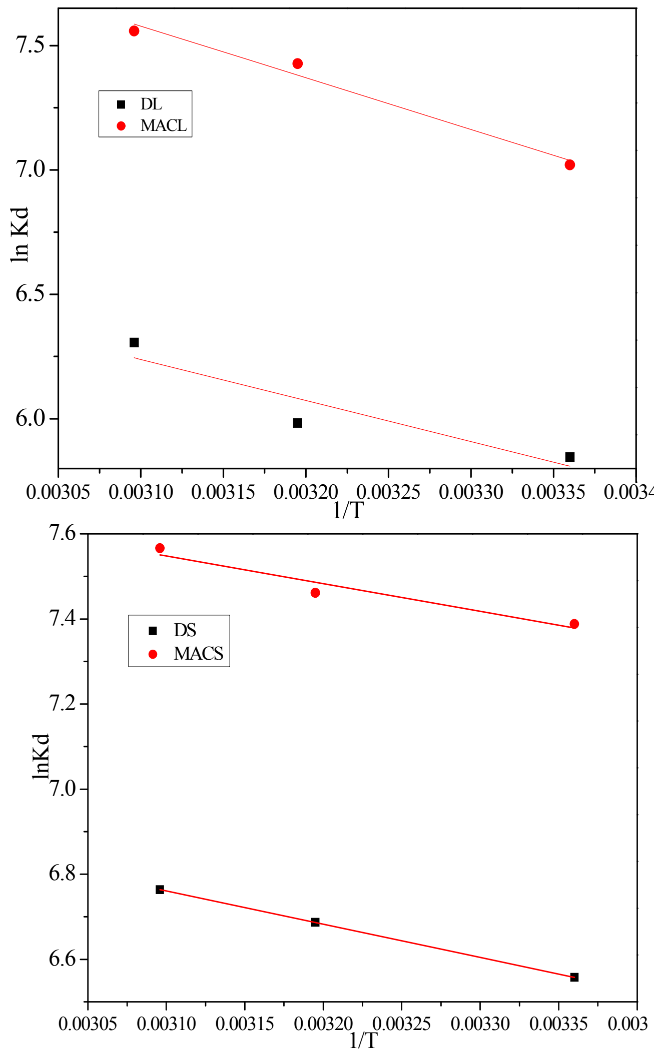


Figure 16: The plots of lnKd versus T^{-1} for estimations of thermodynamic parameters of the adsorption process of $Cd^{+2}$by MACS, MACL, DS and DL Condition :($C_{\circ}$ = 100 ppm, T= 25 – 50 ^{0}C, t= 5h, adsorbent dose = 0.025 g/25 ml)

Table 10: Thermodynamic parameters for adsorption of Cd^{+2} by MACS, MACL, DS and DL at different temperatures

Adsorbents	Mercury concentration (mg/L)	ΔH° (kJ/mol)	ΔS° (kJ/mol)	ΔG° (kJ/mol)		
				298	313	323
MAC S	100	5.405	0.079	-	-	-
MACL	100	17.3	0.166	-	-	-
DS	100	6.429	0.076	-	-	-
DL	100	13.72	0.094	-	-	-

The thermodynamic parameters are given in Table 10. It is clear from the table that the values of ΔG° are negative for DS, DL, MACS and MACL. The negative values of ΔG° at various temperatures indicate the spontaneous nature of the sorption process. The fact that the values of the ΔG° decrease with increasing temperature indicates the increase of spontaneous effect and greater chances of coordination which results in the formation of higher linkages. The positive value of ΔH° confirms the endothermic nature of the sorption process. The positive value of ΔS° also indicates the increased randomness during sorption process due to the liberation of water molecules surrounding the metal ion to the solution.

3.7. Desorption Studies

To develop cost effective adsorbent for Cd (II) removal, it is important that the adsorbed Cd (II) should be easily desorbed for reusability of the media. By studying effect of pH, it is noticed that the adsorption capacity sharply decrease in acidic medium so desorption of Cd (II) was conducted using HCl as desorbing agent. 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 100 ppm of Cd (II) at pH 5 .As the adsorption reaches equilibrium, the metal ion concentration of the solution was measured, Then, the adsorbent loaded with Cd (II) was collected and treated with 25 ml x M HCl to remove the adsorbed Cd (II). The results relating to desorption of Cd (II) by HCl of different concentration are shown in Tables 11, 12. The results show that increase in concentration of HCl. The desorption also increased but remained constant with 0.6 M HCl. The relatively inexpensive HCl desorbed almost all of the sorbed cadmium from carbon. The H^{+} ions from HCl easily displaces cadmium ions bonded to the adsorbent during the desorption stage. The results show that the spent adsorbent can be effectively regenerated for further use easily.

Table 11: Desorption efficiencies of cadmium using 0.3 M HCl after adsorption of 100 ppm

Adsorbent code	q_e	$q_e$desorped	% desorption
MACS	63.5	38.453	60.56
MACL	57.5	35.38	61.351
DS	25.7	16.37	63.69
DL	41.3	25	60.53

Table 12: Desorption efficiencies of cadmium using 0.6 M HCl after adsorption of 100 ppm.

Adsorbent code	q_e adsorbed	$q_e$desorped	% desorption
MACS	63.5	40.022	63.027
MACL	57.5	37.89	65.899
DL	25.7	17.899	69.65
DS	41.3	28.59	69.219

3.8. Mechanism of Adsorption

This study examined the utility of water hyacinth (stems and leaves) and activated carbon prepared from them in the removal of cadmium. Kinetic studies revealed that the removal of Cd (II) was found to be rapid at the initial period of contact time and then to become slow and stagnate with the increase in contact time. This showed blocking of the functional groups by increasing contact time decrease the rate of removal of cadmium. FTIR spectrum confirmed that COO- is the main active groups present in activated carbon and water hyacinth which contains high content of cellulose (30 - 50%), hemicellulose (20 - 40%) and lignine (15 - 30%) and indicated that cadmium was adsorbed as Cd(II) and attached to O- [30]. 0.6 M HCl solution able to desorb Cd(II) from different adsorbents , about 65% desorption yield was obtained for Cd(II). From these results obtained, it seems that, various metal- binding mechanisms are thought to be involved in the bio sorption process including ion exchange (release of H^+), surface adsorption, chemisorption and adsorption-complexion. Metal-Binding mechanisms may be assumed to involve the following four steps:

- Migration of Cd (II) from bulk of the solution to the surface of the adsorbent.
- Diffusion of Cd (II) through the boundary layer to the surface of the adsorbent.
- Adsorption of Cd (II) at an active site (COOH, -OH) on the surface of different adsorbents and release of protons.
- Intra-particle diffusion of Cd (II) into the interior pores of the adsorbent.

3.9 Comparison of the adsorption capacities of sorbents toward Cd (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 Cd (II) [31-36]. 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 Cd (II) removal from aqueous solution.

Table 13: Comparison of the adsorption capacities of Cd (II) onto various adsorbents

Adsorbents	Adsorption capacities (mg/g)	Ref.
MACS	65.9	This work
MACL	58.3	
DS	41	
DL	26.9	
Pomelo peel	21.83	[31]
Akaganeite-type nanocrystals	17.02	[32]
Sugarcane bagasse	6.97	[33]
Rice hus ash	3.02	[34]
Na-zeolitic tuff	18.0	[35]
Sewage sludge for chemical activation with $ZnCl_2$ and pyrolysis.	16.7	
Carbonaceous material	15.0	
ion-imprinted amino-functionalized silica gel	31.6	[36]

4. Conclusion

Dried Water hyacinth (stems, leaves) and Activated carbon (stems, leaves) were successfully evaluated as efficient adsorbents for removal of Cd (II) from aqueous solutions. The results showed that, pH values of solution, contact time, adsorbent dosage, and initial concentration significantly affected the adsorption amount of Cd (II). It was found that the sorption process is pH-dependent and maximum sorption was obtained at pH 5. The sorption studies were carried out using different Cd^{2+} concentrations. It was found that the extent of Cd^{2+} sorption increases upon increasing Cd^{2+} concentration within the range studied. The kinetic studies of cadmium DS, DL, MACS and MACL were performed based on pseudo first-order, pseudo second-order, and intra-particle diffusion rate mechanism. The data indicated that the adsorption kinetics of cadmium on all adsorbents followed the pseudo-second order model at different cadmium concentrations. The equilibrium data were analyzed using the Langmuir and Freundlich isotherms and the characteristic parameters for each isotherm were determined. The results showed that the experimental data were correlated reasonably well by the Langmuir isotherm model. Thermodynamic studies indicated that the adsorption process was an endothermic process.

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