

Synthesis and adsorption properties of Chitosan cross linked with phenol – formaldehyde resin for the removal of heavy metals and dyes from water

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Abstract: A novel activated carbon material has been prepared by carbonization and activation of Phenol-Chitosan-Formaldehyde resin (PCFR) which synthesized by the condensation polymerization method. The physicochemical properties of the PCFR were characterized by SEM, XRD, BET, EDS, TGA and FTIR spectroscopy. The adsorption properties of Pb(II) ion and Methylene blue (MB) onto PCFR were investigated by batch techniques. The particle size of adsorbent was 65-70 μ . Kinetic studies indicated that Pb(II) ion and MB adsorption followed the pseudo-second-order model. The adsorption may be controlled by external mass transfer followed by intra-particle diffusion mass transfer. Equilibrium adsorption was investigated by the Langmuir, Freundlich, Temkin, D-R and Jovanoic isotherms. The thermodynamics parameters of adsorption systems indicated spontaneous and endothermic process.

Keywords: TGA, Lead ion, Methylene blue, Adsorption, Kinetics

I. Introduction:

The contamination of water from toxic compounds, like heavy metal ions and dyes remains a severe environmental and public problem. Heavy metal ions and dyes are often found in the environment as a result of increasing industrial use. They are common contaminants in waste water and known to be toxic and carcinogenic [1]. Lead ion is emitted into the atmosphere by the combustion of fossil fuels, batteries and the smelting of sulfide ores, and in lakes and streams by acid mine drainage [2]. Pb(II) ions dominates in acid while PbOH⁺ predominates in most environmental pHs. The permissible limit of lead ion in drinking water and surface water intended for drinking, as set by EU and WHO, are 0.010 and 0.010 mg/L, respectively [3-4]. Dyes are widely used in textile, paper, plastics coating, etc. The presence of dyes in water consumes oxygen and elevates biochemical oxygen demand destroying the aquatic life [5].

Various technologies and processes are currently used to remove such pollutants from wastewater, like biological treatments, membrane processes, advanced oxidation processes, chemical and electrochemical techniques and adsorption [6-9]. Amongst all, adsorption technique is a feasible option, both technically and economically. Especially, if the adsorbent is inexpensive and readily available then adsorption process provides as an alternative.

The application of biopolymers such as chitosan is one of the most emerging adsorption methods for the removal of dyes and heavy metal ion, even at low concentrations [10]. Chitosan derivatives contain nitrogen, phosphorus and sulfur as heteroatoms. Recently, chitosan composites have been developed to adsorb heavy metals and dyes from wastewater. Various substances have been used to form composite with chitosan such as montmorillonite [11], polyurethane [12], poly vinyl alcohol, poly vinyl chloride and kaolinite [13].

The aim of this work is to improve adsorption capacity of Chitosan by grafting Phenol-Formaldehyde resin on its surface to adsorb lead ion and methylene blue dye and to illustrate adsorption processes and evaluate the feasibility of applying modified PCFR as an adsorbent and ion exchange in practical heavy metal and dye removal. Different physicochemical parameters, i.e., initial concentration of metal ion and dye solutions, adsorbent dose, contact time and temperature were also investigated. To predict the nature of the adsorption process, the equilibrium, kinetics and thermodynamic studies were investigated.

II. Materials and Methods:

2.1. Materials:

The chemicals Con. sulfuric acid (Specific gravity = 1.82), Formaldehyde (37-40% solution) and Phenol (Density = 1.057 gm⁻³) were used in the present study. Chitosan (Chitosan, degree of deacetylation - 85%, average molecular weight - 9.0 $\times 10^5$) was supplied by Merck India. The dye MB (C₁₆H₁₈ClN₃S.3H₂O, molecular weight-373.9) and Lead nitrate (M.W. 331.21) was obtained from RANKEM chemicals, New Delhi, India. All the chemicals used were analytical grade. The double distilled water was used throughout the investigation.

2.2. Preparation of PCFR composites:

Phenol and Con. Sulfuric acid (1:1) and 0.5 mg of Chitosan were mixed slowly with constant stirring in an ice bath. The mixture was then, heated to 70°C for three hours, cooled and kept overnight. The product was polymerized with formaldehyde solution (12 ml) in an ice bath, and then heated to 70°C for three hours and the product was cured, then ground washed with DD water, to remove the free acid. Then the sample was dried at 70°C for 16 h. Then the composite resin was sieved and preserved for characterization and further studies.

2.3. Adsorption Experiments

Batch mode adsorption studies were carried out by adding certain amount of adsorbent and 50ml of dye and 40ml of metal ion solutions of certain concentrations, dose, contact time and temperatures in a thermo stated water bath shaker with a shaking of 200rpm. These samples were withdrawn from the shaker at predetermined time intervals and solutions were separated from the adsorbent by centrifugation at 4000rpm for 5min. To determine the residual dye concentration, the absorbance of the supernatant solution was measured before and after treatment with double beam spectrophotometer (JASCO V530 Spectrophotometer). Lead ion concentration was measured using atomic absorption (Elico SL-173) spectrometry at wavelength of 283.3 nm, experiments were carried out twice and the concentrations given were average values. The initial dye and metal ion concentrations in the test solution and the contact time were changed to investigate their effect on the adsorption kinetics. The pH of the dye and metal ion solution was adjusted by using NaOH or HCl solution. The adsorption studies were carried out at different temperatures (308, 318 and 328K). This is used to determine the effect of temperature on the thermodynamic parameters.

The amount of adsorption in batch experiments and adsorption efficiency were calculated as follows:

$$q = (C_o - C_e) V / m \quad (1)$$

$$\text{Efficiency (\%)} = (C_o - C_e) / C_o \times 100 \quad (2)$$

Where, C_o is the initial concentration (mg/L)

C_e is the equilibrium concentration (mg/L)

V is the volume of solution (mL)

m is the mass of adsorbent (g)

q is the amount of adsorbed (mg/g)

2.4. Desorption experiments

It is known that regeneration of adsorbents is an important aspect of adsorption study. In order to determine the reusability of the PCFR, the adsorption-desorption process was repeated three times. 1.0g PCFR adsorbents loaded into 50 ppm of Pb(II) ion and MB respectively and added into 100mL of 1% (v/v) HNO₃/ 0.05m of Acetic acid solution for 3h at room temperature. The adsorption performance in each cycle was measured. The desorbed dye solution was separated by centrifugation and analyzed as before. The percentage of desorption was calculated. The desorption ratio (E) was calculated as follows:

$$E (\%) = C_d V_d / (C_o - C_e) \times 100 \quad (3)$$

Where E is the desorption ratio, C_d is the concentration of the solutes in the desorption solutions, V_d is the volume of the desorption solution and C_o , C_e and V are the same as defined in Eq. 1 & 2.

III. Results and Discussion

3.1. Effect of adsorbent activity

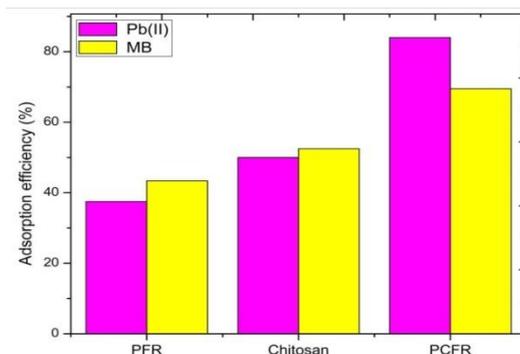


Fig. 1. Adsorbent activity of PFR, Chitosan and PCFR

The activity of adsorbent for the adsorption of Pb(II) ion and MB dye was studied with an initial concentration of 20 & 50 ppm, adsorbent dose of 0.2 g and contact time of 120 min and the results were displayed in Fig.1. Noticeably as shown in the fig.1, the order of adsorption activity for the removal of Pb(II)

ion and MB dye is PCFR > Chitosan > PFR. PCFR composite resin exhibits higher adsorption activity (84% & 69.5%) than Chitosan (50% & 52.5%) and PFR resin (37.5% & 43.4%) of Pb(II) and MB respectively. PCFR composite resin was high removal efficiency than chitosan and PFR resin due to high surface area and facile mass diffusion from the retained interconnected pore system could also be major factors in improving the adsorption potentials.

3.2. Characterization of the adsorbent

B.E.T:

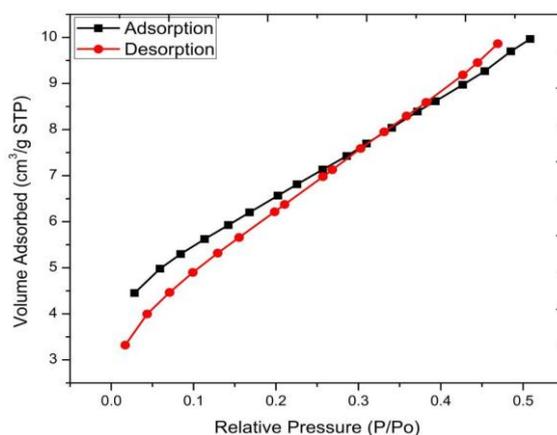


Fig. 2. Adsorption-desorption isotherms of nitrogen at 77 K on PCFR

The surface area of PCFR was determined by nitrogen sorption measurement. The surface area of PCFR was 26.03 m²/g. The average pore radius of PCFR was 48.79 nm and total pore volume was 0.12 cm³/g shown in Fig.2. The relative adsorption performance of different adsorbent is highly dependent on the internal pore structure of each material. With the increase of pore radius, more adsorbate is easier to be adsorbed. Therefore carbon activation offered some attractive advantages. It is not only able to increase the surface area and average pore radius but also reinforce the chemical strength of adsorbents in acidic medium.

FTIR:

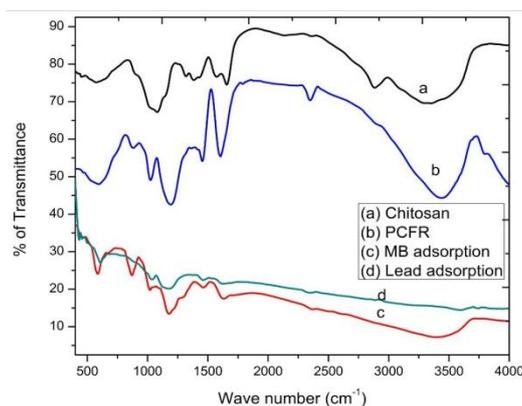


Fig. 3. FTIR spectra of: (a) Chitosan (b) PCFR (c) PCFR-MB (d) PCFR-Pb(II)

FTIR spectra of the Chitosan, PCFR, PCFR-Pb(II) and PCFR-MB were shown in Fig.3. The main bands observed in the IR spectra of Chitosan (Fig. 3a), were the axial stretching of –OH and C-H groups at 3350 and 2907 cm⁻¹ respectively, which appears superimposed to the N-H stretching band; C=O stretching band (amide I) at 1654.9 cm⁻¹, CH₃ symmetrical angular deformation at 1382.9 cm⁻¹ and C-N amino groups axial deformation 1319.3, besides the characteristic polysaccharide bands at 1080.1 cm⁻¹. Fig.3b, presented a strong absorption band at 1633.7 cm⁻¹ attributed to the C=N vibrations characteristic of azomethine [14] which is not observed in chitosan. The bands at 1469 and 881.4 cm⁻¹ were attributed to the C=C and C-H stretching in the aromatic ring, respectively. FTIR data showed that new peak observed at 2349.3 cm⁻¹ attributed to S-H stretching vibrations (Fig.3c). The peaks observed at 3797.8 and 3435.2 cm⁻¹ were assigned to O-H and N-H bands. It may due to MB adsorption onto PCFR.

FTIR data (Fig.3d), showed that the N-H bending vibration wave number at 1633.7 cm⁻¹ before lead adsorption were shifted to 1649 cm⁻¹ after lead adsorption, suggesting the attachment of lead to nitrogen atoms,

which reduced the vibration intensity of the N-H bond due to molecular weight becoming heavier after lead attachment. Another major change in the transmittance can also be observed at the wave number of 2912 cm^{-1} after lead adsorption. This band region may be assigned to both C-H and O-H stretching. As lead ion is unlikely to be attached to a carbon atom, the results may therefore suggest that oxygen atoms in the hydroxyls could also be involved in lead ion adsorption.

XRD:

The XRD patterns as shown in Fig.4 were performed to analyze the crystalline nature. The characteristic 20° - 30° peaks of Chitosan are discernible in carbon; these indicate that they are amorphous carbon.

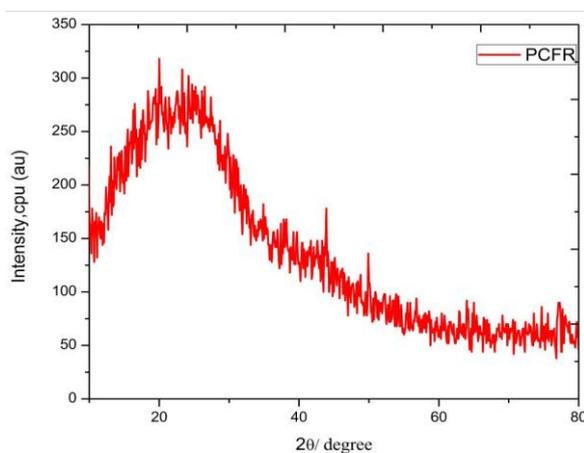


Fig. 4. XRD pattern of PCFR

SEM:

Fig.5, showed the SEMs of PCFR, PCFR-Pb(II) and PCFR-MB dye. However, the particles of PCFR (Fig.5a) are composed of evenly distributed particles. Clearly, there are particle fragments and irregularities structure on the surface. Such cracks and irregularities are beneficial for the metal and dye to diffuse to the inner adsorption sites located in the interior portion of the adsorbent [15]. Fig. 5b and 5c show micrographs of the PCFR surface after adsorbed Pb(II) ion and MB dye, which is covered with some small particulates on the surface, suggesting Pb(II) ion and MB dye have been adsorbed.

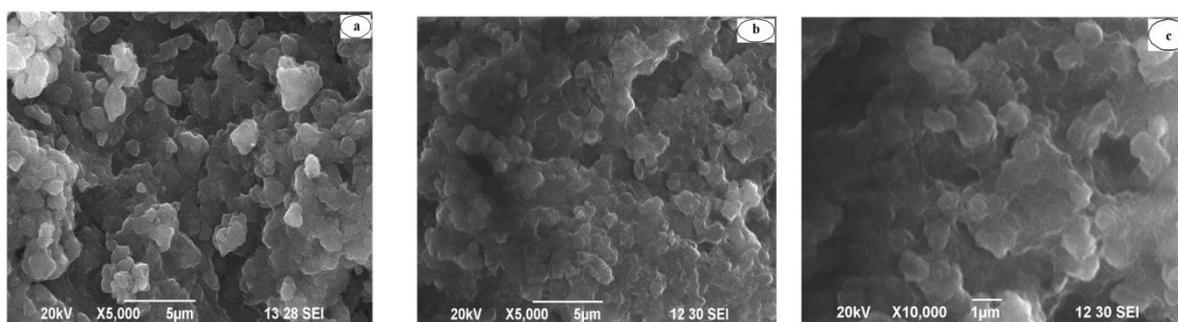


Fig. 5. The SEM images of (a) PCFR (b) PCFR-MB (c) PCFR-Pb(II)

EDX:

Further confirmation of the adsorption of Pb (II) ion and MB dye on PCFR composite was done by energy dispersive X-ray analysis (EDX). Fig.6a for the unloaded PCFR did not show any characteristic signal for metal ions, only shows that the three major constituents, i.e., C, O and S composition were 59.48%, 34.59%, and 5.93%, respectively. The EDS spectrum (Fig.6b) of after adsorption of Pb(II) ion presented a new appearing peak at 2.0 keV, which is associated to Pb element. This provided an evidence for Pb(II) ion adsorption onto PCFR surface. Fig.6c shows three components C, O and S values for the PCFR-MB adsorption composition were 73.18%, 25.11% and 1.71% respectively. To compare both the (Fig.6a and 6c) 'C' atomic percentage was increased, due to adsorption of MB dye onto PCFR.

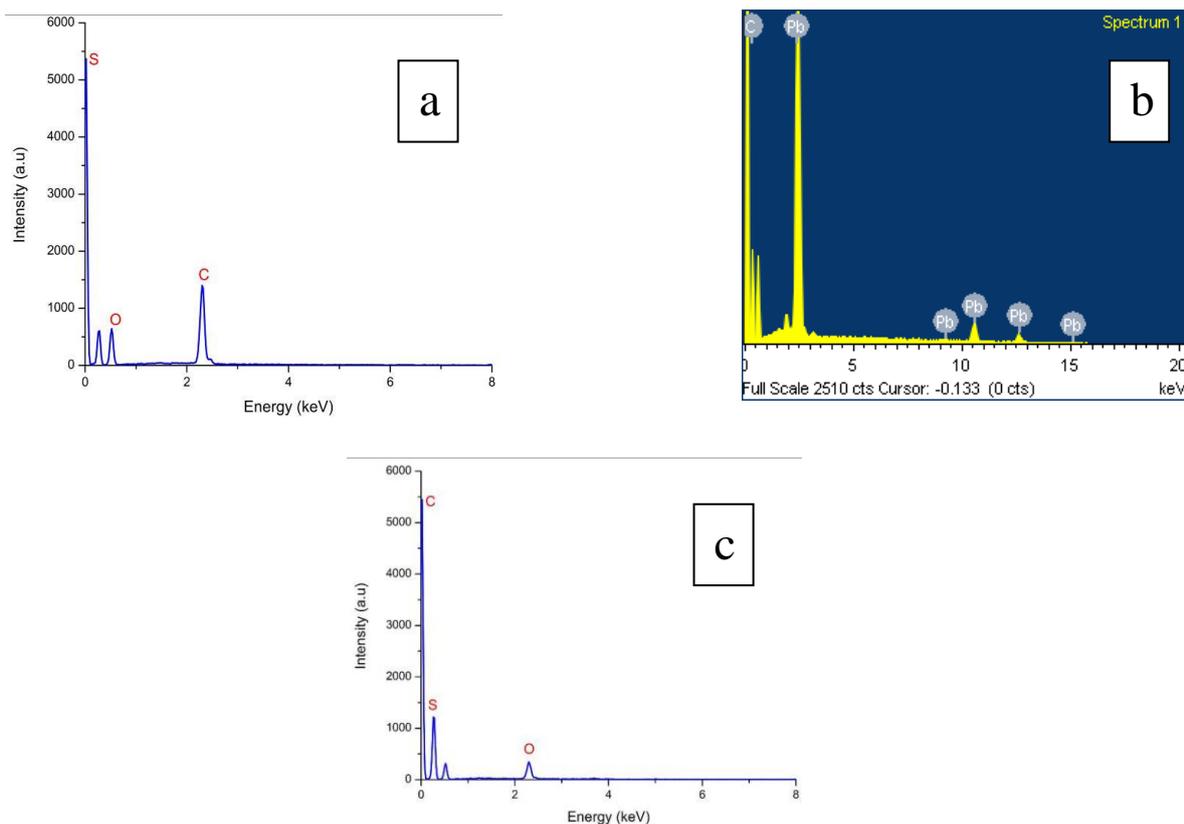


Fig. 6. Energy dispersive spectra of (a) PCFR (b) PCFR-Pb(II) (c) PCFR-MB

TGA:

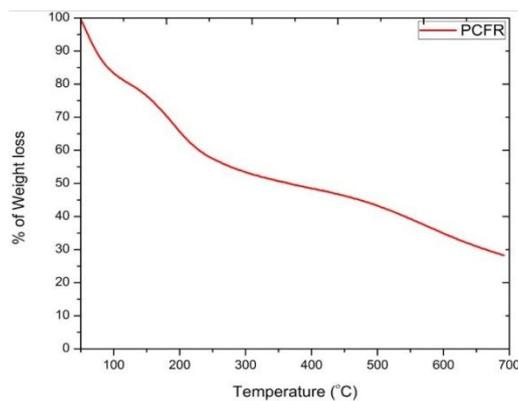


Fig. 7. TGA curve of PCFR

The TGA thermograms for the PCFR samples were shown in Fig.7. The thermo gravimetric profile revealed that the mass loss was occurred in three stages. The first stage at around 50-118 °C, with a mass loss of 18.92%, is related mainly to the loss of water physically adsorbed on the surface of the materials. The second stage showed that the degradation temperature for PCFR was 118-390 °C with a mass loss of 31.76%. The last weight loss was determined above 390-700 °C, which about 20.64%. Finally, no mass loss was detected when the temperature was increased to 700 °C. This result indicates the PCFR are stable at higher temperature. The char residue of PCFR content was 31%.

The characterization results confirmed that the formation of the adsorbent PCFR occurred successfully.

3.3. Effect of initial concentrations

In order to determine the optimum initial concentration of the target metal ion and dye, its value was varied in the range 20 – 60 mg/L and 50-120 mg/L for Pb(II) ion and MB dye respectively, while keeping the temperature, sorbent mass and the contact time constant. The effect of initial concentration on the removal of Pb(II) ion and MB dye by the adsorbent is indicated in Fig.8.

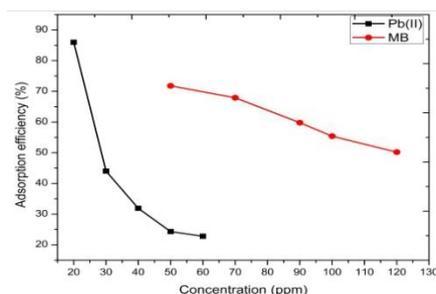


Fig.8. Effect of initial concentrations of Pb(II) and MB dye

It is evident from that percentage of Pb(II) ion and MB dye removal decreases with increase in concentrations, however actual amount of the Pb(II) ion and MB dye adsorbed is increased. This is due to increase in concentration, surface area, and active sites of the adsorbent were saturated and hence percentage removal decreases. In this study Pb(II) ion removal was higher than that of MB dye.

3.4. Effect of contact time

Adsorption was studied at various time intervals (30-240 min) and fixed concentration of Pb(II) ion was 20 ppm and 50ppm concentration of MB dye. The concentration of Pb(II) ion and MB dye was determined at the end of each time. The obtained equilibrium capacities (q_e) were then plotted against the equilibrium time (t) for kinetic modeling. All the results were presented in Fig.9. Adsorption increased rapidly with an increase in contact time from 30 to 240 min. A further increase in time had no effect on the adsorption. A maximum contact time of 180 and 120 min was therefore considered as optimum time for Pb(II) ion and MB dye respectively.

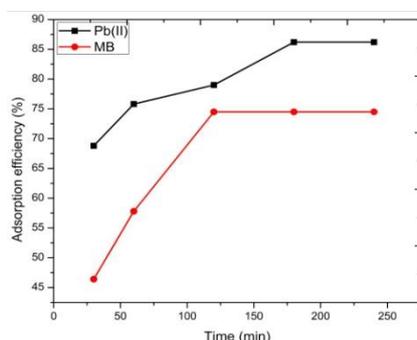


Fig.9. Effect of contact time

3.5. Effect of adsorbent mass:

The amount of adsorbent was optimized to obtain the optimal removal. Adsorption experiments were conducted using different amounts of PCFR, likewise 0.050- 0.250g and 0.010 - 0.070g of Pb(II) ion and MB respectively. The initial concentration of Pb(II) ion 20 ppm and MB concentration was 50ppm, at room temperature and fixed time. The results are presented in Fig.10.

The results showed that adsorption increased sharply for Pb(II) ion was 66.7 to 80.3% with an adsorbent amount of 0.050 - 0.200g and MB was 45.6 to 73.6% with an adsorbent amount of 0.010 - 0.070g. Thus, 0.150 and 0.050g was considered as the optimum adsorbent for the removal of Pb(II) ion and MB respectively.

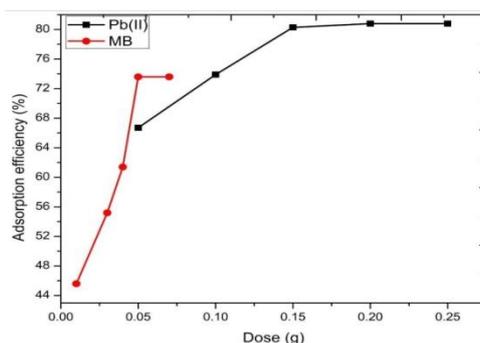


Fig.10. Effect of adsorbent dose

IV. Adsorption isotherms:

The adsorption equilibrium data were tested by five isotherm models, namely the Langmuir, Freundlich, Temkin, D-R and Jovanoic isotherm.

Langmuir isotherm [16], which assumes monolayer adsorption onto a homogeneous surface with a finite number of identical adsorption sites, can be represented in a linear form as follows:

$$\frac{C_e}{q_e} = \frac{1}{K_L \times q_m} + \frac{C_e}{q_m} \quad (4)$$

Where, q_m is the maximum adsorption capacity, K_L is the Langmuir bonding energy coefficient. The K_L and q_m can be calculated from the intercept and slope of the linear plot of C_e/q_e against C_e shown in Fig.11.

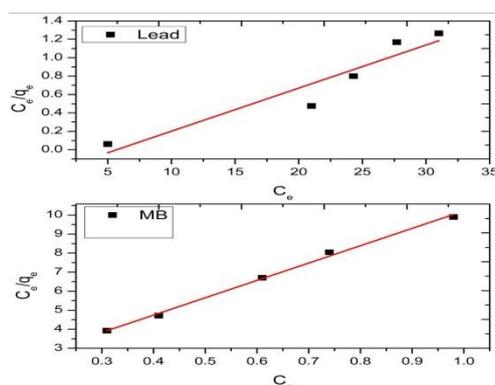


Fig.11. Langmuir isotherm plots for the adsorption of Pb(II) and MB onto PCFR

In order to determine if the adsorption process is favorable or unfavorable, a dimensionless constant separation factor or equilibrium parameter R_L is defined according to the following equation [17]:

$$R_L = 1 / (1 + K_L C_o) \quad (5)$$

Where, K_L is the Langmuir isotherm constant (L/mg) and C_o is the initial dye concentration (mg/L). The R_L value indicates the type of the isotherm to be either unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$), irreversible ($R_L = 0$). The R_L value of MB was higher than compare to that of Pb(II) ion. As it is clear from MB all R_L of values range between 0.915-0.858, indicating the favorable adsorption of MB onto PCFR.

Freundlich isotherm [18], which assumes adsorption onto a heterogeneous surface, can be represented in a linear form as follows:

$$\log q_e = \log K_F + 1/n \log C_e \quad (6)$$

Where, q_e is the amount of dye and metal ion adsorbed at equilibrium (in mg/g), and C_e is the MB and Pb(II) ion concentration in solution at equilibrium (in mg/L). K_F and n are Freundlich constants which indicate capacity and heterogeneity factor. The value of n ranged from 0 to 1, and n value closer to 1 indicates high surface heterogeneity. The K_F and n can be calculated from the intercept and slope of the linear plot of $\log q_e$ against $\log C_e$.

Temkin isotherm [19], which assumes that the heat of adsorption of all the molecules in the layer decreases linearly with coverage due to adsorbent-adsorbate interactions and characterized by a uniform distribution of binding energy, can be represented in a linear form as follows:

$$q_e = B_1 \ln K_T + B_1 \ln C_e \quad (7)$$

Where, B_1 and K_T are constants, representing adsorption capacity and retention intensity of adsorption. The B_1 and K_T can be calculated from the intercept and slope of the linear plot of q_e against $\ln C_e$.

In order to determine the type of adsorption, D-R isotherm has also been tested for the adsorption of both MB and Pb(II) ion onto PCFR. The D-R equation can be defined by the following equation [20].

$$\ln q_e = \ln q_m - \beta \epsilon^2 \quad (8)$$

Where, β a constant related to the adsorption energy (mol^2/kJ^2), q_m is a constant that indicates the sorption degree characterizing the sorbent (mg/g) and ϵ is the Polanyi potential shown in Eq. 8:

$$\epsilon = RT \ln (1 + 1/C_e) \quad (9)$$

Where, T is the absolute temperature (K) and R is the ideal gas constant ($R = 8.314 \text{ J/mol/K}$).

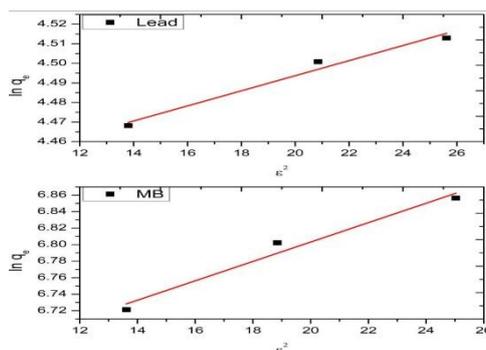


Fig.12. D-R isotherm plots for the adsorption of Pb(II) and MB onto PCFR

By plotting $\ln q_e$ versus ϵ^2 (Fig.12), it is possible to determine the value of β from the slope and the value of q_m from the intercept, which is $\ln q_m$.

The mean free energy E (kJ/mol) of sorption can be estimated by using β values as expressed in the following equation [21].

$$E = 1 / (2\beta)^{1/2} \quad (10)$$

The magnitude of E may characterize the type of the adsorption as chemical ion exchange ($E = 8-16$ kJ/mol), or physical adsorption ($E < 8$ kJ/mol). The mean free energy of adsorption for the present study was found to be Pb(II) ion has 12.9 and MB was 6.79 kJ/mol. This implies that, the adsorption of Pb(II) ion on PCFR may be considered as chemical adsorption process, the MB was physical adsorption process.

The Jovanoic isotherm [22], which is based on the same assumptions of the Langmuir isotherm, also considers the possibility of some mechanical contacts between the adsorbing and desorbing molecules on the homogeneous surface and can be represented in a linear form as follows:

$$\ln q_e = \ln q_m + K_J C_e \quad (11)$$

Where, q_m is the maximum amount adsorbed (in mg/g) and K_J (in L/mg) is the constant related to the energy of adsorption. The q_m and K_J can be calculated from the intercept and slope of the linear plot of $\ln q_e$ against C_e .

To understand the adsorption equilibrium behavior, five isotherms, namely Langmuir, Freundlich, Temkin, D-R and Jovanoic isotherm models were tested, and the Table.1 summarizes the isotherm parameter values. The best fitted models are selected on the basis of coefficient Langmuir isotherm and D-R isotherm model. The Langmuir isotherms were best fit model for the adsorption of MB, The maximum adsorption capacity of MB was 10.96 mg/g. The D-R isotherm model well described in both Pb(II) ion and MB onto PCFR. The maximum amount adsorbed was 260.6 and 369.8 mg/g for Pb(II) ion and MB respectively.

Table 1. Different adsorption isotherm model parameters for the adsorption of Pb(II) and MB on PCFR

Mathematical models	parameters	Pb(II) ion	MB
Langmuir isotherm	R^2	0.901	0.996
	K_L	1.723×10^{-3}	8.35×10^{-4}
	q_m (mg/g)	21.73	10.96
Freundlich isotherm	R^2	0.899	0.942
	K_F	331.1×10^3	787.0×10^4
	n	1.517	5.7142
Temkin isotherm	R^2	0.968	0.840
	B_1	32.3	0.101
	K_T	135.4	6.497
D-R isotherm	R^2	0.978	0.974
	β	0.003	0.011
	q_m (mg/g)	260.6×10^2	369.8×10^4
	E kJ/mol	12.9	6.74
Jovanoic isotherm	R^2	0.954	0.902
	K_J (L/mg)	0.050	0.296
	q_m (mg/g)	4.689	6.614

V. Kinetic Studies:

The applicability of the pseudo-first-order model, pseudo-second-order model and Intra particle diffusion model was investigated to identify the mechanism of Pb(II) ion and MB adsorption on PCFR as follows:

5.1 Pseudo-first-order mode:

The Lagergren pseudo-first-order model illustrated the adsorption kinetic data, which is the earliest known equation describing the adsorption rate based on the adsorption capacity. The integral form of the pseudo-first-order model is generally expressed as [23]

$$\ln (q_e - q_t) = \ln q_e - k_1 t \tag{12}$$

Where, k_1 (L/ min) and predicted q_e can be determined from the slope and intercept of the linear plot between $\ln (q_e - q_t)$ and t , respectively.

5.2 Pseudo-second-order model:

The adsorption kinetic may be described by the pseudo-second-order model. The differential equation is generally known and described as [24].

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{13}$$

Where, k_2 (g/mg/min) is the second-order rate constant of adsorption. The plot of t/q_t versus t shows a linear relationship. Values of k_2 and equilibrium adsorption capacity q_e were calculated from the intercept and slope of the plot shown in Fig.13.

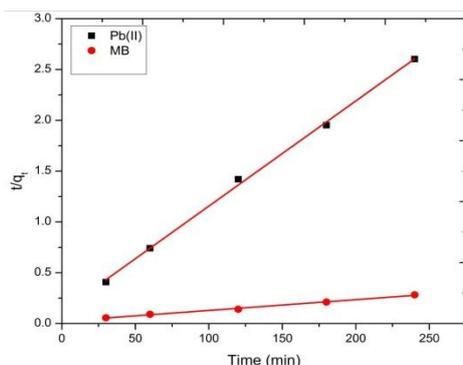


Fig. 13. Pseudo-second-order kinetic plots for adsorption of Pb(II) ion and MB onto PCFR

5.3 Intra-particle diffusion model:

The adsorption proceeds in several steps involving transport of solute molecules from the aqueous phase to the surface of the solid particles and then interior of the solid. According to [25], for most adsorption processes the amount of adsorption varies almost proportional with $t^{1/2}$, which can be expressed as

$$q_t = k_{id} t^{0.5} + C \tag{14}$$

Where, q_t is the adsorption capacity at time t , $t^{0.5}$ is the half life time in second and k_{id} (mg/g/min^{0.5}) is the rate constant of the intra-particle diffusion model and C (mg/g) reflects the boundary layer effect. The k_{id} and C can be determined from the slope and intercept of the linear plot of q_t against $t^{0.5}$.

Table 2. Kinetic parameters for the adsorption of Pb(II) ion and Methylene blue dye on PCFR

Mathematical models	parameters	Pb(II) ion	MB
First-order kinetics	R ²	0.735	0.246
	k ₁ (min ⁻¹)	0.007	0
	q _e (mg/g)	10.11	209.4
Second-order kinetics	R ²	0.998	0.996
	k ₂ g/mg/min	0.0833	0.0454
	q _e (mg/g)	100	1000
Intra-particle diffusion	R ²	0.946	0.835
	k _{id} g/mg/min ^{1/2}	1.885	32.99
	C (mg/g)	64.6	397.6

The pseudo-first-order, pseudo-second-order and intra-particle diffusion models were used to understand the kinetic nature of Pb(II) ion and MB onto PCFR adsorption system. All the values are presented in Table.2. Based on linear regression (R²) values, the kinetics of Pb(II) ion and MB adsorption onto the PCFR can be described well by second-order equation. The value of pseudo-second-order rate constant, k_2 , for Pb(II) ion was 0.0833 and MB was 0.0454 g/mg/min.

VI.

Effect of temperature and

thermodynamic data

The adsorption tests were performed by batch technique in single system at 308K, 318K and 328K respectively. For kinetic studies, a series of 250ml flask were used and each flask was filled with PCFR at mass

loadings 0.150g for Pb(II) ion solution and 0.050g for MB solution at 20ppm and 50ppm initial concentrations respectively. The percentage removal of Pb(II) ion and MB are presented in Fig.14.

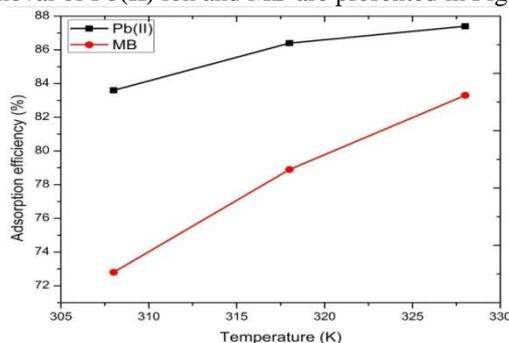


Fig. 14. Effect of temperature

The energy and entropy considerations are very important in order to understand the kinetics of adsorption. The amount of Pb(II) ion and MB adsorbed at equilibrium at different temperature has examined to obtain the thermodynamic parameters. The K_L value is used in the following equation to determine the change of Gibbs free energy of adsorption (ΔG°).

$$K_L = \frac{q_e}{C_e} \quad (15)$$

$$\Delta G^\circ = -RT \ln K_L \quad (16)$$

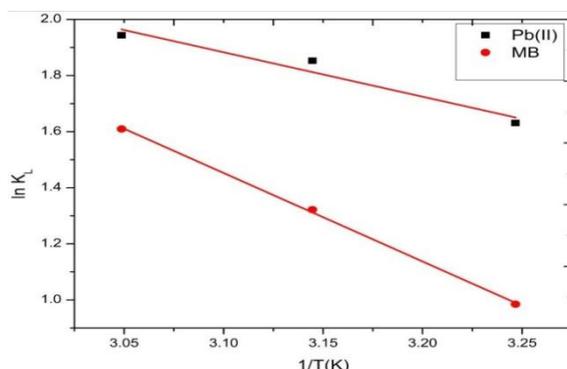


Fig. 15. van't Hoff plots of $\ln K_L$ versus $1/T$ for the adsorption of Pb(II) ion and MB onto PCFR

The change in enthalpy (ΔH°) and entropy (ΔS°) was determined from the slope and intercept of van't Hoff plot of $\ln K_L$ versus $1/T$ plot (Fig.5.15), according to the following equation:

$$\ln K_L = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (17)$$

Where, K_L is Langmuir constant. Where R is constant (8.314 J/mol K), T is the temperature (in K). The

Dyes	R^2	Thermodynamics parameters				
		ΔH° J/mol	ΔS° J/mol K	$-\Delta G^\circ$ (kJ/mol) $\times 10^2$		
Pb(II)	0.952	13.44	64.56	308K		
				318K		
				328K		
				66.88	74.90	79.72

the constant. the gas temperature estimated

thermodynamic parameters are presented in Table 3.

MB	1	24.84	146.4	202.9	217.5	232.2
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Table.3. Thermodynamic parameters for the adsorption of Pb(II) ions and MB dye on PCFR

The correlation coefficient for the linear plot for Pb(II) ion and MB was $R^2 = 0.952$ and $R^2 = 1$ respectively. The negative values of ΔG° at all temperatures indicate the spontaneous nature of the adsorption of Pb(II) ion and MB on PCFR. The ΔG° was negative and increased towards negative side with rise in temperature, indicating the adsorption process to be spontaneous in nature without any induction period and more favorable at higher temperature.

The standard enthalpy and entropy changes of adsorption determined from the Eq. (17) were 13.14 kJ/mol and 64.56 J/mol/K for Pb(II) ion, 24.84 kJ/mol and 146.49 J/mol/K for MB, respectively. The positive value of ΔH° suggests the endothermic nature of adsorption. The positive value of ΔS° confirmed the increased randomness at the solid-solute interface during adsorption process, which suggests that Pb(II) ion and MB replace some water molecules from the solution previously adsorbed on the surface of adsorbent. These displaced molecules gain more translation entropy than lost by the adsorbate ions, thus allowing the prevalence of randomness in the system [26].

VII. Desorption studies:

An important characteristic of adsorbents is the desorption efficiency. The results show that the amounts of Pb(II) ion and MB adsorbed on PCFR from three repeated adsorption-desorption cycles. It is found that the adsorbents can be used repeatedly without changing significantly their adsorption capacities with high desorption percentages 98% for Pb (II) ion and MB studied here.

VIII. Conclusion:

This study showed the characterization of PCFR and Pb (II) ion and MB adsorption behavior by PCFR. The PCFR was mainly composed of hydroxyl, esters and secondary cyclic alcohols on the surface of PCFR. The equilibrium adsorption can be fitted by Langmuir for MB and D-R isotherm for both Pb(II) ion and MB adsorption. The kinetic process can be predicted by pseudo-second-order model. The adsorption may be controlled by external mass transfer followed by intra-particle diffusion mass transfer. The thermodynamics parameters indicated spontaneous and endothermic process. The treated PCFR are much effective adsorption for Pb(II) ion but less adsorption in MB.

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