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ADSORPTIVE REMEDIATION OF CHROMIUM (VI) AND COPPER (II) IONS ONTO MICROWAVE ASSISTED PHOSPHORIC ACID ACTIVATED CARBON PREPARED FROM AERIAL ROOT OF *FICUS BENGHALENSIS L*

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ABSTRACT

The research was conducted with an aim to assess the efficiency of phosphoric acid activated carbon prepared from Aerial root of *Ficus Benghalensis L* as an adsorbent in removing Cr(VI) and Cu(II). The effects of different system variables, *viz*, adsorbent dosage, initial metal ion concentration, pH and contact time were studied. The results showed that as the amount of the adsorbent was increased, the percentage of metal ion removal increased accordingly. Optimum pH value for metal adsorption is determined as 2.0 for Cr(VI) and 4.0 for Cu(II) ions. Maximum metal is sequestered in 180 min for both ions after the beginning of every experiment. The adsorption of metal ions followed a Pseudo second order rate equation. Freundlich adsorption model is suitable for describing the sorption of Cr(VI) and Cu(II) on PAC. Furthermore, the natural organic matter is characterized by FTIR specra. The removal efficiency of PAC from Aerial root of *Ficus benghalensis L* is Cr(VI) > Cu(II).

Keywords: Cr (VI), Cu (II), Isotherms, Kinetics, FTIR.

1. INTRODUCTION

The water pollution due to contamination by heavy metal ions is of high concern worldwide. The main sources of heavy metals are mining, metallurgical, chemical manufacturing, tannery, battery manufacturing Industries, fossil fuel, chemical industry etc [1]. The presence of copper and chromium metal ions in water bodies, their bioaccumulation, potential activity and adverse health effects were a matter of serious concern for the last few decades [2, 3]. Heavy metals removal from aqueous solution has been commonly carried out by process, chemical precipitation, several solvent extraction, ion exchange, reverse osmosis or adsorption [4, 5]. Chemical precipitation in particular, is the most prevalent method but not suitable for removing low concentration of heavy metal ions. Adsorption process are promising and widely used method to remove heavy metal ions due to its high efficiency for trace ions, easy handling, economical effectiveness and availability of various adsorbents [6-8]. Nowadays, research has been focused on the production of activated carbons from cheaper, abundantly available, and renewable precursors.

The biological materials (fruit stone and shells, agricultural waste and marine algal biomass, etc.) have been considered as potential precursors for activated carbons because of their abundance and renewable nature [9].

The bio-based porous carbon prepared from Aerial root of *Ficus benghalensis L*. Microwave assisted phosphoric acid activation of carbon has been carried out for effective adsorption of heavy metal ions. Microwave heating has been widely used in the activation of carbon. It is based on dielectric heating in which energy is absorbed by ions or molecules that are either induced or permanent dipoles. Unlike conventional heating, the energy conversion occurs by two mechanisms: ion conduction and dipole rotation inside particles [10, 11]. So, the treatment time can be appreciably reduced as a result of microwave heating. Generally, H_3PO_4 acts as a dehydrating catalyst, which can promote decomposition of the cellulosic precursor at a lower heat treatment temperature [12].

The aim of this study is to assess the evaluation of viability of microwave radiations for the preparation of

activated carbon from Aerial root of Indian banyan tree via H_3PO_4 activation. The adsorption capacity of the activated carbon was attempted for Cr(VI) and Cu(II) removal from the aqueous phase. The effect of various reaction parameters such as solution pH, metal ion concentration, contact time, adsorbent dose were investigated. Moreover, adsorption equilibrium isotherms and kinetics studies were also outlined.

2. MATERIAL AND METHODS

2.1. Preparation of adsorbents

The aerial root of *Ficus benghalensis.L* were cut into small pieces and powdered in a pulveriser 20 g of the powdered aerial root was mixed with 75 mL of H_3PO_4 solution of desired concentration (20, 40 and 60%). The slurry was kept at room temperature for 24 hours and then subjected to microwave heating of pre-determined duration (8, 10 and 12 minutes). Thus the carbonized samples were washed with 0.5 M HCl followed with hot distilled water and cold distilled water until the pH of the washings reach 7. Afterwards, the carbon was designated as phosphoric acid activated carbon (PAC) [13, 14].

2.2. Adsorbate Solutions

The stock solution (1000mg/L) of metal ions was prepared by dissolving their corresponding salts $\{\text{CuSO}_4.5\text{H}_2\text{O}, \text{K}_2\text{Cr}_2\text{O}_7\}$ in distilled water. The solution was further diluted to the required concentrations before use.

Table 1: Weight of the salts taken for thepreparation of stock solutions

Metal ion	Metal salt	Weight (g)/liter
Cr(VI)	$K_2Cr_2O_7$	2.828 g
Cu(II)	CuSO ₄ .5H ₂ O	3.9294 g

2.3. Adsorption experiments

The effect of parameters such as adsorbent dose, contact time, initial concentration and pH of the solution was studied by batch mode techniques. Pre determined dose of the adsorbent was taken in 250mL iodine flask and 50mL and predetermined concentration of Cr(VI) and Cu(II) solutions was poured into the flask. The content of the flask was agitated using rotary shaker with 180rpm for pre-determined duration. Then the aliquot was centrifuged. Concentration of the centrifugate was measured after proper dilution using Systronics Double Beam UV-visible spectrophotometer: 2202. The effect of pH was calculated via bringing the preferred pH of the solutions by adding con. 0.1 N HCl / 0.1NNaOH solution [15].

3. RESULTS AND DISCUSSION

3.1. Effect of Adsorbent dosage

The adsorption studies of Cr(VI) and Cu(II) ions onto PAC was studied by varying the quantity of adsorbent from 10 to 100 mg. The influence of adsorbent dosage in removal percentage of Cr(VI) and Cu(II) ions is shown in fig 1. The adsorption of Cr(VI) increased from 39 to 99 % and Cu(II) increased from 50 to 100% respectively by increasing the dosage from 10 to 100 mg/mL under equilibrium conditions. The results showed that the adsorption increased with the increase in the dose of PAC. The increase in the removal percentage is due to the increase in active sites on the adsorbent and thus making easier penetration of the metal ions in to the sorption sites.



Fig. 1: Effect of Dose on Cr(VI),Cu(II) ions onto PAC

3.2. Effect of contact time

The results of the effect of contact time on the adsorption of Cr(VI) and Cu(II) ions onto PAC are shown in fig 2. It was revealed that the adsorption of Cr(VI) ions onto the adsorbent is relatively faster. In all subsequent experiments, the equilibrium time was maintained at 80 min for Cr(VI) and Cu(II). The fast metal ions uptakes by the adsorbent was due toit's highly porous and mesh like structure which provided ready to access and a large surface area for the adsorption of the metal ions onto the binding sites [12].

3.3. Effect of initial metal ions concentration

The effect of initial metal ions concentration onto PAC was shown in fig. 3. Adsorption experiments were carried out with varying initial metal ion concentrations from 5 to 15 mg/L for Cr(VI) and 10 to 30 mg/L for Cu(II) using 20 mg/50 mL activated carbon. The removal percentage decreased as the initial concentration increased because there is a lack of adsorption sites while

increasing the concentration of metal ion. The amount of metal ions adsorbed on PAC was found to increase from 3.55 to 10.30 for Cr(VI) and from 6.90 to 20.80 for Cu(II) ions at the temperature (305K,310K,315K). The increase in uptake capacity of the adsorbent might be due to the fact that the high metal ion concentration provides higher driving force for the transfer process to overcome the mass transfer resistance [16, 17].



Fig. 2: Effect of Contact time on Cr(VI), Cu(II) onto PAC



Fig. 3: Effect of initial concentration on Cr(VI),Cu(II) onto PAC

3.4. Effect of pH

pH of the solution is the most important parameter affecting the metal ion adsorption. The effect of pH on metal ion adsorption onto PAC is shown in fig. 4. The removal of Cu(II) ion increases with increase in pH, attains maximum adsorption at pH 4 and decreases. This is because of generation of negative charged metal ions when dissolved in water at low pH, the positive charge accumulates on the surface of the adsorbent and facilitates more adsorption of metal ions. After pH 4, both adsorption and precipitation would have been occurred. The formed precipitate blocks the adsorption sites and so adsorption decreased.

Moreover at low pH, the concentration of OH- ions was meagred [18] in Cr(VI) ions onto PAC increased significantly with a decrease of pH value and the maximum removal was attained at pH 2.0. Among the active forms such as $HCrO_4$ -, Cr_2O_2 -, $HCrO_4$ - ion is stable at only lower pH range which leads to high removal of Chromium. The concentration of this form decreases with the increase of pH [19]. At low pH hydrogen ion competing with the positively charged metal ions on the active sites of the adsorbent and hence the surface charge of the adsorbent will be positive so maximum adsorption is favourable. While increasing pH the competition will be lesser extent, the same charge repulsion occurred and adsorption decreased.



Fig. 4: Effect of pH on Cr(VI),Cu(II) onto PAC

3.5. Isotherm studies

The adsorption isotherm reveal the specific relation between the concentration of the adsorbate and its adsorption degree onto adsorbent surface at a constant temperature. To quantify the adsorption capacity of PAC for the removal of Cr(VI) and Cu(II) ions from aqueous solution, the Langmuir, Freundlich isotherm models were used.

3.5.1. Langmuir isotherm

This isotherm is founded on the following expectations, such as limited absorption for monolayer coverage, that all surface bases are the same site with one type of adsorbate and that a molecule is capable of absorbing on a assumed site independently of its neighbouring sites. This equation is often written in linear form as

$$C_e / Q_e = 1 / Q_0 b + C_e / Q_0 \dots 3.7$$

Qe is the solvent adsorbate in a unit weight of the adsorbent (mg/g), the equipoise attention of the solute in total solute (mg/L), Q_0 is the maximum monolayer absorption capacity or concentration (mg/g) and b is the absorption energy is the mutual of the concentration reaching half the concentration of the adsorbent. The linear form of this equation is often preferred because of its ease and suitability [20].

The essential characteristics of Langmuir isotherm can be described by a separation factor, R_L , which is defined by the following equation

 $R_L = 1 / (1 + bC_0) \dots 3.2$

3.5.2. Fredunlich isotherm

The Freundlich model designates sorption only within the restricted range. It is accomplished of recitation the sorption of organic and inorganic complexes in a variability of sorbents [21]. This equation has the following form:

 $\log q_e = \log K_f + 1/n \log C_e \dots 3.3$

where qe is the quantity of adsorbate adsorbed (mg / g) in equilibrium, Ce is the symmetry attention of adsorbate in solution (mg / L), and K_f and n are constants covering all the influences that distress the absorption capacity and intensity of absorption, respectively [21].

3.6. Kinetic study

3.6.1. Pseudo first order kinetics

The linearized form of the pseudo-first order equation of Lagergren is generally expressed as follows:

 $\label{eq:qe} \begin{array}{l} \log{(q_e - q_t)} = \log{q_e} - \frac{k_1}{2.303} \times t.....3.4 \\ \text{where, } q_e \text{ and } q_t \text{ are the adsorption capacity at equilibrium} \\ \text{and at timet respectively (mg/g). } k_1 \text{ is the rate constant} \\ \text{of pseudo first-order adsorption. The plot of } \log{(q_e - q_t)} \\ \text{versus t should give a linear relationship; } k_1 \text{ and } q_e \text{ can be} \\ \text{calculated from the slope and intercept of the plot,} \\ \text{respectively [22].} \end{array}$



Fig. 5: Langmuir isotherm on Cr (VI),Cu(II) onto PAC



Fig. 6: Freundlich isotherm on Cr(VI), Cu(II) onto PAC

	Table 2: Results o	f Langmuir Freundlic	h isotherm plots for t	he adsorption of Cr	[.] (VI), Cu(II)onto PA(
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Isothorms	Paramotors	Cr(VI)			Cu(II)		
isotherms	rarameters -	305 K	310 K	315 K	305 K	310 K	315 K
	\mathbf{q}_0	25.000	25.510	26.316	41.667	47.619	52.632
Langmuir	b	0.107	0.129	0.149	0.048	0.065	0.091
	R^2	0.992	0.986	0.985	0.992	0.98	0.982
	C_{i}	5 mg/L	10 mg/L	15 mg/L	10 mg/L	20 mg/L	30 mg/L
		0.6514	0.4837	0.3844	0.6756	0.5077	0.4074
	R _L	0.6079	0.4366	0.3406	0.6060	0.4354	0.3396
		0.5730	0.4016	0.3091	0.5235	0.3539	0.2675
	n	1.3193	1.3550	1.4184	1.3106	1.4663	1.6502
Freundlich	$ m K_{f}$	2.6853	2.9992	3.3884	2.9174	4.1115	5.3456
	R^2	0.999	0.999	0.999	0.9990	0.996	0.999

3.6.2. Pseudo second order kinetics

The pseudo second order kinetic model (Ho equation) is represented by the following linear equation [23]:

$$/q_{t} = 1/k_{2}.q_{e}^{2} + 1/q_{e}t.....3.5$$

where, q_e and q_t are the adsorption capacity at equilibrium and at time t respectively (mg/g).

The initial adsorption rate, h (mg/(g min)), as t \rightarrow 0 can

be defined as

The Plot is drawn between of t/q_t and t. Theoretical adsorption capacity (q_e) , and the second-order rate constants k_2 (g/(mg min)) can be determined experimentally from the slope and intercept of plots.

3.6.3. Test for kinetics models

Best fitting kinetic model for a system can be determined by using the statistical tool percentage of sum of error squares (SSE) [24]. The sum of error squares is given as follows;

SSE $(\%) = \sqrt{\sum [(q_e)_{exp} - (q_e)_{cal}]^2} / N..... 3.8$

Where, N is the number of data points, (q_e) expise the experimental q_e and (q_e) calis the calculated q_e .

The parameters generated from the plots of pseudo first and second order kinetic models for the adsorption of Cr(VI) and Cu(II) on PAC are tabulated in table 3. The values of the parameters as presented in table 3 show clearly that pseudo second order kinetic model described well the adsorption process for both Cr(VI) and Cu(II) with high regression coefficient (R2) values. This suggest that adsorption of Cr(VI) and Cu(II) ions onto PAC was based on chemical reaction between the metals and active site of the adsorbent [25,26].

3.7. Fourier transformer infrared spectroscopy (FTIR)

The functional groups responsible for adsorption of Cr(VI) and Cu(II) ions on PAC were investigated by FTIR analysis shown in fig. 7. Results from FTIR analysis for PAC shows the presence of -OH, C-H, N-H, C-O,

C=O, and C=C functional groups .All the bonds are in stretch mode. After adsorption of Cr(VI) and Cu(II), slight changes were observed in some frequencies. The changes in adsorption magnitude and shifts were attributed to adsorption of metal to the functional groups [27, 28]. This adsorption includes the substitution of hydrogen atoms by metals on the surface of PAC is either through complexation or physical by weak electrostatic interaction or weak vanderwall's force [29]. The broad and intense peak at the ranging from 3200-3900 cm⁻¹ is assigned to the stretching of -OH group due to inter and intra molecular hydrogen bonding of polymeric compounds [30]. The clear band at 2924 cm⁻¹ indicates symmetric or asymmetric C-H stretching vibration of aliphatic acids. The existence of peaks at range between 2300 and 2100 cm⁻¹ infers the presence of $C \equiv C$ Stretching [31]. The peaks at 1700 -1600 cm⁻¹ may be attributed to C=C, C=O and N-H stretching vibrations. Moreover, the band at 1100cm⁻¹ to 1000cm can be connected to the existence of stretching vibrations of C-O of alcohol groups and carboxylic acids. The Peaks at the range 950-750cm⁻¹ indicates that the unsaturated group present in PAC might have involved in the bond formation with metal [32].

Table 3: Pseudo-first-order and pseudo-second-order models for the adsorption of Cr(VI) and Cu(II) ions onto PAC

Model / Parameters		Cr(VI)			Cu(II)	
Pseudo first order	5 mg/L	10 mg/L	15 mg/L	10 mg/L	20 mg/L	30 mg/L
$K_1(\min^{-1})$	0.0484	0.0461	0.0484	0.0576	0.0461	0.0484
Qe(mg/g)	2.1330	3.9446	6.0117	4.5604	7.9433	11.9674
\mathbf{R}^2	0.988	0.989	0.994	0.991	0.990	0.994
Pseudo second order	5 mg/L	10 mg/L	15 mg/L	10 mg/L	20 mg/L	30 mg/L
$K_2(g mg^{-1}min^{-1})$	0.0589	0.0289	0.0195	0.0327	0.0138	0.0095
Qe(mg/g)	3.7037	6.9930	10.1010	7.1942	13.6986	19.6078
$\mathbf{R}^{\mathcal{I}}$	0.998	0.997	0.997	0.998	0.997	0.997



Fig. 7: Lagergren plot for Cr(VI), Cu(II) ions onto PAC



Fig. 8: HO plot for Cr(VI), Cu(II) ions onto PAC



Fig. 9: FTIR spectra of PAC (a) unloaded PAC (b) Cr(VI) loaded (c) Cu(II) loaded

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Peak Position of PAC	Cr(VI) PAC	Cu(II) PAC	Possible Functional group
3865	3888	3838	-OH Stretching
3739	3796	3789	-OH Stretching
3425	3495	3475	-OH Stretching
2844	2859	2935	C-H Stretching
2324	2385	2154	$C \equiv C$ Stretching
1693	1905	1700	C = C Stretching
1609	1582	1600	N- O Stretching
1125	1029	1191	C- O Stretching

 Table 4: FTIR spectra of PAC (a) unloaded PAC (b) Cr(VI) loaded (c) Cu(II) loaded

4. CONCLUSION

In the present study microwave assisted phosphoric acid activated carbon as an adsorbent was prepared from the aerial root of Ficus benghalensis. L and investigated its potential for the removal of Cr(VI) and Cu(II) ions from aqueous solution. Batch experiments were carried out using various parameters. The extent of adsorption was found to be proportional to the time of contact and adsorbent dosage. The equilibrium time for the adsorption of Cr(VI) and Cu(II) ions onto adsorbent (PAC) was 80 minutes. The percentage of removal for a given adsorbent dose, decreased with an increase in initial metal ion concentration and increased with increase in temperature. The quantity adsorbed for a given adsorbent dose, increased with an increase in initial metal ion concentration. The maximum removal of the metal ions was observed at the pH 2.0 for Cr(VI) and 4.0 for Cu(II). The adsorption capacity and other parameters were evaluated using Langmuir and Freundlich isotherm models. The equilibrium data were found to be well represented by Freundlich isotherm which shows that the surface is heterogeneous in nature. The kinetic studies indicated that equilibrium in the adsorption of Cr(VI), and Cu(II) ions on PAC followed pseudo-second order model. The FT-IR spectrum of PAC unloaded and loaded adsorption of Cr(VI), and Cu(II) ions indicated that the adsorption were physisorption. Taking into consideration of the above results, it can be concluded that the PAC is a suitable adsorbent for the removal of Cr(VI) and Cu(II) ions from aqueous solution in terms of low cost, natural and abundant availability.

Conflict of Interest

None declared

5. REFERENCES

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