

**A STUDY ON THE REMOVAL OF HEAVY METAL IONS FROM
AQUEOUS SOLUTION USING ACTIVATED CARBON PREPARED
FROM PONGAMIA PINNATA (L) PIERRE**

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Abstract:

Activating carbon converted to from the leaf Pongamia pinnata under the process in order to remove the heavy metals ions from the aqueous using kinetic water treatment method. A study made regarding the influence initial concentration adsorbent dose contact time and temperatures during the process. A pseudo second order kinetic appears in the adsorption chosen and adsorbent examined in FT-IR studies, Powder X-Ray Diffraction and the scanning electron micrograph images shown what it reacts.

Keywords: Adsorption, Kinetics, FT-IR, PXRD, SEM and Pongamia pinnata

INTRODUCTION

As one of the most common heavy metal ions, too much Cu²⁺ in the human body will cause gastrointestinal problems, liver and kidney damage, nausea, hair loss, severe headache and even death. (Rahman MS et al., 2009) Therefore, how to remove organic dyes and heavy metal ions in wastewater has become a hot topic in environmental protection. There are many removal methods, such as adsorption method, (Tang WW, et al., 2012) ion exchange method (Sapari N, et al., 1996) and chemical precipitation method. (Chen QY, et al., 2009) Among these methods, the adsorption method is widely used because of its high adsorption efficiency, simple operation and recoverability. (Asuha S, et al., 2010)

Types of contaminants

Biological Contaminants: These include organisms living in water, such as, parasites, bacteria, protozoa and viruses,

Chemical Contaminants: These include pesticides, salts, toxins, bleach, metals and so on. Chemical contaminants can be either manmade or they can occur naturally. This kind of water contaminated by chemicals is extremely hazardous to our health.

Physical Contaminants: The contaminant which alters the physical properties of water are called Physical Contaminants. Sediment and other organic matter are considered as Physical Contaminants. This kind of water contaminated water can be visually identified.

Radiological Contaminants: Unstable radioactive chemical elements such as uranium, plutonium, or cesium can cause incredibly hazardous to all living organism.

1.2 Heavy Metals

Chromium, copper, cobalt, iron, magnesium, manganese, molybdenum, nickel, selenium zinc, arsenic, mercury, and lead are examples for heavy metals. Few heavy metals are important for physiology and few are toxic taken in very small amount.

Exposure to heavy metals: Heavy metal pollution is mostly found in areas where smelters, mines, metal processing refineries, paper and wood preservation.

Toxicity of heavy metals: Toxicity by each heavy metal depends on method of exposure, dosage, gender, age and genetics. Tissue damage is the adverse effects.

Chronic degenerative problems are due to heavy metal exposure and the symptoms are mental disorders, gastro-intestinal disorders, pain in muscle and joints, chronic fatigue, vision problems, and susceptibility to fungal infections.

Alzheimer's, Parkinson's, muscular dystrophy, and multiple sclerosis are all due to the above said effect and (<https://www.hydroviv.com/blogs/water-smarts/heavy-metal-toxicity>).

Chromium (Cr): It is used in steelmanufacture, paints, electric cell, photography, rubber goods, and matches. Hexavalent chromium (greater than 70 mg) is very toxic. It causes anuria, cancer, gastrointestinal ulceration, nephritis and damage the central nervous system.

Nickel (Ni): Higher amount (more than 30 mg) may change the muscle, lung, brain, kidney and liver, and also cancer. Sometimes it is responsible for tumor, paralysis, and even death.

Silver (Ag): 100 mg and above in human body can cause changes in gastroenteritis, blood cells, diarrhea, and decrease the blood pressure

Gold (Au): Soluble gold compounds in man causes fever, violent diarrhea and gastritis.

Zinc (Zn): Zinc more than 165 mg in human body cause renal damage, vomiting, and cramps.

Cadmium (Cd): Cadmium is toxic to all animals. Its toxicity causes diarrhea, vomiting, abdominal pains, , loss of consciousness, bone deformation, growth retardation, impaired kidney functioning and reproductive function, tumor formation, hypertension and teratogenic effects.

Mercury (Hg):Its toxicity may cause abdominal pain, headache, diarrhea, hemolysis, and tremors. Hg vapor causes breathing problem, acute tightness and pain.

Lead (Pb): About 800 mg of lead is dangerous. Mild anemia, vomiting, convulsion, brain damage, loss of appetite, uncoordinated body movements, and stupor.

Manganese (Mn): When its concentration exceeds 100 ppm, causes fever, growth retardation, muscular fatigue, sexual impotence, and eye blindness.

MATERIALS AND METHODS

Preparation of Activated carbon

Activated carbon was prepared from the leaves of *Pongamia pinnata* by sulfuric acid treatment. The leaves of *Pongamia pinnata* were cut into smaller pieces and soaked in concentrated H₂SO₄ with 1:1 ratio (W/V) for 48 hours and activated at 433 K temperature for 6 hours. The activated carbon was washed several times with distilled water until the pH of the water used for washing become neutral. The carbon obtained was dried at 383 K temperature for nearly 2 hours to remove the moisture. The above prepared carbon was designated as *Pongamia pinnata* leaves carbon hereafter referred to as PLC and it was kept in a desiccator (Stephen Inbaraj et al., 2006)

Determination of Characteristics of activated carbon

(ISI,Method, 1989)

Determination of pH_{zpc}.

The pH at the zero point charge (pH_{zpc}) of PLC was measured using the pH drift method (Lopez-Ramon et al., 1999). For this, first the pH of a solution of 0.01 M NaCl was adjusted between 2 and 12 by adding either HCl or NaOH solutions as needed. The dissolved carbon dioxide in the solution was removed by bubbling nitrogen gas through it till the pH stabilized. To

50 mL of this solution, 0.15 g of PLC was added. After the pH had stabilized (typically after 24 h), the final pH was recorded. A graph was drawn between initial pH and final pH. The pH_{zpc} is the point where the curve pH (final) vs pH (initial) intersects the straight line connecting the points showing equal pH values in “x” axis and ”y” axis .(Lopez-Ramon et al., 1999; Faria et al., 2004).

Bulk density: A 100 mL graduated cylinder was weighed accurately. For the determination of bulk density, the PLC was filled in the cylinder using a trip balance. The carbon was filled in 50 mL mark. It was weighed accurately. The bulk density was calculated by dividing by 50.

Surface area: A SarloErbaSorptomatic – 1800 was used and the surface area of the adsorbents determined at liquid nitrogen temperature by direct reading. The measurement was done assuming that the adsorbed nitrogen forms a mono layer and possesses a molecular cross sectional area of 16 \AA^2

Moisture content: 10g of the sample was weighed and heated at a temperature of $378 \pm 5 \text{ K}$ for about 4 hours. The dish was covered, cooled in a desiccator, and weighed.

$$\% \text{ of Moisture content} = \frac{(M - X) \times 100}{M}$$

where, M = mass in grams of the material taken for test

X = mass in grams of the material after drying

Fixed Carbon Content

Fixed carbon is a calculated value and it is obtained by subtracting the summation of percentage of moisture content, ash content, and volatile matter content from 100.

Fixed carbon (%) = $100 - (\text{moisture, \%} + \text{ash, \%} + \text{volatile matter, \%})$.

Loss on ignition: Each adsorbent at 1 g was taken in pre-weighed silica crucibles ignited at 1273 K for 4 hours. Then it was cooled in a desiccator for 1 hour. The final weight was measured. The weight loss was calculated as loss on ignition.

Water-Soluble matter: Ten grams of the PLC of known moisture content was weighed accurately and transferred into a beaker (1 L capacity). Distilled water, 300 mL, was added to the sample and heated to boiling for 5 minutes. The boiled mixture was filtered This procedure was repeated four times. Then the filtrate was concentrated to 100 mL. 50 mL of the concentrate was evaporated to dryness. The residue was finally dried at $378 \pm 5\text{K}$.

$$\% \text{ of Water soluble matter} = \frac{M \times 100 \times 2}{M1 (100 X) / 100}$$

where, M = mass of the residue in grams

M_1 = mass of the material in grams taken for test

X = % of moisture content

Acid-soluble matter: The carbon under study (10 g) was weighed accurately and transferred into a beaker (1 L capacity). To this, 300 mL of 0.25 N HCl was added and heated to boiling with continuous stirring. Stirring was continued for about 5 minutes, after the flame was removed. The supernatant liquid was filtered. It was repeated three times with the residue using 300 mL of acid each time. After the fourth treatment, the combined filtrate was concentrated to 100 mL. Exactly 50 mL of the concentrate was evaporated to dryness. The residue was dried at 378 ± 5 K temperature.

$$\% \text{ of Acid soluble matter} = \frac{M \times 100 \times 2}{M_1 (100 X) / 100}$$

where, M = mass of the residue in grams

M_1 = mass of the material in grams taken for test

X = % of moisture content

Preparation of metal ion solutions

The metal ions chosen for the adsorption studies in the present work are Cr(VI), Ni(II), and Cu(II). 1000 mg/L of stock solutions of these metal ions were prepared using distilled water. While making up the copper ion solution, 1 mL of HCl was added to avoid the hydrolysis of cupric ions. The weights of the respective salts taken are listed in Table 1.

Table 4.1 Weight of the salts taken for the preparation of stock solutions

Metal ion	Metal salt	Weight (g) dissolved in 1 L
Cr(VI)	Potassium dichromate	2.828
Ni(II)	Nickel Ammonium Sulfate	6.729
Cu(II)	CuSO ₄ .5H ₂ O	3.929

6 Determination of concentrations of metal ion/dye solutions

Estimation of Cr (VI)

A 0.25% (W/V) solution of diphenyl carbozide was prepared in 50% (V/V) acetone. The sample solution (1 mL) was pipetted out into 25 mL standard flasks. To this, 1 mL of 6 N H₂SO₄ was added and then 1 mL of diphenyl carbozide was added and was made up to 25 mL using double distilled water. Concentration of Cr (VI) solution was determined by measuring the optical density of the reddish brown color solution at 540 nm wavelength with Systronics Double Beam UV-visible Spectrophotometer: 2202 at the wave length of 540 nm (Gohulavani, G., 2013).

Estimation of Cu (II)

Quantification of Cu(II) was done by a spectrophotometric method by the formation of a Cu–Potassium ferrocyanide complex. Potassium ferrocyanide complexing agent (5%) 2 mL was added to 10 mL of Cu(II) ion solution to form a reddish brown color. This solution was diluted to exactly 20 mL using distilled water and the absorbance was measured at 620 nm (Mehlig, J., 1941).

Estimation of Ni (II)

The concentration of Ni (II) ions in solution was determined spectrophotometrically as a nickel–dimethylglyoxime (Ni-DMG) complex. To about 10 mL of the sample solution containing Ni (II), 0.5 mL of 0.5 N HCl, 0.2 mL of 0.25 N sodium citrate, 1 drop of 0.05 N iodine, and 0.8 mL of 0.5% Dimethyl Glyoxime were added. The concentration of rosy red coloured Ni-DMG complex was measured at 445 nm (Gohulavani, 2013).

Concentration of colored metal complex/dye solution (mg/L) was measured using Systronics Double Beam UV-visible Spectrophotometer: 2202. The wavelength of maximum absorbance for the Malachite green, Bismarck -R and Reactive Red F3B are 618 nm, 516 nm, and 539 nm, respectively.

RESULTS AND DISCUSSION

Characteristics of Adsorbent

The characteristics of Activated carbon was prepared from the leaves of *Pongamia pinnata* by sulfuric acid treatment (PLC) were determined using ASTM. The determined characteristics are presented in Table 2.

Table 5.1 Physicochemical characteristics of PLC

S. No.	Properties	Values
1.	pH_{zpc}	6.2
2.	Particle size (mm)	0.11 – 0.21
3.	Bulk density (g/mL)	0.35
4.	Surface area (BET) (m^2/g)	368.52
5.	Moisture content (%)	3.87
6.	Loss on ignition (%)	86.5
7.	Water-soluble matter (%)	0.78

pH_{zpc}

The functional groups present on the surface of the adsorbent render the sites on the surface either negative or positive depending on the pH. The point of zero charge (zpc) is the pH required to obtain a net superficial charge equal to zero (pH_{zpc}). (Hector Ruizi, et al., 2015). The existence of surface functional groups depends on the preparation conditions of activated carbon and on the nature of the precursor (Mattson and Mark, 1971). When the adsorbent is poured into a solution having a certain pH, which is lesser than the pH_{zpc} of the adsorbent, the surface of activated carbon would acquire positive charge and when the pH of the solution is greater than pH_{zpc} of the adsorbent, the surface of activated carbon would acquire a negative charge. Thus, depending upon the pH_{zpc} of the adsorbent and the solution pH, electrostatic interaction between the adsorbent surface and the adsorbate will take place (Al-Degset al., 2000). pH_{zpc} of PLC is 6.2. So when the adsorption process is carried out with the adsorbate solution having pH less than 6.2, the PLC surface will attract anionic adsorbates because of positively charged surface and will not favor the approach of cationic adsorbate by electrostatic repulsion. Similarly, when the adsorption process is carried out with the adsorbate solution having pH greater than 6.2, the PLC will facilitate adsorption of cationic adsorbate and not favor the adsorption of anionic adsorbates. Figure 1 shows the plot drawn for the determination of pH zpc of PLC.

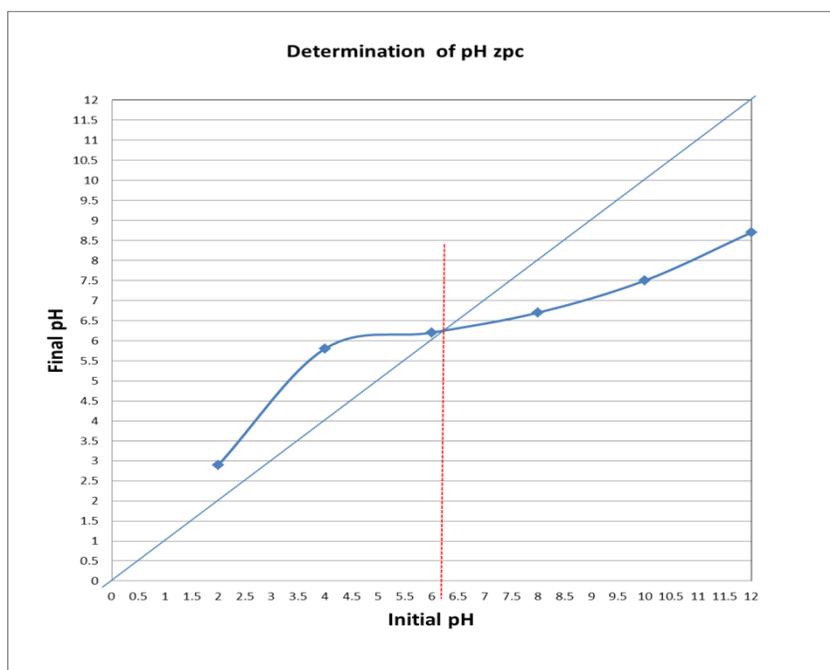


Fig. 5.1 Determination of pH_{zpc}

Particle size

Smaller the particle size more will be the surface area in general and hence more will be the adsorption capacity. But particle of very small sizes might have lower bulk density and lower mechanical strength. Therefore, particle sizes ranging from 0.105–0.212 mm were chosen for the present study, balancing between the surface area and mechanical strength.

Bulk density (g/cm³)

Settling rate of the sludge is proportional to the bulk density and the volume of sludge that has to be handled is inversely proportional to the bulk density. Further, the bulk density value gives an idea about the space that would be occupied by the material in the column. Thus, adsorbent having higher bulk density is preferable. Bulk density calculated for the PLC is 0.35 g/mL, which is reasonable.

Surface area (m²/g)

Surface area of adsorbent is the most important criteria for an adsorbent – more the surface area more will be the adsorption capacity of the adsorbent. Surface area of the activated carbon depends upon the precursor material and the preparation method. Removal of

compounds, which form the organic content such as lignin, esters, humic substances, and waxes, by the chosen activated method, is responsible for the surface area gained.

Moisture content

Having lower moisture content is good for a good adsorbent because the moisture present in the carbon will dilute the adsorbent when mixed with adsorbate solution, and thus might require additional weight of adsorbent than the estimated mass. The moisture content of PLC is 3.87%. This higher value may be due to the extensive porosity formed during acid treatment and absorption of water during washing in these pores.

Fixed Carbon content

Fixed Carbon content of the PLC was 68.3%. The presence of more carbon content is beneficial, which follows that a more carbonaceous adsorbent with a good skeleton of carbon is present in the chosen plant material (Yang and Lua, 2003).

Acid-soluble matter: Water-soluble matter and acid-soluble matter indicate the amount of impurities present in the adsorbent, which affect the quality of water. However, it has been found that PLC contains very low amount of acid-soluble matter that is 3.4 percentages only.

Ash content: Ash content indicates the amount of inorganic content present in the adsorbent. PLC contains a very low amount of ash content that is 10.4 percentages only.

Infrared spectra of PLC

Infrared spectra analysis is useful for the identification of the organic functional groups on the surface of the adsorbent. An examination of the PLC surface before and after adsorption provides information regarding the participation of surface groups involved in the adsorption process. FTIR spectrum of the PLC determined between the wave number 400 and 4000 is shown in Fig. 5.1. Functional groups present on PLC identified from the peak positions are alcoholic, O–H; carbonyl, $>C = O$; alkene, $C=C$; aliphatic amine, and amide (www.compoundchem.com) (Table 5.2). These groups may assist adsorption through ion-exchange mechanisms.

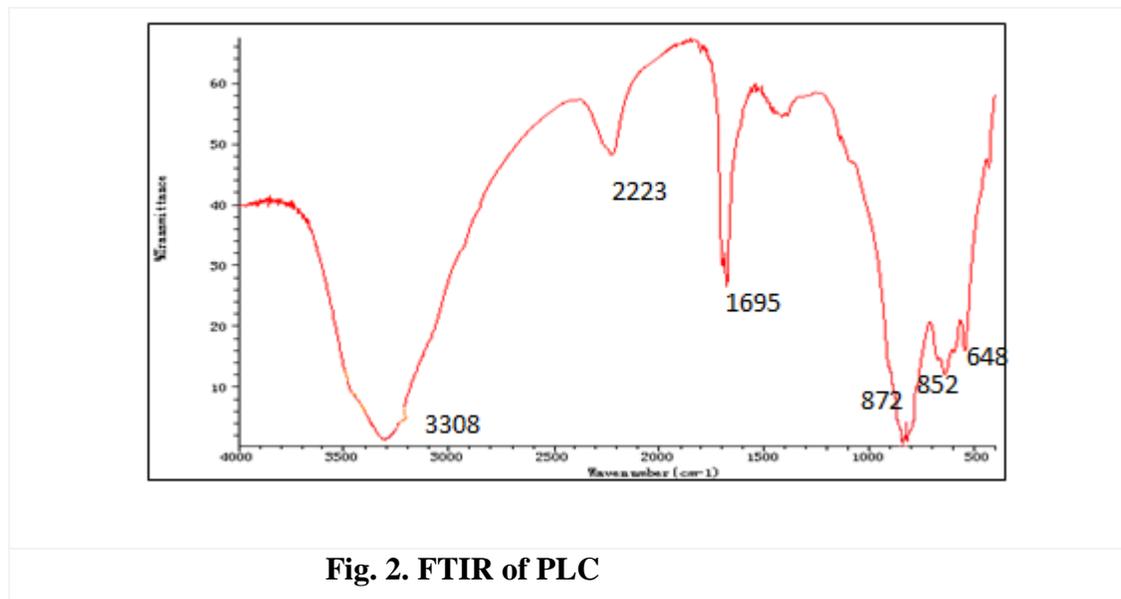


Fig. 2. FTIR of PLC

Table 3. FTIR peaks and functional groups on PLC

Band position cm^{-1}	Description
3308	O–H stretch in alcohols and phenols N–H stretch in primary and secondary amine, amide
2223	$\text{C}\equiv\text{C}$ stretch in alkyne group $\text{C}=\text{N}$ stretch in nitrile group
1695	$\text{C}=\text{O}$ stretch in carbonyl group
858, 872	$\text{C} = \text{C}$ Symmetric stretching in alkene
648	$\text{C} = \text{C}$ Bending vibration in alkene

SEM images of PLC

The scanning electron micrograph images of PLC are shown in Fig. 3. These figures clearly show the surface texture and porosity of carbon. Pore diffusion in the adsorption process is an important step. Pore diffusion means the migration of adsorbate molecules through the interior pores to reach the adsorption site. More the number of pores more will be the adsorption capacity.

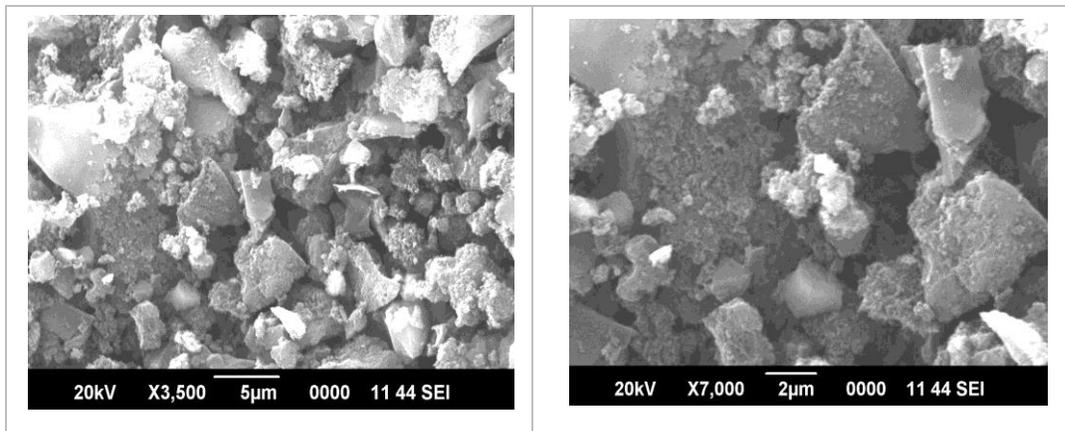


Fig. 3. SEM images of PLC

X-Ray Diffraction pattern of PLC

X-ray diffraction (XRD) imaging is a nondestructive technique used to characterize crystalline materials. Information on structures, crystal orientations (texture), average grain size, strain, crystallinity, and crystal defects can be known (Grimshaw, 1971).

The X-Ray Diffraction pattern of PLC is shown in Fig. 4. There is no sharp peak which indicates the absence of crystalline nature and the broad peaks indicates the amorphous nature of PLC.

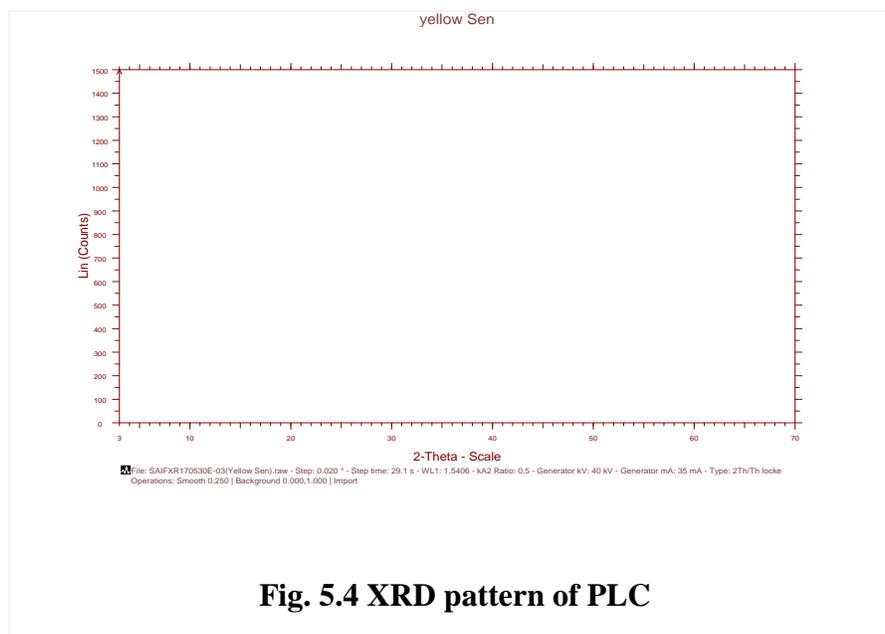


Fig. 5.4 XRD pattern of PLC

Adsorption study

Batch mode adsorption experiments were conducted with the chosen adsorbates: Malachite green (MG) dye, Bismarck brown (BB) dye, Red F3B(R)dye, heavy metal ions Cr(VI), Ni (II), and Cu (II) using PLC as an adsorbent. The results obtained for the effects of pH, dosage of PLC, contact time, initial concentration, and temperature are discussed in detail. Equilibrium data were analyzed with Langmuir, Freundlich, Sips, Temkin, and Dubinin–Radushkevich isotherm equations. Inferences obtained from the isotherm constants were recorded.

Effect of contact time data was processed with Lagergren, Ho, and Webber Morris kinetic equations. Best fitting kinetic equation was identified using Mean of Summation of Error Squares (MSSE) test.

Thermodynamic parameters such as enthalpy change (ΔH°), entropy change (ΔS°), and Gibbs free energy change (ΔG°) were determined from the equilibrium experiments conducted at different temperatures with different initial concentrations of adsorbates and using Van't Hoff plots. Significances of the results are discussed.

Effect of pH

The pH of the solution strongly influences the sorption process. Its effect is twofold. First, it affects the functional groups of the adsorbents and hence alters the surface charge of the adsorbent and second, it governs the speciation of the adsorbate. Surface charge and the speciation of adsorbate decide the extent of adsorption. Hence, the study of the effect of pH was initially carried out to fix an optimum pH for the further adsorption study.

In this present study, the chosen adsorbates were allowed to adsorb on the PLC with different pH solution ranging from 2–11. The desired pH of the solution was achieved by the addition of drops of 0.1 N HCl or NaOH solutions as required. Initial concentrations of the adsorbate solution and the chosen dosage of PLC for each adsorbate are given in the Table 5.3. The effect of pH on the percentage removal of solute from the aqueous phase was found to be different for different solutes for the same adsorbent depending upon the nature of the adsorbate.

Table 3 Effect of pH on dye adsorption

Time: 120 minutes Temp: 303 K

pH	Percentage of removal		
	MG (20 mg/L) Dose: 50 mg/50 mL	BBR (50 mg/L) Dose: 25 mg/50 mL	RR (20 mg/L) Dose: 50 mg/50 mL
1	28	32.2	69.6
2	36	37.6	65.7
3	51	51.2	61.3
4	56	56.4	55.2
5	59	64.7	40.6
6	64	69.3	31.2
7	71	71.2	30.5
8	72	72.6	29.4
9	73	73.5	26.1
10	74	74.6	24.3

Effect of pH on cationic dye adsorption: MG and BBR dyes belong to the class of basic dyes, which will give colored cations when dissolved in water. MG dye is yellow in color when the solution pH is below 1.8 and it is colorless when the solution pH is above 3.2.

(https://en.wikipedia.org/wiki/Malachite_green)

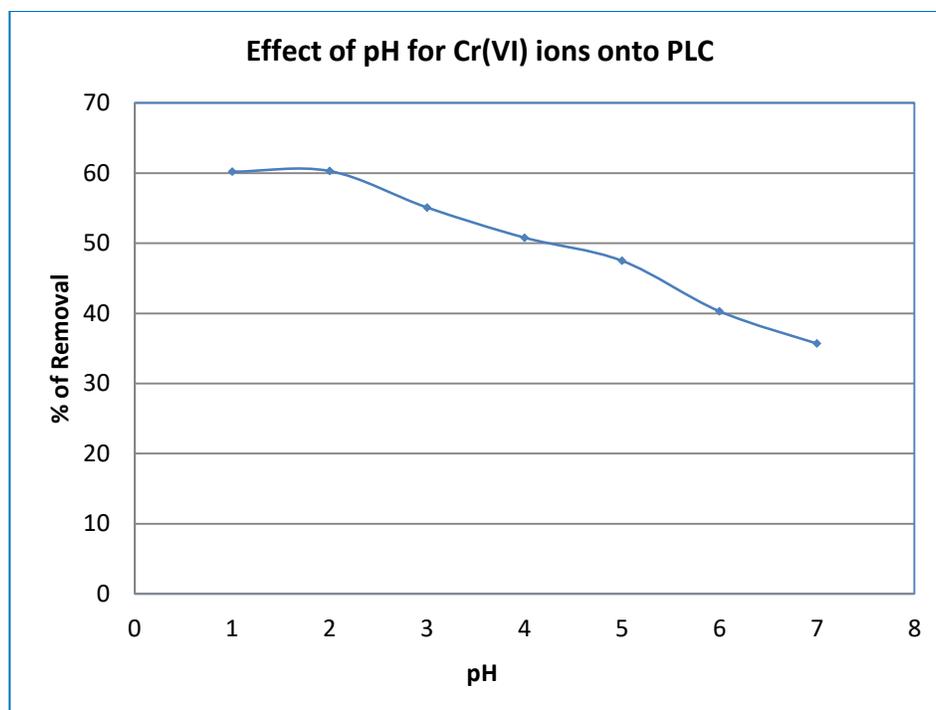
Figures 5 and 6 show the effect of pH on percentage removal of MG dye and BBR dye, respectively. At low initial pH, the percentage removal of dye was low and it increased with the increase of solution pH. This is due to variation of charge density on the surface of adsorbent and also on the dye molecule. At lower pH, protonation on the on the adsorbent as well as on dye molecule are high. Nitrogen atoms of the dye undergo for protonation. (Yahya, et al., 2008) pH_{zpc} of the PLC is 6.2. When the pH of the solution is below pH 6.2, the adsorbent surface possesses positive charge. The positive charge on the surface of the PLC prevents the adsorption of positively charged dye due to electrostatic repulsion. As the pH of the solution is raised, deprotonation of the dye and the adsorbent surface occurred and more due to decrease of proton density in the solution. (Gupta et al., 2004). When the pH of the solution, exceeds the value of pH_{zpc} of the adsorbent, the surface of the adsorbent acquires negative charge and therefore the electric double layer changes its polarity, and hence the dye uptake increases. A similar result

was reported for adsorption of Malachite green dye onto activated carbon prepared from lignite (Onalet al., 2006). The increase in percentage of removal is very meager with the increase in pH of solution from 7 to 11. Therefore experiments are conducted with the neutral solution (pH 7) in order to avoid neutralization of the effluent.

Effect of pH on adsorption of Cr(VI) ions: Figure 5.8 shows the effect of pH of initial solution on the percentage removal of Chromium(VI). The percentage of removal of Chromium (VI) ions decreased significantly, with the rise of the initial pH value of the solution and maximum removal was found at pH 2.0. This is because, the stability of different forms of chromium (HCrO_4^- , $\text{Cr}_2\text{O}_7^{2-}$ and CrO_4^{2-}) in aqueous solution is depend upon the pH of the system. The active form of Cr(VI) to be adsorbed is the bichromate form (HCrO_4^-). This bichromate form is stable only at lower pH range. So a higher percentage of removal was observed at pH 1–2. But the concentration of this bichromate form decreases with the rise of pH (Kulkarnisunil,et al. 2013; Supriya Singh, et al.2013; KhadkaDebaBahadur and Mishra Paramatma, 2014). Based on this result, further adsorption studies of Cr(VI) were carried out at pH 2. Optimum pH used for the adsorption of Cr(VI) ions by few of the earlier researches are collected in Table 5.8

Table .4 Optimum pH used for the adsorption of Cr(VI) ions

S. No.	Adsorbent	Optimum pH	References
1	Sugarcane bagasse	1.62	IshitaSinha, et al. (2016)
2	Activated carbon derived from Tendu (<i>Diospyros melanoxylon</i>) leaf refuse (CA-TLR)	2.	Maneet al. (2010)
3	Surfactant-modified coconut coir pith	2	Namasivayam and Sureshkumar, (2008)
4	Zeolite NaX	4	Pandeyet al., (2010)

**Fig. 8**

Effect of pH on adsorption of Ni(II) ions :The results inferred that the maximum uptake of Ni(II) ions occurred at initial pH of 7 (Fig. 5.9). At low pH, the adsorption percentage is low due to competition between the protons and Ni(II) ions for the active surface sites as well as electrostatic repulsion rendered by the positive charge on the surface towards Ni(II) ions. Electrostatic repulsion and the competition exerted by the protons decrease with increase of pH, which increases metal ion adsorption on the surface. Therefore, the optimum pH is 7.0. Similar result was obtained by Kadirvelu, et al., 2001; PremPrakash Vishwakarmam, et al., 1989; Manal El-Sadaawy, et al., 2014.

But pH 6 was selected for further experiments as some researchers suspected that the hydrolysis of Ni(II) might occur at pH > 6. (PrzemyslwBartczak, et al., 2011). Optimum pH used for the adsorption of Ni(II) ions by few of the earlier researches are collected in Table 5.9.

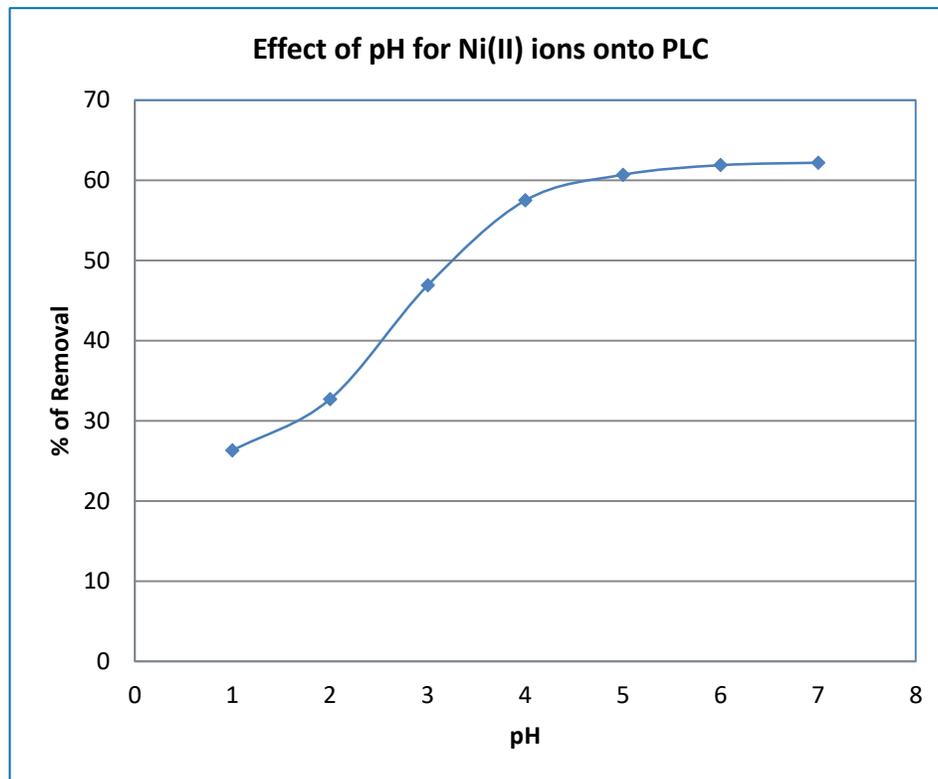


Fig. 5.9

Table 5. Optimum pH used for the adsorption of Ni(II) ions

S. No.	Adsorbent	Optimum pH	References
1	Leaves of <i>Araucaria cookie</i>	6	Deepa et al. (2013)
2	<i>Odinawodier</i> bark	6.5	Vijayakumaran et al., (2011)
3	Fly ash based on zeolite	5	Khadseshaila, et al. (2015)
4	Powder of mosambi fruit peelings	4	Hemakrishna et al., (2011)
5	Orange peel	5	FerdaGonen, et al. (2011)
6	Peanut hull carbon	4	Periasamyand Namasivayam, (1995)
7	Granular activated carbon	4	

Effect of pH on adsorption of Cu(II) ions: Effect of pH on the percentage removal of Cu(II) ions is shown Fig. 10. Percentage of removal of Cu (II) ions increased appreciably up to 60.9%

with an increase of pH from 2 to 5. This kind of increase was reported for other materials (Lee and Davis, 2001; Alkan and Dogan, 2001; Uceret al., 2006).

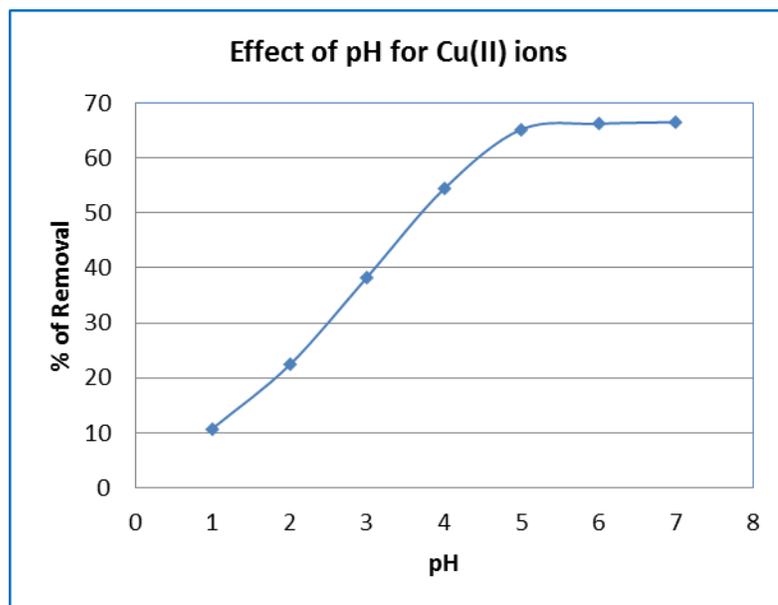


Fig. 10

The effect of pH on the removal of Cu(II) can be explained considering electrostatic interaction. When pH is below 6.5, the predominant species is Cu^{2+} , beyond that pH, Cu(II) undergo hydrolysis to give $(\text{Cu}(\text{OH})^+)$ and $(\text{Cu}_2(\text{OH})_2^{2+})$ (Jing Wang, et al., 2013). The pH_{zpc} of the PLC is 6.2. When the solution pH is below the pH_{zpc} of the adsorbent, positive charge begin to accumulate on the surface of the PLC. As the adsorbate also positive, the adsorption is not favored. Moreover, H^+ ions present in the solution at a higher concentration compete with Cu(II) ions for the adsorption sites. Hence, there is low adsorption is at low pH. The positive charge on the surface of the adsorbent decreases with the rise of pH and therefore the adsorption of positively charged Cu(II) and $\text{Cu}(\text{OH})^+$ species increases.

Based on this result, further adsorption studies of Cu(II) was carried out at pH 5. Neutral pH is avoided because Periasamyand Namasivayam (1996) pointed out that Cu(II) ion in the solution phase undergoes both adsorption and precipitation processes at pH above 5.4. Optimum pH used for the adsorption of Cu(II) ions by few of the earlier research works are collected in Table 5..

Table 6. Optimum pH used for the adsorption of Cu(II) ions

S. No.	Adsorbent	pH	References
1	Peanut hull carbon	5.4	Periasamyet al. (1996)
2	Commercial activated carbon	5.4	
3	<i>Elaeisguineensis</i> kernel activated carbon	5	NajuaDelailaTumin, et al. (2008)
4	Malawian baobab fruit shells	6	Ephraim Vunain, et al. (2017)
5	<i>Azadirachta indica</i> bark	9	Balakrishnanet al. (2010)
6	Maghnite	5.5	Mohamed Amine Zenasni, et al. (2012)
7	Carboxylate group functionalized single-walled carbon nanotube	7	Moradi, et al. (2011)
8	Single-walled carbon nanotube	7	

Effect of adsorbent dosage

Adsorbent dosage determines the capacity of the adsorbent for a given adsorbate and determines the sorbent–sorbate equilibrium of the system (Kilic, et al., 2011). After deciding the optimum pH, experiments were conducted to decide the optimum adsorbent dosage for each adsorbate by varying the PLC dose from 10 to 100 mg, taken in 50 mL of adsorbate solution of desired concentration. The adsorbate solutions with PLC were stirred in a rotary shaking machine at 150 rpm for 120 minutes at 303 K.

The percentage of removal of adsorbates from aqueous solution increased with the increase of PLC doses. Representative graphs are shown in Figs.11 and .12.

It is reasonable to say that higher percentage of removal at higher dose of adsorbent is attributed to more availability of exchangeable sites because of greater surface area at higher dosage (Tumin, et al. 2008; Babel and Kurniawan., 2004; Namasivayam,, et al., 1996).

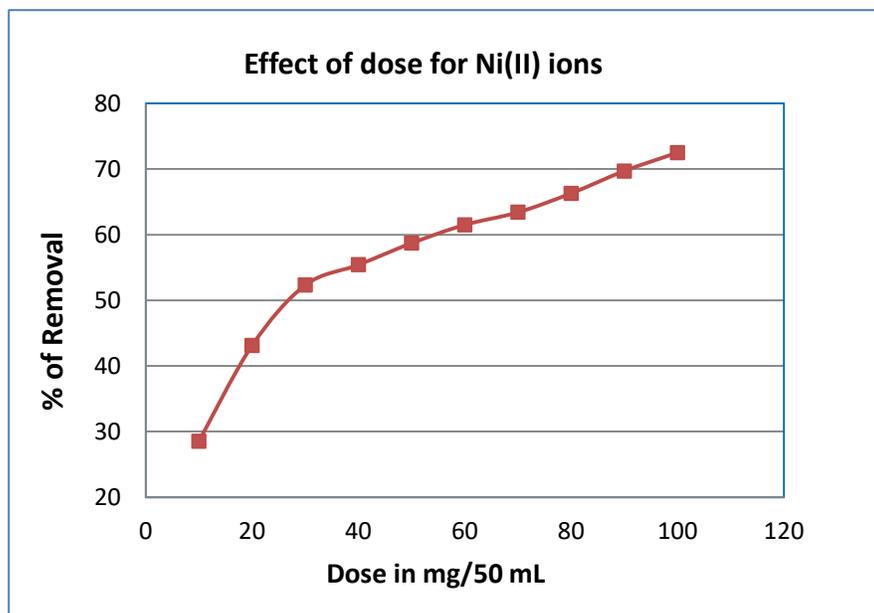


Fig. 5.11

Table 7. Optimum dose of PLC for chosen adsorbates

Adsorbate	C_i (mg/L)	Chosen dose (mg/50 mL)	% of Removal
MG	20	50	65.2
BBR	50	25	69.5
RR	20	50	69.6
Cr(VI)	20	75	60.3
Ni(II)	20	60	61.5
Cu(II)	30	100	65.2

The differences in the percentage of removal for different adsorbates are due to difference in the size, charge density, atomic mass/molecular mass, hydration radii in the case of metal ions and structure in the case of dyes, and also pore size and nature of functional groups of the adsorbent. Adsorbent dose, which gave 60–70% removal of adsorbates were chosen for further studies (Table 7).

Conclusion

To eliminating heavy metal ions from pollutants water and achieved by different techniques viz., water treatment method adsorptions methods different kind of adsorbents, preparation and activated carbon with the help of surface morphology an attempt is made to

studies FT-IR, SEM, PXRD. Eventually shown results apparently help to reuse kinetically treated water for the well growth of the plants in this adsorbent adsorption system.

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