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BIOSORPTION OF HEAVY METALS IN POLLUTED WATER USING NATURAL MATERIALS AS BIO-ADSORBENT

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ABSTRACT

Anthropogenic exercises create and release wastes containing heavy metals into the water resources, making them inaccessible and frightening to human wellbeing, just as the environment. Customary strategies for the extrusion of metal ions are incredibly costly. Treating a lot of water cause inadequate metal expulsion and produces vast amounts of muck and other poisonous items that require careful removal. The purpose of the investigation is to explore the impending efficiency of natural biosorbent to expel heavy metals from polluted water. The optimum pH, contact time, initial metal concentrations were investigated, and the sample is further studied for FTIR and SEM analysis. The result shows that the natural bio-adsorbent shows a high potential for heavy metal removal.

Keywords: Biosorbent, Heavy Metal, Water Pollution, Wastewater Treatment

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INTRODUCTION

Heavy metals are emitted into the environment in quantities and have a high density as compared to water.[1] Heavy metals are toxic and produce a poisonous effect on the body when exposed at lower level.[2] Recently, attention has been focused globally on the public health issues and ecological imbalance caused by heavy metal associated with environmental pollution.[3] Various factors are directly and indirectly affecting the environment and have become a significant issue for human wellbeing and other organisms, which can cause life-threatening diseases.[4-6] Nowadays, water pollution is considered a global problem, priority has been given to stop and control further pollution.[7] Many pollutants, organic materials, and metals like copper, lead, cyanide, arsenic etc., are present in industrial and municipal wastes and need effective treatment to spread contamination.[8] One of the most hazardous and highly poisonous chemicals like cyanide, enters the water body from various industrial wastes, particularly from the steel and automobile industry.[9] It is also toxic to human beings and animals and causes acute or chronic poisoning when binds with the enzyme cytochrome oxidase (an iron-containing enzyme for cell respiration).[10] Regulatory agencies have well defined the cyanide content in drinking water and surface water. The Central Pollution Control Board (CPCB) of India has set a minimum acceptable standard for cyanide 0.2 mg/L in drinking water.[11] Another toxic pollutant, lead, is abundantly available in nature and introduced in the environment through industrial effluents discharged to the soil. The trace amount of information can produce severe health complications in human life. However, lead poisoning is considered as cumulative toxicity of all lead compounds.[12,13] The most dreaded outcome from lead poisoning is the impairment of the nervous system, liver, kidney, gastrointestinal tract, brain, and sometimes death.

The primary source of lead contamination is the discharge of large quantities of wastewater from various industries like steel, power, battery, printing and metal soldering. Lead contamination also occurs in drinking water and domestic water due to the leaching of the lead component from corroded lead pipes, fittings and joints in household plumbing.[14-16] According to the Environment Protection Agency (EPA) and Bureau of Indian Standards, the acceptable level of lead in drinkable water is 0.05 mg/L and 0.1 mg/L respectively.[17-19] Other volatile metals like Hg, Se, As and Sb can exist as a gas or enrich as particulate systems, whereas metals like Pb, Cu and Zn are transferred as particles[20] and creates an adverse effect on the biota and human health.[21] The aquatic systems are affected by metal contaminants mainly through runoff and transport of industrial mobile colloids.[22,23] Heavy metals are well known for their toxic effect on living organisms. The unexpected availability of heavy metals in

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the surface and underground water causes serious risk in ecosystems.[24] The potential and persistence bioaccumulation property of heavy metals urge to eliminate it from the water has turned into a challenge and significant environmental task.[25]

A variety of modern convectional wastewater treatment technologies have been introduced to remove or recover heavy metal ions from solution in recent years.[26,27] The main drawback of the conventional treatment and its associated technologies is the use of expensive chemicals and toxic sludge production. The disposal of chemical sludge is not eco-friendly and costly too.[28-29] To overcome these problems, considerable approaches have been made to study the elimination of heavy metals from water samples by adsorption technology utilizing natural resources. The abundantly available natural bio-adsorbents have good potential to remove the metal ions from the pollutants in large quantities and well known for their low cost and environment friendly.[30] In short, biosorption is defined as the removal of toxic substances from the contaminated water by means of the physical and chemical process using biomaterials.[31,32] Several studies have been reported on the biosorption properties of microbial systems like algae, bacteria and fungi[33,34] and most recently, the development of bio-adsorbent and their effectiveness have been investigated for the removal of toxic metals in peat,[35] fly ash,[36,37] biomass and bioproducts from agricultural origins like soya bean hulls,[38] walnut hulls,[39] sugarcane bagasse[40] and corn cobs.[41] Biadsorptive removal of cyanide ion and divalent lead from contaminated water using tea leaves and shells from almond was reported in the previous studies.[42,43] These studies said that the maximum adsorption capacities estimated for cyanides and lead (II) per gram of almond shells and tea leaves are 25.44 mg and 65 mg, respectively. The study further suggested the need for bio-adsorbent modification for active binding of metals and ease of availability for the adsorption process. Hence, the current research has been designed to introduce agricultural wastes as a bio-adsorbent to remove heavy metals from contaminated water.

EXPERIMENTAL

The shells of *Prunus amygdalus* (PAS) were collected from the local market of Bilaspur and Neem bark was obtained from the campus of Chouksey Engineering College, Bilaspur, India. The shells of *Prunus amygdalus* were washed with double distilled water to remove the dirt and dried at 100°C temperature for 24 hours in an oven. The dried shells were then crushed into powders[44]. The exact process was followed for Neem bark. After the barks' collection, muddy materials were removed by running water and final washing was done with distilled water and sun-dried. The barks were then cut into small pieces and dried at 105 ± 5°C temperature in a hot air oven for 6 hours to eliminate the excess moisture. After cooling at room temperature, the bark was grounded and homogenized and washed with distilled water to remove residual dust and color. Finally, the grounded bark was dried in an oven at 105 ± 5°C temperature and placed in desiccators to cool for further use.[45,46]

All the chemicals used in the experiments were of analytical grade and were purchased from Prism Sales, Raipur, India. The cyanide stock solution was prepared by dissolving 1.88 g of sodium cyanide and 1.6 g of sodium hydroxide pellets in doubled distilled water to concentrate 1000 mg/L.[47] The lead nitrate salt [$Pb(NO_3)_2$] was used for the stock solution of lead. Briefly, 1.61 g of $Pb(NO_3)_2$ was weighed and placed in a 1000 ml volumetric flask containing 200 ml of distilled water. Two drops of concentrated nitric acid (HNO_3) were added to the flask and mixed thoroughly. The final volume was adjusted to 1000 ml with distilled water to concentrate 1mg Pb (II) per 1ml solution. The required test concentration was prepared from the above standard stock solution by appropriate dilution with distilled water.

In the beginning, prepared bio-adsorbents were evaluated for surface area, morphological examination and surface functional group analysis. The BET (Brunauer-Emmet-Teller) analysis was carried out to measure the surface area.[48] In contrast, different functional groups present on the surface of bio-adsorbents were determined by performing FTIR (Fourier transform infrared spectroscopy) studies. The surface morphology and porosity of the bio-adsorbents were investigated by SEM (Scanning Electron Microscopy) analysis.

The various test batches were prepared from the cyanide standard stock solution. Every 100 ml of cyanide solution with known concentrations was taken into the conical flasks placed on the incubator shaker. The bio-adsorbent with predetermined doses were added to each conical flask and shaken at 110 to 120 rpm for 1 hour. In the same way, different concentrations of test solutions were also prepared from the standard lead solution with proper dilution and with bio-adsorbent. The pH of prepared test solutions was adjusted by adding 0.1(N) HCl or 0.1(N) NaOH solution dropwise and continuous stirring. For each solution, the time to reach an equilibrium condition was recorded. Then,

the content inside the flasks was filtered using filter paper. The cyanide concentration in the filtrate was analyzed spectrophotometrically at 520 nm wavelength using picric acid method.[49] The concentration of the lead in the resultant solution was determined using an absorption spectrophotometer.[50] The ranges of the operating parameters are shown in Table-1. The removal of metals from the test solutions and equilibrium adsorption capacity (q_e) were estimated individually from the following equations:

$$\text{Removal of heavy metals (\%)} = \frac{Ci - Cf}{Ci} \times 100$$

$$\text{Equilibrium adsorption capacity } (q_e) = (C_i - C_f)$$

Where,

C_i is the initial concentration of metals, C_f is the equilibrium concentration of metals in mg/L and q_e is the amount of cyanide or lead adsorbed in mg/g. All experiments were performed in triplicate and average values were reported.

Table1: Various experimental Parameters studied
(pH, Contact time, Initial Metal ion Concentration and Adsorbent Dose)

Study performed	Experimental Parameters	
	PAS	Neem bark
Influence of pH on metal ion removal	pH- 2 to 10 [CT- 120 min, ICC- 100 mg/L and AD- 20 g/L]	pH- 2 to 10 [CT- 120 min, ILC- 25 mg/L and AD- 7.5 g/L]
Effect of adsorbent dose	AD- 5, 10, 15, 20, 25, 30 and 40 g/L [CT- 120 min, ICC- 100 mg/L and pH: 7]	AD- 4, 8, 10, 12, 16, 18 and 20 g/L [CT- 120 min, ILC- 25 mg/L and pH- 5]
Contact time with bio adsorbent	CT- 15, 30, 45, 60, 90, 120 and 150 min [AD- 20 g/L, ICC- 100 mg/L and pH-7]	CT- 20, 40, 60, 80, 100, 120 and 140 min [AD- 7.5 g/L, ILC- 25 mg/L and pH- 5]
The initial concentration of metal in the solution	ICC- 25 to 800 mg/L [AD- 20 g/L, CT- 120 min and pH- 7]	ILC- 20 to 140 mg/L [AD- 7.5 g/L, CT- 120 min and pH- 7]

Note: ICC: Initial Cyanide concentration, ILC: Initial Lead concentration, CT: Contact time and A.D.: Adsorbent dose.

RESULTS AND DISCUSSION

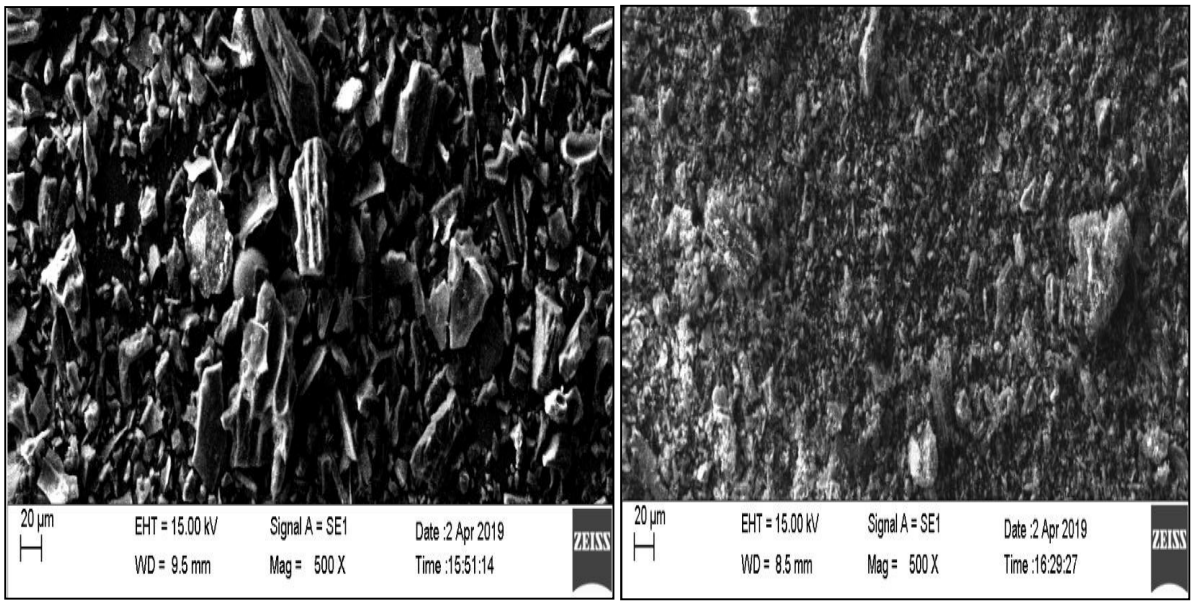
Evaluation of Bio-adsorbents

The surface area measured by BET analysis of PAS and neem bark was 48.97 m^2/g and 3.8 m^2/g, respectively. The SEM was carried out for both the bio-adsorbents before and after treatment with pollutant samples (Fig.-1A and B; Fig.-2A and B). The SEM micrograph of neem bark bio-adsorbent revealed the irregular and porous surface due to the presence of cellulosic content with tannin and lignin. It was also observed that both the bio-adsorbent had prominent porous and irregular surfaces (Fig.-1A and Fig.-2A) before treatment and the surface become smooth after treatment (Fig.-1B and Fig.-2B). The smooth surface may be due to the adsorption of heavy metals on the bio-adsorbent surface.

FTIR Spectroscopy

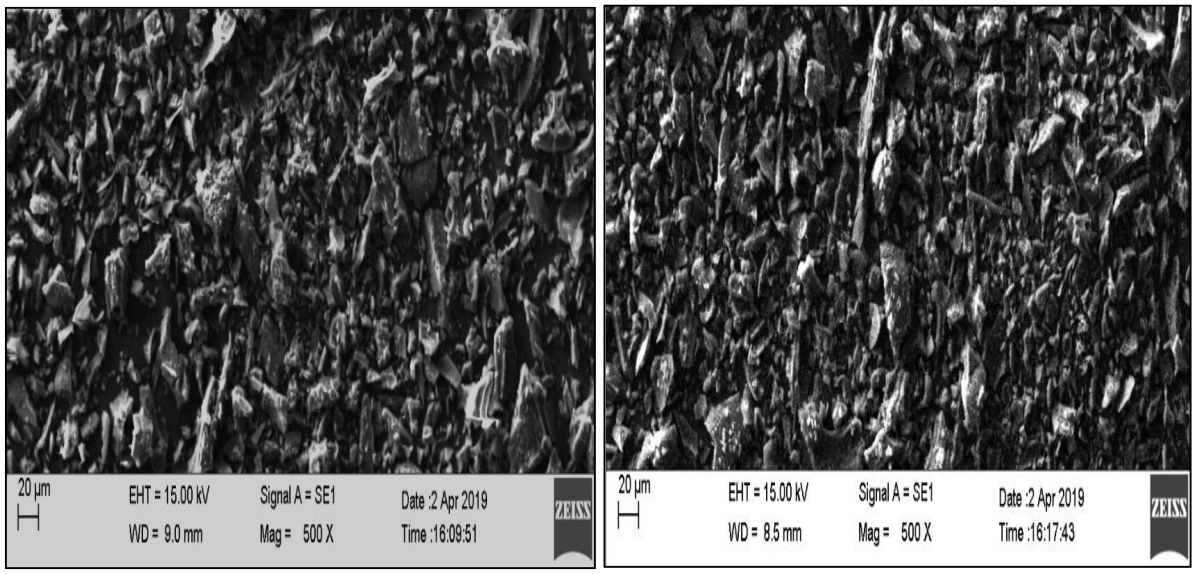
Fourier transform infrared spectroscopy, or simply FTIR, was performed to identify the major functional groups present in the bio-adsorbent, responsible for adsorbing heavy metals. Functional groups are the primary keys, which reflect the probable mechanism of metal ion binding on the bio-adsorbent surface. Preliminary investigation revealed that functional groups like carboxyl, methyl, hydroxyl, amide, phenolic, amine, and sulphonate were present on the neem bark and PAS surface. The prominent peaks of functional groups were initially observed on the bio-adsorbent surface before treatment. But after treatment, the peaks were disappeared and some peaks had shifted from their original position. The shifting and disappearance of peaks suggest the interaction of metal ions with functional groups present on bio-adsorbent surface. Two bio-adsorbents were scan in the wavenumber range from 4000 cm^{-1} to 400 cm^{-1} to identify the functional groups. Various characteristic peaks at different wavenumbers and probable functional groups to the corresponding peaks are summarized in

Table-2. PAS's surface contains functional groups responsible for cyanide adsorption, which was evident from the shifting and broadening of peaks. Shifting of the peak from wave number 1631.14 cm^{-1} to 1633.36 cm^{-1} may be the reason for cyanide adsorption. The presence of a peak at wave number 1121.18 cm^{-1} indicates the presence of an aliphatic amine.



(A) (B)

Fig.-1: SEM Analysis of PAS Bio-adsorbent Before Treatment (A) and After Treatment (B)



(A) (B)

Fig.-2: SEM Analysis of Neem Barks Bio-adsorbent Before Treatment (A) and After Treatment (B)

Moreover, after treatment with bio-adsorbent, the peak shifted to 1118.14 cm^{-1} from its original position. The attachment of cyanide ion into the aliphatic amines may be the reason for peak shifting. The shifting of peaks from 1333.13 cm^{-1} to 1327.13 cm^{-1} and from 2921.01 cm^{-1} to 2918.71 cm^{-1} is due to cyanide ion sorption by aromatic nitro compound and aliphatic C-H stretching in PAS, respectively. However, in bio-adsorbent from neem bark, noticeable numbers of peaks were shifted after treatment of lead polluted water. This shifting is highly associated with loaded metal on bio-adsorbent surface. The functional group, carboxylic acid, contains O-H and C-O stretching. The clear sifting of the C-O stretching group peak at the wave number 1249 cm^{-1} indicated the potential adsorption of lead ion on the bio-adsorbent surface. Also, it proved that carboxylic acid is involved in metal binding. There was no significant peak shift for C-N stretching. Still, shifting peak at wave

number 3295 cm^{-1} from 3314.1 cm^{-1} for N-H stretching firmly suggested the adsorption of lead by neem bark be interpreted as N-H stretching in the amine group with metal adsorption. The S-O stretching in the sulphonate group also showed the peak shift from 746.2 cm^{-1} to 757.1 cm^{-1} confirmed the adsorption of lead ion by neem bark and the result further suggested that the sulphonate group being strongly acidic, will be able to absorb metal ion from polluted water. The possible functional groups that may be involved in metal binding by bio-adsorbents are illustrated in Table-2. It is important to note that FTIR analysis neither provides any information regarding the affinity of bio-adsorbent to the metals nor the quantitative analysis of metals adsorbed by bio-adsorbents. The only mechanism of adsorption of cyanide and lead ion by bio-adsorbent is physical adsorption. FTIR analysis only suggested the possibility of coupling between critical functional groups in bio-adsorbents and metals ions in pollutants.

Table-2: Bio-adsorbents containing various Functional Groups with their Wavenumber

Bio-adsorbent Sample	Wavenumber (cm^{-1})	Functional Group
Prunus amygdalus Shell	3421.47	O-H
	2921	Methylene C-H stretching
	2854.95	C-H
	1632.14	Amide
	1121.18	Aliphatic amines
Neem Bark	2916 1249.6	Carboxylic acid C-O and O-H stretching,
	3314.1	Amine C-N and N-H Stretching, Amide
	1603.8	Sulphonate with C-O stretching
	746.2	S-O stretching

Influence of pH on Metal Removal

The influence of the pH on cyanide removal from the PAS sample solution was investigated at various pH levels ranging from 2 to10, using ICC of 100 mg/L, CT of 120 min and A.D. of 20 g/L as shown in Fig.-3A. It was observed that the increasing pH of solution initially increased the % removal of cyanide and the maximum value of 89.5 % was observed at pH 7. The percentage of removal was then decreased as the solution become basic. This suggests that the maximum removal of cyanide occurs at neutral pH. On the other hand, the removal of lead from the solution was also examined over a pH range of 2 to 10 (Fig.-3B) with ILC 25 mg/L, CT 120 min and AD 7.5 g/L. The maximum percent removal of lead was 86.6 at acidic pH 5. Therefore, the biosorption study of heavy metals by PAS and neem bark powder was carried out throughout the experiments by maintaining pH 7 for cyanide and pH 5 for the lead. The pH of a solution plays an important role in several chemical reactions like complexation, ion exchange, oxidation/reduction, and electrostatic interactions. It seems the surface charges of the adsorbents are altered by the pH of the solution, which in turn affects the degree of ionization and convergence of contaminants. In the event of pH change, the adsorption phenomena on the bio-adsorbent surface occur through the functional group's dissociation. Hence, fixing the suitable pH of effluents or waste, water-heavy metals can effectively be removed by bio-adsorbent.

Effect of Bio-adsorbent Dose

The various PAS and neem bark doses were examined for removal of cyanide and lead from the solution keeping another parameter constant as depicted in Table-1 and Fig.-4A and 4B. The doses were selected in the concentration ranges from 0 to 50 g/L for both the bio-adsorbents. The results showed that removing metals from the solution was effective with increasing the dose of PAS and neem bark. But after a specific dose, there were no noticeable changes observed in the removal efficacy.

The maximum effective dose of PAS for removing cyanide was 20 g/L. On the other hand, the neem bark's maximum removal efficacy was observed in the dose of 7.5 g/L. Therefore, for the further experiment, the doses of bio-adsorbents were fixed at 20 g/L for PAS and 7.5 g/L for neem bark.

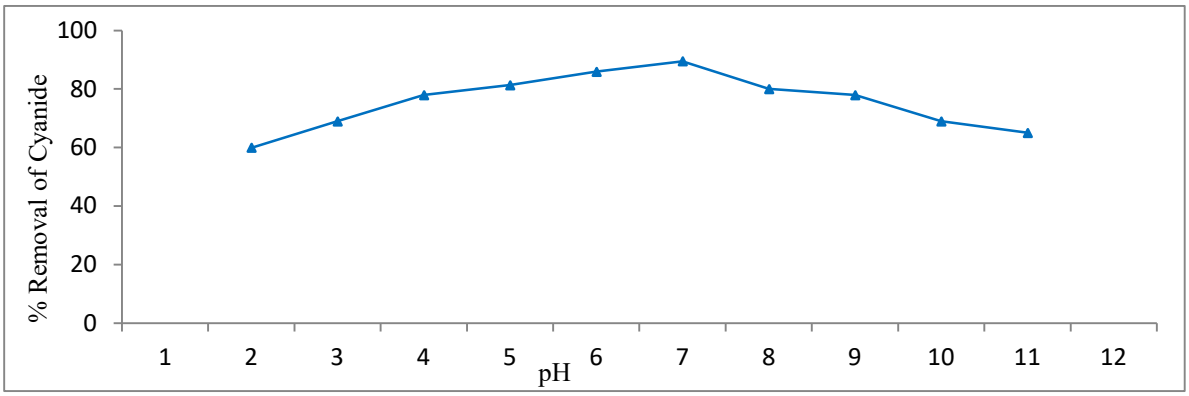


Fig.-3A: Influence of pH on Cyanide removal by PAS

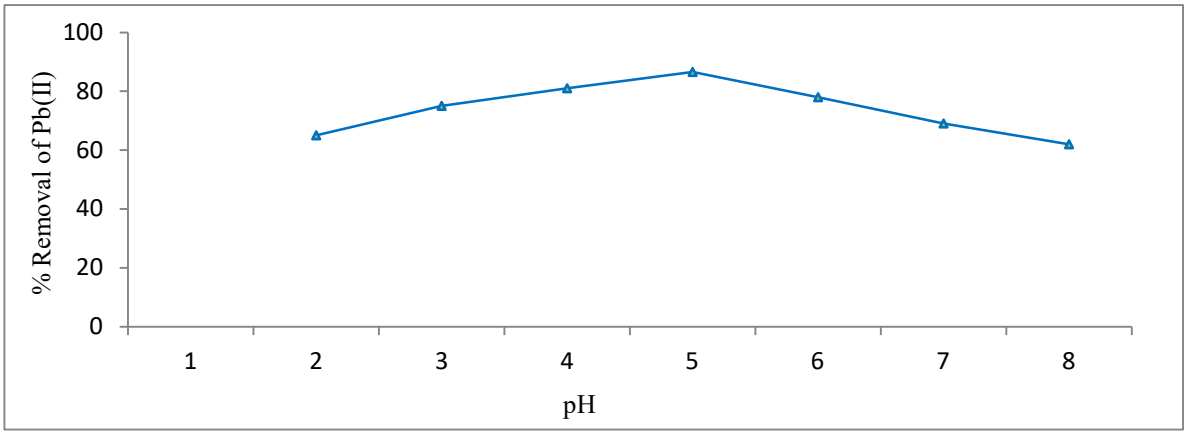


Fig.-3B: Influence of pH on Lead removal by Neem bark

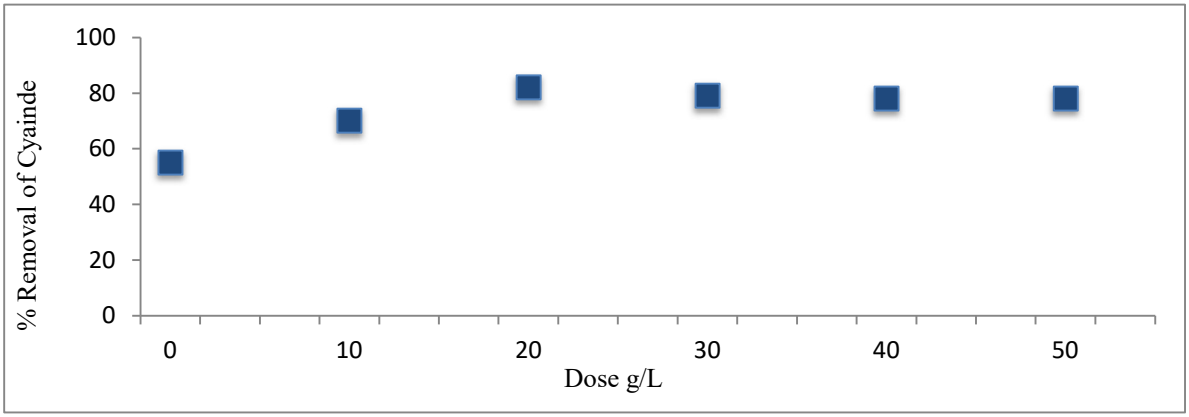


Fig.-4A: Effect of Bio-adsorbent (PAS) Dose on the Removal of Cyanide

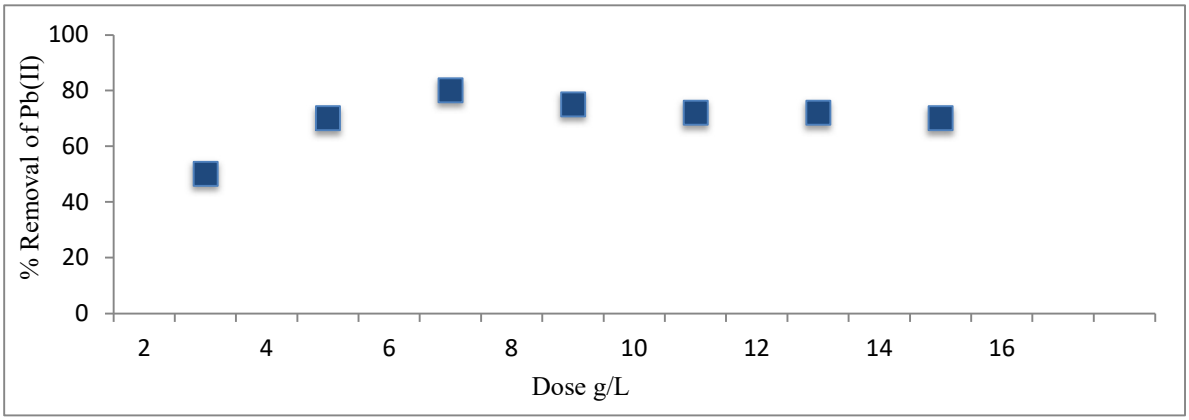


Fig.-4B: Effect of Bio-adsorbent (Neem Bark) Dose on the Removal of Lead

Effect of Contact Time on Biosorption

The contact time is another critical parameter to measure the efficacy of bio-adsorbent for removing heavy metals from the effluents of contaminated water. The experimental conditions for measurement of the effective time of exposure are given in Table-1. The study showed that with an ICC of 100 mg/L, almost 55% of cyanide was removed within a short time span of 15 min by the PAS powder (Fig.-5A), and within 60 min maximum of 82%, cyanide was eliminated. After 90 min, the PAS becomes equilibrium with cyanide ion and no more

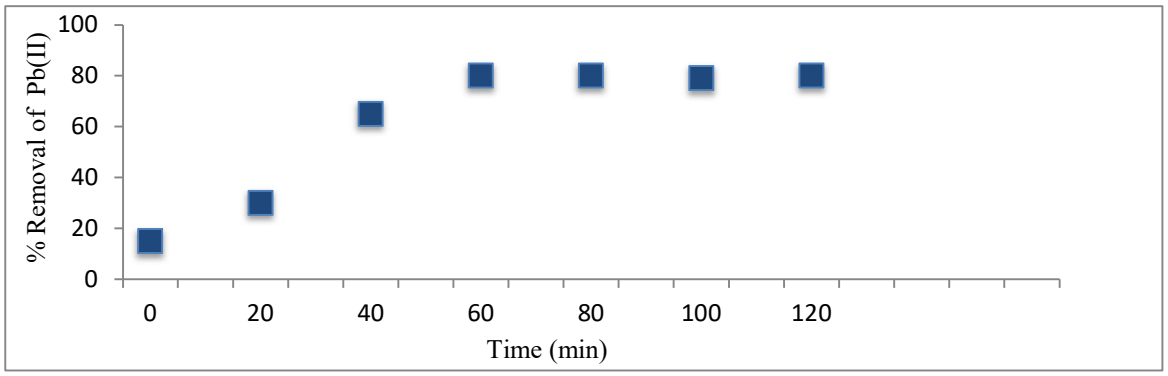


Fig.-5A: Effect of C.T. (PAS) on Cyanide Removal

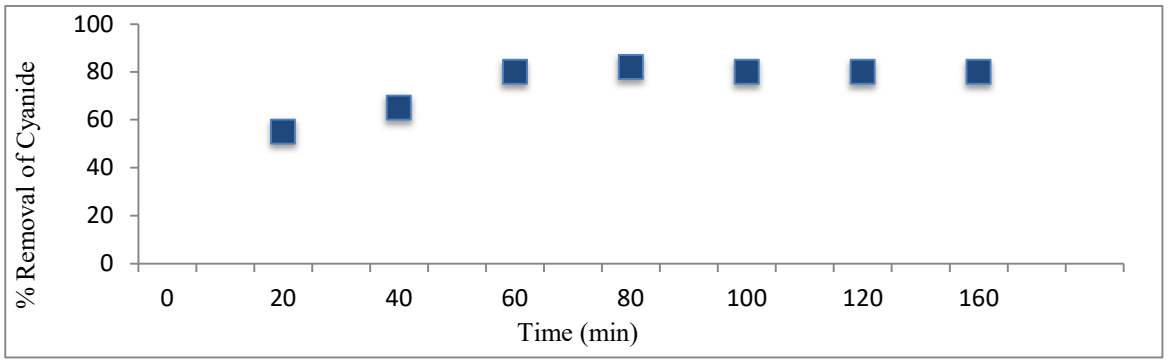


Fig.-5B: Effect of C.T. (Neem Bark) on Lead Removal

For Neem bark, the experiment was carried out to investigate the optimum contact time for effective removal of lead from the solution. The contact time was varied from 0 min 160 min by keeping the other parameter constant (Table-1). The lead's initial adsorption was very slow concerning time and reached the maximum adsorption level in 80 min (Fig.-5B). After 90 min, the equilibrium is achieved, and no more lead adsorption occurs by the neem bark. It suggests that the nature and site of sorption play an important role in reaching the equilibrium condition.

Influence of Initial Metal Ion Content

The effect of adsorption with initial cyanide concentration ranges from 25 mg/L to 800 mg/L was investigated for PAS with predetermined experimental conditions (Table-1). The PAS powder initially showed the high quantity removal of cyanide from the solution with ICC 25 mg/L (Fig.-6A).

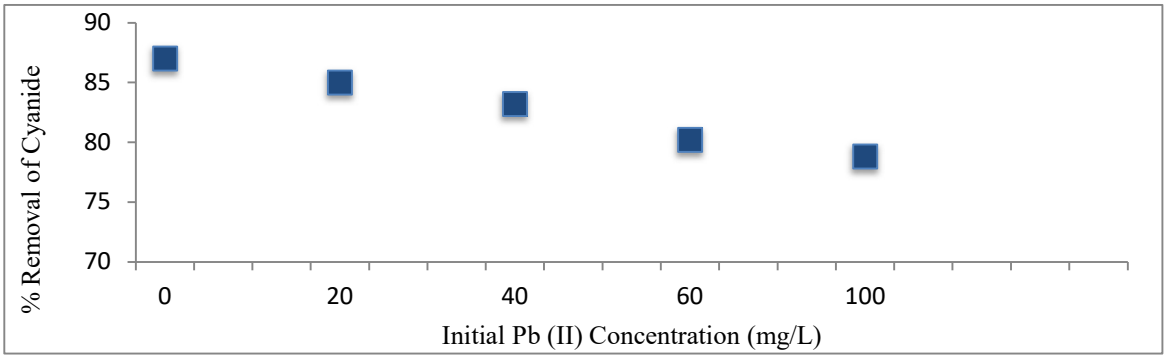


Fig.-6A: Effect of ICC on Cyanide Removal by PAS

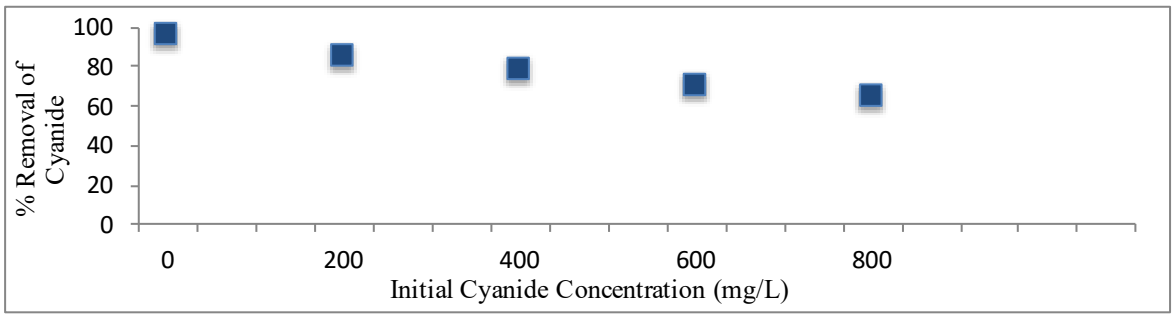


Fig.-6B: Effect of ILC on Lead Removal by Neem Bark

From Fig.-6A, it was observed that about 95% of cyanide was eliminated with the initial cyanide concentration of 25 mg/L, and with the highest concentration of 800 mg/L, only 63.6% cyanide was removed. However, the increase of cyanide concentration in the bio-adsorbent decreases the percent removal of cyanide from the solution. The percentage removal of lead from the solution was also investigated with concentration ranges from 20 mg/L to 140 mg/L and depicted in Fig. 6B. The elimination of lead from the solution by neem bark powder was decreased gradually with the increasing initial concentration of the lead at constant pH. PAS's uptake of cyanide was measured with ICC 25 mg/L and 800 mg/L and found to be 1.2 mg/g and 24.4 mg/g, respectively. Similarly, the lead uptake with lower ILC was 0.52 mg/g, whereas; with higher ILC, it was recorded as 16.5 mg/g.

CONCLUSION

In the present study, a batch adsorption experiment investigates the removal of harmful metals cyanide and lead from the aqueous solutions. The bio-adsorbents from natural resources are selected due to their abundant availability and low cost. Preliminary investigations are carried out by BET surface analysis, SEM and FTIR for suitability of bio-adsorbents. FTIR analysis of PAS and neem bark provides basic information about functional groups that may be responsible for the metal-binding process. The bio-adsorbents are evaluated for their adsorption activity by examining the pH, contact time, initial concentration of metal ion, and the dose. The study observed that pH played an essential role in the effective adsorbent of metals. It was also found that bio-adsorbent from various sources have different potential, and they are active in specific pH of the effluent/wastewater, as evident from the study. The maximum uptake of metal ions depends on the optimum dose of the bio-adsorbent (adsorbent dose of 20 g/L for PAS and 7.5 g/L for neem bark) with a specific condition. The contact time of bio-adsorbent with pollutants and initial metal ion concentration played an essential role in removing metals. The encouraging findings reveal that *Prunus amygdalus* and Neem bark shells may be used as promising bio-adsorbent for the economical treatment of wastewater containing cyanide and lead.

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