WWW.IJRPR.COM

International Journal of Research Publication and Reviews

Journal homepage: www.ijrpr.com ISSN 2582-7421

Synthesis and Characterization of Natural Adsorbent Using *Citrus Sinensis* Plant Material and its Application in Removal of Heavy Metal Lead

Sandeep R. Gadhave [a], Harshal S. Kharde [a], Rupali S. Kale [b], Pooja N. Kasar [b]

[a] Assistant Professor, Department of Chemistry, Padmashri Vikhe Patil College of Arts, Science and Commerce, Pravaranagar, Maharashatra, India.
[b] Post Graduate Student, Department of Chemistry, Padmashri Vikhe Patil College of Arts, Science and Commerce, Pravaranagar, Maharashatra, India.
DOI : https://doi.org/10.55248/gengpi.6.0125.0639

ABSTRACT

Natural agricultural solid waste material is very cost effective for synthesizing adsorbent utilized in the removal of heavy metal ions from economic and non-economic waste waters, which are numerously exploded in environmental soil and water resources. *Citrus sinensis* (orange peel powder CSPP) was synthesized into particle in the removal of Lead metal ions. The adsorbent was synthesized in a yellowish manner in an aqueous medium. A batch adsorption study was carried out with parameters including the effect of pH (pH 7, 79.00%), adsorbent dose (2.5gm, 72.10%), the concentration of metal ion (300ppm, 83.40%), the effect of temperature (40^{o}C, 76.35%), and the effect of contact time (90 min. 70.88%). Characterization on study of CSPP before lead metal ion adsorption and after lead metal ion adsorption was conducted. Including X-ray diffraction analysis, Fourier transforms infrared spectroscopy, Ultraviolet - visible spectroscopy and elemental detection analysis.

Keywords: Lead, Adsorbent, characterization, synthesis, Removal

I. INTRODUCTION

Lead contamination of waste water causes toxicity to aquatic life, the ecological and water quality and causes many human disfunction and diseases thus, it is necessary to remove lead from waste water before discharging it into the environment. Orange peel and orange peel powder doped iron (III) oxide - hydroxide (OPF) were synthesized, characterized and examined lead removal efficiency by batch experiment, adsorption isotherm kinetic, and desorption experiment [1]. Affecting the quality of drinking water due to their high content of dyes and toxic substances, arguing the need for finding simple and cost-effective remedies to remove such contaminants. Utilising a variety of analytical approaches, it was determined how process variables like contact duration, pH, adsorbent affected the dye removal efficiency. Studies on the kinetic, isothermal, and thermodynamic [2,3]. The aim of this study is to review several instances in the existing literature on the adsorption of various pollutants by orange peel and identify structural properties of the peel that influence contaminants adsorption. In achieving this, SEM images and FTIR spectra of raw and modified orange peels would be extensively studied to determine properties of the peel that influence biosorption [4]. It is well known that the processing of heavy metal by human body is a very difficult since they settle down in dissimilar internal orange and could lead to serious damage of body system. The objective of this study was to investigate orange peel by grafted copolymerization for the removal of lead, cadmium, nickel ions from water by adsorption [5,6]. The oxide group material has semiconductor properties where the material has a band gap energy in the U.V region, so it is able to absorb U.V rays. In this study, the manufacture of natural material based photocatalysts composite material using orange peel was carried out. The objective of this study was to characterise and to evaporate the applicability of orange peel biomass as an adsorbent so remove methylene blue textile dye through characterization test of an adsorbent prepared from in natural orange peel and adsorption isotherm of the dye [7,8]. The removal and recovery of toxic heavy metal ions such as copper, cadmium from contaminated environments is of great importance. Fruit peel is a major source of cellulose, which can offer an effective solution of this issue for .example orange peel due to its natural abundance, waste resources and minimal processing, could be a potential low-cost adsorbent for waste pollutants hence supporting the principal of circular economy and sustainability [9]. The aim of this study was to modify orange peel by sodium hydroxide to enhance the adsorption capacity of the by product and investigate the adsorption of methylene blue on it. Environmental and human health risks derived from toxic heavy metal ions and nitrate have promoted the investigation of different potential solutions, including photocatalysis [10,11]. In this work a novel magnetic nano adsorbent was developed by the surface modification of Fe_3O_4 nanoparticles (MNP) with OOP with the aim of exploring the feasibility of adsorbents for the removal of cadmium taken as a model toxic metal ion. In this work a novel magnetic nano adsorbent was developed by the surface variation of Fe_3O_4 nanoparticles (MNP) with OOP with the aim of exploring the feasibility of adsorbents for the removal of cadmium taken as a model toxic metal ion [12]. The shortage of drinking water is increasing continuously in the world. It is estimated that approximately one third of the world's population use groundwater for drinking purposes. Heavy metal especially arsenic polluted drinking water has been emerging as a problematic issue around the globe. Arsenic, one of the world's most hazardous chemicals, is found to exist within the shallow zones of ground water of many countries like Argentina, Bangladesh, India in various concentration. Adsorption technique is one of the alternative treatments, especially the widespread industrial use of low-cost adsorbents for waste water treatment [13,14]. The influence of various operating parameters as adsorbent dosage, contact time, initial pH, and temperature on the removal efficiency was studied [15]. The presence of pollutants in the natural water body above the allowable limit creates damaging effects on the comments of living organisms and especially on human health orange peel principally consists of cellulose, hemi-cellulose, pectin substance, chlorophyll second pigment and other low molecular weight compound [16,17]. The main objectives for this study were to investigate the effect of variable adsorbent dosage, contact time, pH, temperature and initial Metal ion concentration. Adsorption of nickel was confirmed by taking the FTIR spectrum of adsorbent before and after.

II. MATERIAL AND METHODS

2.1 Synthesis of Adsorbent: Citrus Sinensis

In this study natural adsorbent plant was selected *citrus sinensis* fruit peel. *Citrus sinensis* is a widely available medicinal product belonging to the rutaceae family. *Citrus sinensis* fruit peels were locally available and collected from Fruit Market loni village, Rahata taluka of Maharashtra state (India). The peels were washed with distilled water severally to avoid dust and other soluble impurities. Then washed *citrus sinensis* fruit peels were dried in sunlight for 5-6 days till it became crispy. Small size pieces of dried *citrus sinensis* fruit peel have been grinded for 240-320 mesh fraction. The grinded bark is not further treated. Dried *citrus sinensis* fruit peel powder is used directly for the removal of lead.

2.2 Batch Adsorption Studies:

Removal of lead ions was studied through various parameters employed by orange peel powder (OPP). The chemicals used were of AR grade for parametric study with purity of high range. Adsorbate stock solution contained 1000 mg/L of lead has ion prepared by dissolving lead nitrate with accurate measurement in double distilled water [18]. The stock solution for investigation was diluted for the initial working solution. Adsorption experiments were carried out with 50ml of lead ion solution of desired concentration with the addition of 200 mg. *Citrus sinensis* fruit peel powder in a stoppered flask of 250 ml, as an experiment of adsorption was managed at 30 degrees sensuous which is near room temperature further stripping the mixture combination for 60 min at pH 3 was altered with solution of 1N NaOH and 1N HCl [19]. Lead ion solution was removed from the stirred in a proper time for 15 min. and separation of adsorbent was practiced with Whatman filter paper No. 41. Lead ion samples were examined on UV- visible spectrophotometer for the study of parameters including pH, adsorbent dose, initial metal ion concentration and effect of temperature. Reaction time for this study is 240 min with 15 min of time interval. The formula derived the % of removal of lead metal ion from absorbance.

% Removal = A_o- A_t / A_o

Where A_o = Absorbance at initial time

A_t = Absorbance at final time

III. RESULT AND DISCUSSION

Characterization of Natural Adsorbent *Citrus Sinensis* fruit peel

3.1 FTIR Analysis:

Fourier transform infrared spectroscopy for the leaves extract of *Citrus Sinensis* fruit peel was implemented for the identification of biomolecules and phytoconstituents present in extract which has the ability to produce a stable nanoforms and having the property of stabilizing agent as well as capping agent. The analysis spectrum of leaves extract shows various peaks of functional groups which due to the presence of biomolecules and the phytoconstituents capped on the surface of the synthesized nanoparticle. The spectrum peaks at 3928.64 cm^{-1} and 3758.24 cm^{-1} are due the stretching frequencies of -OH hydroxyl group of the inner surface. Peak at 3552.46 cm^{-1} is the stretching frequency of phenolic -OH stretching present in the biomolecules. The broad and sharp peak is observed at 3414.11 cm^{-1} and gives the presence of the O-H stretching frequency of amines. 3236.01 cm^{-1} gives the stretching of N-H functional group of amides peak at 2920.05 cm^{-1} and 2853.29cm^{-1} gives the presence of C-H group of alkanes. Peak at 2563.67 cm^{-1} is due the presence of carbonyl group of carboxylic acid present in the leaves extract. The peak at a 2034.18 cm^{-1} gives the presence of silicon compounds which may be due to plant phytoconstituents. 1740.81 cm^{-1} sharp peak show the stretching of the presence of ketonic group of the plant biomolecules. The stretching frequency peak at 1638.81cm^{-1} and 1617.85cm^{-1} is due to the -C= C- alkenes vibrational stretching. Peak 1583.80cm^{-1} is due the presence of -N-H- group of primary amines the presence of peak at 1507.26 cm^{-1} results in the presence of aromatic -C-C- stretching frequencies due to presence of aromatic components present in the extract of the *Citrus Sinensis* fruit peel. The broad peak of 1432.58 cm^{-1} is the result of carbonyl group -C=O- of carboxylic acid of phytoconstituents peaks at 1406.49cm^{-1} is due to the -C-O-H stretching, the peak at 1384·41cm^{-1} is due to the presence of -CH_3- group. 1330 cm^{-1} stretching frequency is due the -CH-CH_3- groups of the constituents in leaf extract. The stretching at the 1257·33 cm^{-1} is due to wagging of -CH- of alkyl halides. The peaks at 1232·32, 1147·68, 1050·95 cm^{-1} gives the presence of the -C-O- functional group of alkyl ester, ethers and the presence of -C-O-C group peak at 851·56 cm^{-1} is the stretching frequency of =C-H alkenes which is out of the plane peak at 883·20 cm^{-1} is may be due to -C-O-C, -C-OH, -CH ring and also vibration of some side groups 822·22 cm^{-1} stretching frequency is of asymmetric vibrations of ring stretching which may be due to presence of the carbohydrates. Peak at 803·28cm^{-1} gives the presence of the aromatic compounds in the plant constituents peaks at 740·84cm^{-1}, 689·54cm^{-1}, 626·11cm^{-1}, is due to stretching vibration frequency of presence of halogen compounds of chlorine peak at 480·33 cm^{-1} assigns the presence of halogen compounds.

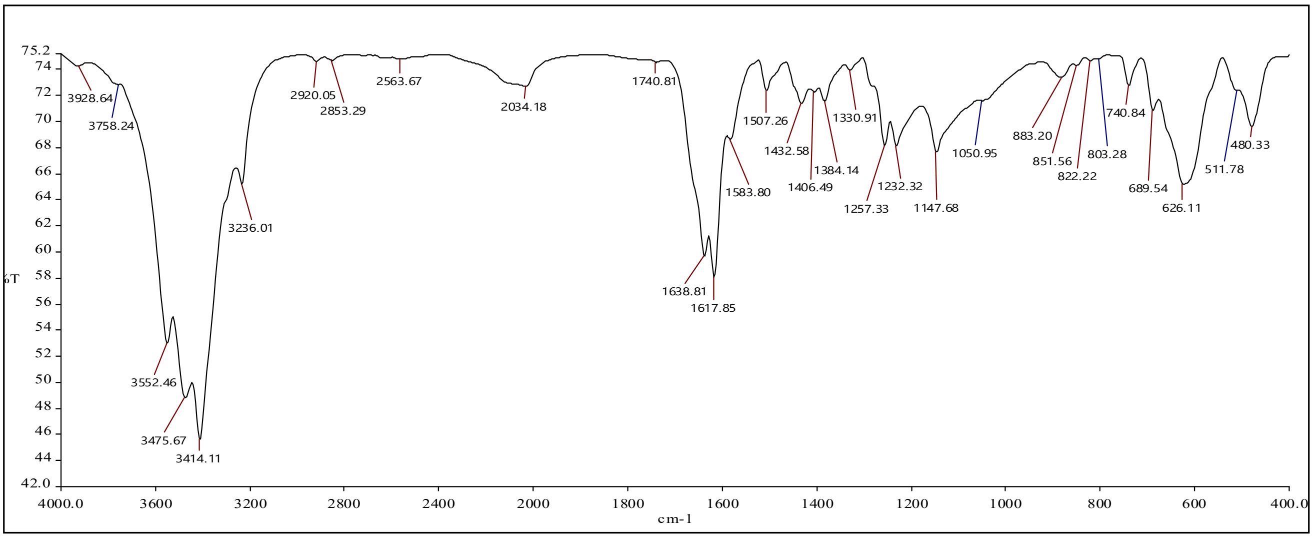

Figure 3.1.1. FTIR spectrum of *Citrus Sinensis* fruit peel before lead (II) adsorption

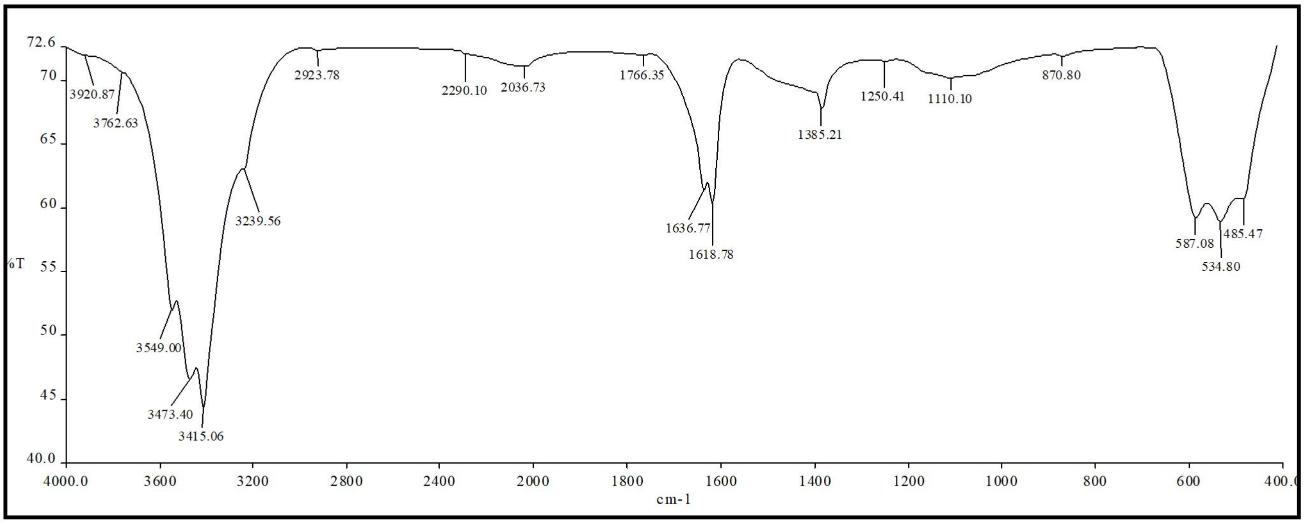

Figure 3.1.2. FTIR spectrum of *Citrus Sinensis* fruit peel after lead(II) adsorption

3.2 Energy Dispersive X-ray Analysis (After lead ions absorption):

The elemental analysis was studied using Energy dispersive X-ray analysis. The presence of Pb and O with higher atomic percentage respectively was confirmed by EDX micro analysis summarized. EDX is based on the fundamental principle that each element has a unique atomic structure allowing a unique set of peaks on its electromagnetic emission spectrum.

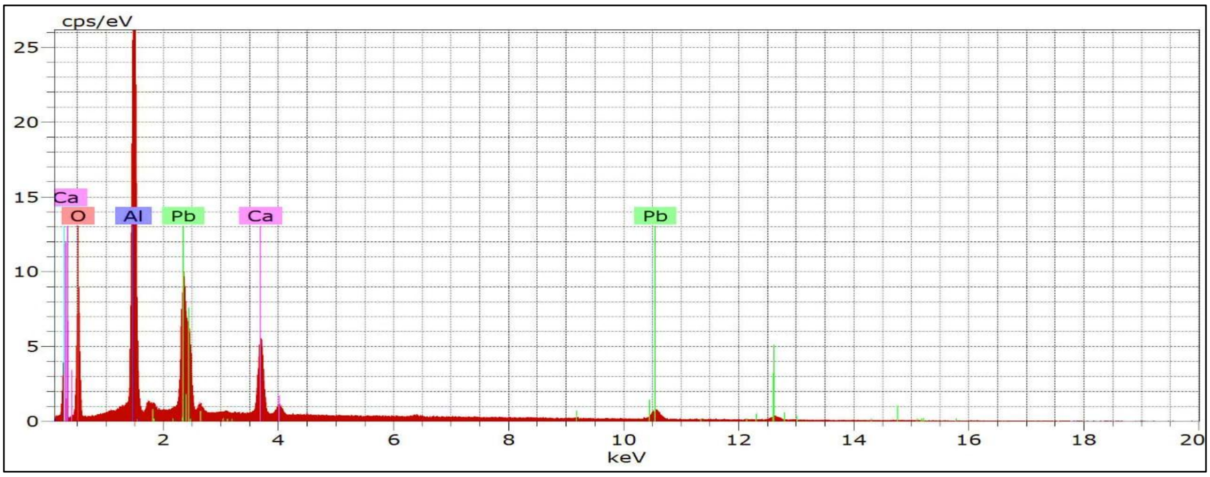

Fig 3.2: EDX of *Citrus Sinensis* plant adsorbent

3.3 XRD of Citrus Sinensis plant adsorbent

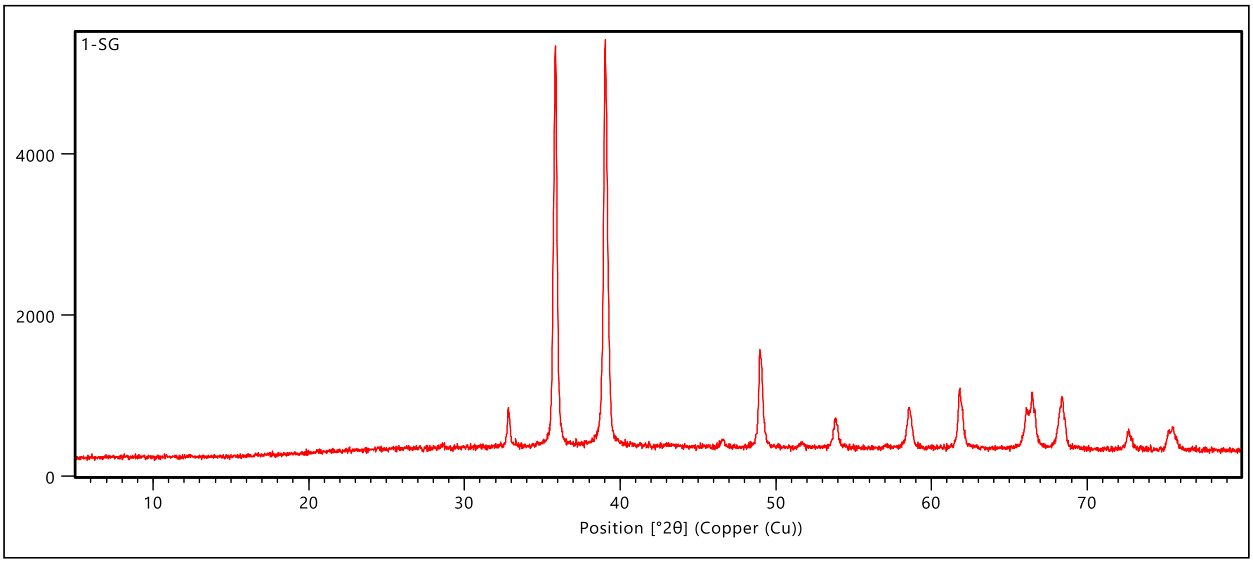

Fig 3.3: XRD of *Citrus Sinensis* plant adsorbent

3.4 Ultra violet visible spectroscopy

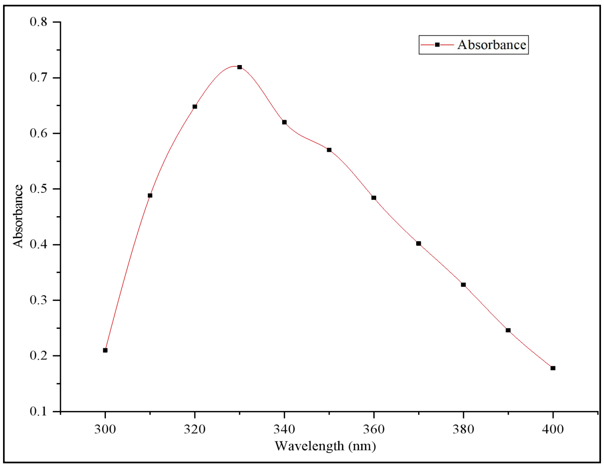

Fig 3.4.1: U.V. Visible for plant extract shows maximum absorbance

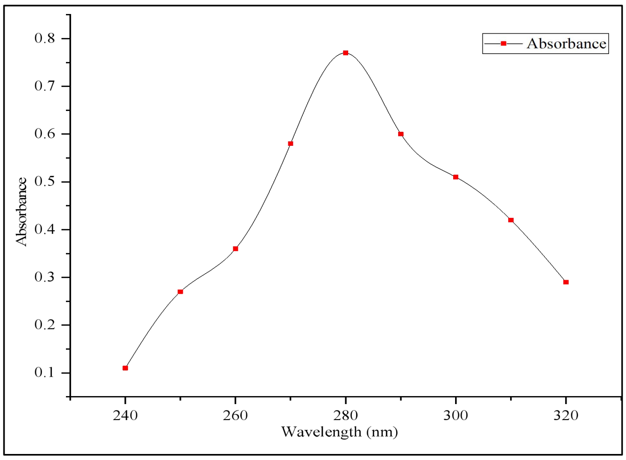

Fig 3.4.2: U.V. Visible for Lead(II) metal ion shows maximum

at 330nm absorbance at 280nm

3.5 Effect of Adsorbent dosages

In this study, after transferring 25.0 ml of nickel solution having concentration of 5.0 mg mL^{-1} is taken in100 ml Erlenmeyer flask and adsorbent dose is varied from 0.5 to 2.5 gm with keeping all other conditions constant. The outcome obtained indicates that the percentage removal of lead (II) increases with increasing *Citrus Sinensis* fruit peel (adsorbent) dose from to a maximum at 2.5 gm, beyond 2.5 g, percentage removal of lead (II) decreases slightly is shown in Figure 3.5 and Table 1. The maximum removal of lead was observed 72.0% with an adsorbent dosage of 2.5gm. It is seen that the initial increase in percentage of lead (II) may be due to increase in surface area of the sorbent, thus making it probable that the lead (II) ions are adsorbed on to the adsorption sites.

Adsorbent dose(g)	%Removal
0.5	**54.10**
1.0	**63.30**
1.5	**68.10**
2.0	**70.70**
2.5	**72.10**
3.0	**72.35**

Table 1: Effect of Adsorbent dosages

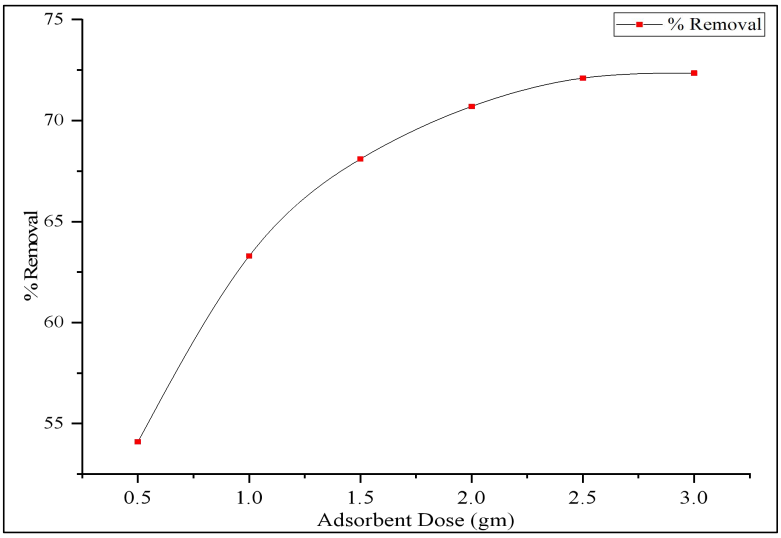

Fig 3.5: Maximum % removal at 2.5 gm adsorbent dose

3.6 Effect of Contact time

Contact time plays a crucial role in the adsorption of metal. In this study, the retention of heavy metal on the surface of adsorbent was found to be higher with increasing contact time for a fixed concentration of lead (II) 5.0 µgml^{-1} and adsorbent dose of 2.5g at 150 rpm and allowed to stand for different time intervals from 15 to 90 minutes (Figure 3.6). The lead (II) sorption increased steeply with time up to 60 minutes and afterwards showed steady adsorption rend. This may be due to the slower diffusing of solute into the interior of the biosorbent. The maximum uptake of lead (II) ions was 71.0 % was found at optimum contact time 60 minute (Table 2). The gradual increase of percentage removal of Lead (II) ions with time on the surface of *Citrus Sinensis* fruit peel powder may be attributed to the binding of those lead (II) ions which are very close to the free absorption sites on the surface of biosorbent.

Contact time (min)	% Removal
00	00
15	49.65
30	62.10
45	69.10
60	71.55
90	71.80

Table 2: Effect of contact time

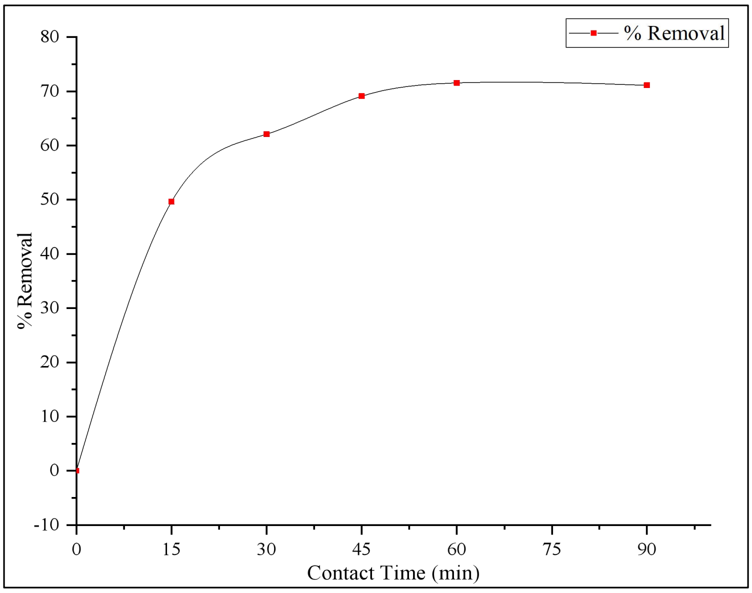

Fig 3.6: Maximum % removal at 60 min contact time

3.7 Effect of pH

The pH plays an important role on the sorption of adsorbents on the surface of adsorbate. pH is one of the most important factors that influences surface charge of the adsorbent, degree of ionization and speciation on adsorbate. In order to establish the effect of pH on the adsorption of lead (II) ion on *Citrus Sinensis* fruit peel, different pH values were carried out in the range of 4to 8 for a constant 2.5 g *Citrus Sinensis* fruit peel dose and initial metal ion concentration of 5.0 µgml^{-1} for a period of 60 minutes. It is seen (Figure 3.7) that percentage removal of lead (II) ion shows an increasing trend with increasing pH from 4 to 7. Beyond pH 7, the adsorption was not carried out due to the formation of lead hydroxide precipitate at basic medium. In this study it has been seen that with increased pH, the percentage of adsorption of lead increased from 48.20 % to 79.0 % (Table 3). At low pH, there might be occupation of the negative sites by the H^+ which gives to the reduction of the vacancies for the metal ions and it causes decrease in the metal ion adsorption.

pH	%Removal
4	48.20
5	56.30
6	65.10
7	79.00
8	66.10

Table 3: Effect of pH

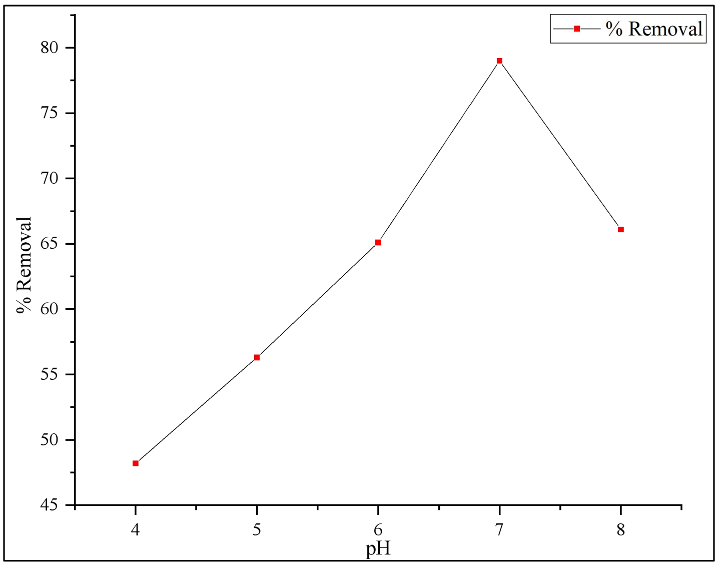

Fig: 3.7: Maximum % removal at pH 7

3.8 Effect of Temperature

Temperature is one of the most important factors for the adsorption of lead. In this study, the effect of temperature on the lead removal was studied in the range of 10-50°C with an initial metal ion concentration 5.0 mg mL^{-1} at pH 7, with 2.5 g adsorbent dose. The solutions were kept for about 60 minutes with 150 rpm shaking. The lead (II) removal increased significantly to 76.35% as the operating temperature was raised to 40°C and minimum

28.10% at 10⁰C (Figure 3.8 and Table 4). Beyond 40°C there is no increase in percentage removal of Lead. When the temperature rises, the pores enlarge and more surfaces will be available for the adsorption of lead (II) ions. At high temperature pores size changes, dissolution of lead ions and increase in intra particles diffusion it increases the adsorption of lead.

Temperature (^{0}C)	%Removal
10	28.10
20	52.30
30	63.65
40	76.35
50	65.10

Table 4: Effect of Temperature

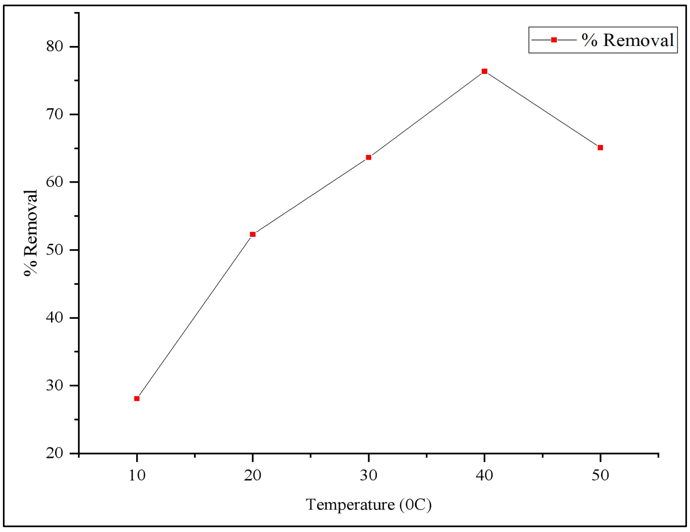

Fig: 3.8: maximum % removal at 40°C

3.9 Effect of Initial metal ion concentration

Initial concentration of metal ions is a crucial parameter as it offers the driving force for overcoming the mass transfer resistance of metal ions between the aqueous and solid phase. The lead (II) ion uptake is particularly reliant on the initial metal ion concentration. The effect of change in adsorption efficiency with initial ion concentration (Figure 3.9 and Table 5). In this experiment initial ion concentration was varied from 50 to 300 µgmL^{-1} treated with 2.5g *Citrus Sinensis* fruit peel dose, at pH 7 for 60 minutes. The graph plotted showed that the percentage adsorption of lead (II) removal using *Citrus Sinensis* fruit peel increases from 22.20 % to 83.45 % on increasing initial lead (II) ion concentration up to 50 mg mL^{-1}. The results indicate that the metal ion uptake tends to saturate as the initial concentrations increased. At higher concentration, metal ion diffuses to the adsorbent surface by intraparticle diffusion and the hydrolyzed ions diffuse at a slower rate decreasing the percentage removal.

Metal ion conc. (µgmL^{-1})	%Removal
50	22.20
100	48.70
150	55.36
200	70.45
250	74.20
300	83.40

Table 5: Effect of initial metal ion concentration

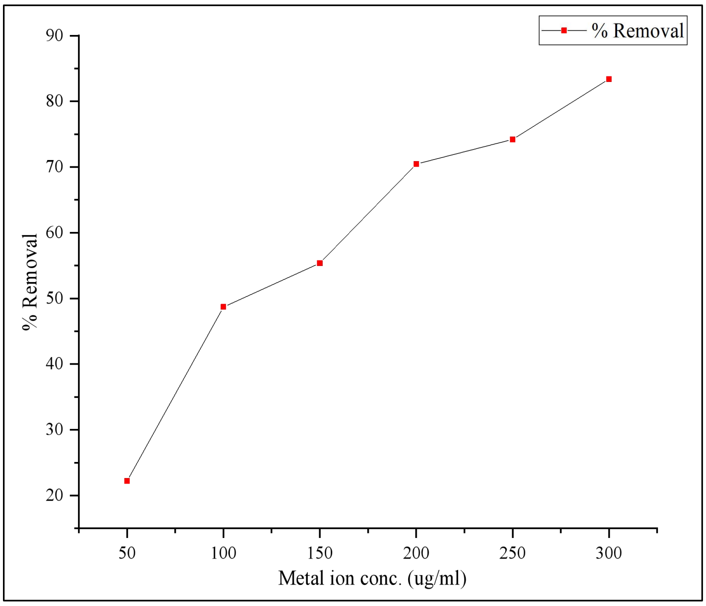

Fig: 3.9: maximum % removal at 300µg/ml

IV. CONCLUSION

The results obtained in this study, shows that lead (II) ion sorption on *Citrus Sinensis* fruit peel was significantly affected by experimental parameters. i.e. adsorbent dosage, contact time, pH of solution, temperature and initial metal ion concentration. The optimum adsorbent dose is 2.5 g whereas optimum pH found for the lead (II) ion removal is 7 Higher percentage removal of lead (II) ions is obtained by keeping the *Citrus Sinensis* fruit peel for contact time of 60 minutes at agitating speed 150 rpm. It is found that adsorption capacity increases with increasing initial metal ion concentration up to 50 µg mL^{-1} and beyond that percentage removal decreases. The endothermic nature of reaction shows that increase in temperature increases the percentage removal of lead (II)metal ion. The results obtained from FTIR spectrum of *Citrus Sinensis* fruit peel before and after lead (II) adsorption confirms that the vibrational frequencies of functional groups such as OH, -C=O, -NH present on the surface of *Citrus Sinensis* fruit peel after adsorption of lead(II) ions as compared to the vibrational frequencies that of *Citrus Sinensis* fruit peel indicated the active participation of these groups in the adsorption of lead (II) onto *Citrus Sinensis* fruit peel surface confirmed the occurrence of chemisorption's process. In this study, it is concluded that the recovery of lead (II) ions was found to be very effective using *Citrus sinensis* peel powder. As *Citrus Sinensis* has no commercial value, is easily available and its utility as an adsorbent will be economical. It can be successfully used as a low-cost environment friendly adsorbent for the removal of heavy metals from industrial waste waters.

REFERENCE

1. Pornsawai praipipat, Pimplloy Ngamsurach and Tanyaporn joraleeprasert, 2023**,** Synthesis, characterization and lead removal efficiency of orange peel powder and orange peel powder doped iron (III), oxide-hydroxide, Scientific Reports, nature portfolio, 13:10772. https://doi.org/10.1038/s41598-023-38035-7

2. Saedah R. Al- Mhyawi, Nader A.H, Abdel. T, M. EI Nashar, 2023**,** Synthesis and characterization of orange peel modified Hydrogels an Efficient Adsorbents for Methylene Blue, polymers, 15-277. https://doi.org/10.3390/polym/5020277

3. Asmaa. K, Chirangano. M, Mohamed A. Salem, Safaa. R, Ahmed EI. N, 2024, Orange peel magnetic activated carbn for removal of acid orange 7 dye from water, Nature, Scientific reports,14:119. https://doi.org/10.1038/s41598-023-50273-3.

4. Uloau M. I, Samuel J. A, Augustine O. I, Eyou. Eyo, 2023**,** Modified orange peel waste as a sustainable Material for Adsorption of contaminants, Denis A. Vinnik and Asif Afzal, 16, 1092.

5. Temilade F.A, Edwin A.D, Abideen L.A, Peter A,2020, Orange peel low-cost adsorbents in the elimination of Cd (II)ion: kinetic isotherm Thermodynamic and optimization evaluation, Akinhanmi, Bioresour, Bioprocess. https://doi.org/10.1186/540643-020-00320-Y.

6. Mayowa.J, Ningchian. F, Xueyi. G, Sha. L, Yansu. Z, 2011, Biosorption of heavy metals from aqueous solution by chemically modified orange peel, Journal of Hazardous materials, 0304-3894, 49-54. doi: https://doi.org/10.1016/j.jhazmat.2010.08.114

7. Aulia D. R, 2022, The effect of orange peel waste addition on ZnO characteristics and its ability to degrade methyl orange, Earth and Environmental Science, 1041, 012008. doi:10.1088/11755-1315/1041/1/012008.

8. Aline. H, Eliane. P. D, 2021, characterization and application of orange peel as an adsorbent for cationic dye removal from aqueous solution, REGET, Santa Maria, 2236-1170. https://doi.org/10.5902/2236117065271

9. Awash. Y, Om P.Y, and Tania. D, 2021, Waste Orange Peel Adsorbent for Heavy Metal Removal From Water, Pollution, 8(2): 553-556. doi: https://doi.org/10.22059/poLL.2021.3311561193

10. Taghried A. S, Mayasa I.A, 2016, Potential application of Natural and modified orange peel as an Eco-friendly Adsorbent for Methylene Blue dye, Iraqi Journal of Science, 0067-2904, Vol.57, 1-13.

11. Maryam. A, Seyedeh Z. M, Mohaddeseh. T, and Fatemeh. S. T, 2024, Synthesis, characterization and Biosorption ions from an aqueous solution using Bioch orange peel, Scientific Reports, Nature, 35195363. https://doi.org/10.1038/541598-024-52455-Z.

12. V. K. Gupta, Arunima. N, 2012, Cadmium removal and recovery from aqueous solution by novel adsorbent prepared from orange peel and Fe_2O_3 nanoparticles, chemical Engineering Journal, 1385-8947, 81-90. doi: https://doi.org/10.1016/j.cej.2011.11.006

13. Mazhar I. Khaskheli. Samia Q. Memon, Ali N. Siyal. M.Y, Khuhawar, 2011, Use of Waste for Arsenic Remediation of drinking water, Springer Science Business Media B.V 2:423-433. doi: https://doi.org/10.10071512649-011-9081-7

14. LIANG Sha, Guo Xue-yi, FENG. N. C, TIAN Qing-hua, 2014**,** Effective removal of heavy metal from aqueous solution by xanthate, Science Direct, 5187-5191.

15. Inioluwa C. A, Segun I. P, Olugbenga S. B, 2020, Modelling pseudo-second order kinetics of orange peel paracetamol adsorption process using artificial neural network, Journal Pre-proof ,50169-7439(20)3002-3. https://doi.org/10.1016/j.chemolab.2020.194953

16. Mohsina. A, Fouzia. M, Abu. N, 2019, Development, characterization, and utilization of magnetised waste as a novel adsorbent for the confiscation of crystal violet dye from aqueous solution, Journal Pre-proof, 52352-801 X(19) 30161-4. https://doi.org/10.16/j.95d.2019:100322

17. Xiaomin Li, Yanru Tang, Xiuju Cao, Dondan Lu, Fang Luo, Wenjing Shao, 2008, Preparation and evaluation of orange peel cellulose adsorbents for effective removal of Cadmium, Zinc, Cobalt and Nickel, Science Direct, 0927-7757, 317(2008)-517-521. doi: 10.1016/j.colsurfa.2007.11.031
18. Kharde HS, Maurya C, Aher HR. Removal of Cobalt Metal Ion from Aqueous Solution using *Punica granatum* Stem Powder as Biosorbent. J Adv Sci Res. 2024;15(4): 10-15 DOI: https://doi.org/10.55218/JASR.2024150402
19. Kharde HS, Maurya C, Aher HR, Green synthesis of charcolated adsorbent derived from *Punica grantanum* stems and its application in dye removal of methyl orange, chromoseint blue, eriochrome black -t and malachite green, J Adv Sci Res. 2023; 14 (11): 14-19, DOI: https://doi.org/10.55218/JASR.2023141103