



Abatement of Pb(II) ion from the Wastewater Using Surface Coated Activated Carbon Derived From the Bark of *Ziziphus mauritiana*: Kinetic and Equilibrium Study

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ABSTRACT

Water contamination is a major concern to human health. Most of the ground water is polluted with heavy metals, has become a serious problem today. Heavy metals are poisonous and non-biodegradable environmental pollutants that seriously threaten human health. Particularly, Pb is highly toxic and directly associated with health risks such as damage to kidney, liver and central nervous system. Thus there has been an honest deal of attention given to advance technologies for junking of heavy metal ions from contaminated water. Adsorption is one in every of the effective methods for removal of toxic heavy metal like Pb(II). In this study, the removal of Pb(II) from wastewater using chitosan based activated carbon deduced from the bark of *Ziziphus mauritiana* was estimated. The prepared chitosan coated activated carbon were verified by Fourier transform infrared (FTIR) spectroscopy, X-ray diffraction (XRD), thermogravimetric analysis (TGA) and scanning electron microscopy (SEM). The concentration of Pb²⁺ ions were measured by flame-atomic absorption spectroscopy. Batch experiments were conducted to search out the influence of operating variables like pH effect, contact time, adsorbent dosage and initial concentration. The amount of Pb(II) adsorbed was found to vary with pH of the solution and maximum adsorption was found at a pH value of 5.5. The extent of Pb(II) uptake (mg/g) was found to increase with increase in initial concentration and contact time. Equilibrium was reached at 130 min. The experimental adsorption data were fitted to the Langmuir and Freundlich adsorption model and therefore the maximum adsorption capacity (q_m) of CCZMAC was found to be 13.346 mg/g. Thus this disquisition verifies that the new advanced chitosan coated activated carbon prepared from the bark of *Ziziphus mauritiana* as valuable material used as cost effective and less energy intensive adsorbent for the removal of Pb(II) from aqueous solution and wastewater waste with none chemical treatment, creating it user friendly bio-sorbent.

Keywords: Activated Carbon, Adsorption, Bark of *Ziziphus mauritiana*, Lead, Chitosan

1. Introduction

Water and land contamination by heavy metals discharged from industrial wastes has become a global problem during the current years [1]. Water may be valuable human resource but not permanent. Now a days, the source of water for living and natural waters in developing countries is now increasing polluted, especially heavy metals contamination.[2,3,4,5]. Toxic heavy metals are one amongst the most contaminant of water resources [6]. Among the metals that are commonly released are copper, lead, zinc, silver, arsenic, antimony, iron selenium, chromium etc.[7]. Heavy metals and metalloids affects the standard of surface water and ground water resources mainly because they are non-biodegradable, toxic at low concentration and straightforward to accumulate within the tissue of assorted living organisms [8,9]. They will cause serious harm to human health from cancer to nervous system problems [10,11,12]. Lead is one amongst the foremost common and most toxic heavy metals found in industrial wastewater. Lead is a substantial heavy metal found in wastewater from the paint industry which is toxic to life, even at low concentrations, and can affect the nervous and reproductive system [13, 14]. It is released into the environment through mining, melting, galvanizing, and industrial metallurgical processes and from batteries, paints, ceramics, munitions, lead piping, etc. [15,16]. This could have serious effects on the human nervous, reproductive, and circulatory systems, kidneys, and liver, with children the foremost vulnerable to intoxication [17,18]. The maximum contaminant level as per US Protection Agency (USEPA) is 0.006 mg/L, which is far more near to mercury [19]. Thus it's necessary to review and development of sustainable technology to get rid of these pollutants have gained attention in recent years. Various technologies are employed to get rid of heavy metals from contaminated water like chemical precipitation [20,21], ion exchange [22,23], adsorption [24,25], membrane filtration [26-27], reverse osmosis [28-29], solvent extraction [30], electro dialysis and electrochemical treatment [31,32], photo catalysis [33,34]. However these methods possess some drawback like inapplicability to large scale units together with expensive energy and chemical intensiveness. The adsorption process has gained growing research interest due to its easy operation and flexibility. Biosorption is an attractive method due to large availability, low cost, operation facility and high heavy metal adsorption efficiency of the adsorbents. An outside number of researchers have tried to use conventional

and non-conventional adsorbents like carbonized biomass, un-carbonized powder biomass and activated carbon for removing lead from wastewater. Activated carbons prepared from agro-wastes are likely to possess properties cherish to those of commercially available activated carbon. Actually, agro waste from crops and fruit production may be used as best suited material for preparation of low cost activated carbon. Most researchers have tried adsorption from aqueous solution utilizing different agricultural-based biosorbents, like tangerine peels [35], green marine macro algae, *Caulerpa scalpelliformis* [36]; orange, pineapple and pomegranate peels[37]; sunflower, potato, canola and walnut shell residues[38]; almond shell [39]; walnut shell [40]; potato peel, lemon peel, orange peel, watermelon peel, tomato peel, coffee waste, apple peel, banana peel, decaf coffee waste, eggplant peel, carob peel and grape waste[41]; orange peel [42]. Activated carbons prepared from apricot stone, coconut shell, groundnut husk, pecan nut shell, *Terminalia arjuna* nuts, etc. were successfully used for water and wastewater remediation by several researchers. The present work reports the studies administered for the removal of lead from aqueous solution using activated carbon derived from bark of *Ziziphus mauritiana* on which chitosan was coated. It's one among the most important families of seed plant belong to Fabaceae family and extensively employed in Ayurveda, Unani and Haemeopathic medicine and has becomes a cynosure of contemporary medicine[43]. Chitosan, {2-acetamido-2-deoxy- β -D- glucose-(N acetylglucosamine)} a biopolymer, was chosen because it's excellent physicochemical properties. A polymeric sorbent like chitosan was used for water decontamination because it is an eco-friendly biopolymer that has attractive properties like biodegradability, biocompatibility, non-toxicity, is widely used and could be a low-cost adsorbent for metal-ion removal because of its high ratio of hydroxyl to amine groups [44,45]. The composite sorbent was characterized by FTIR and Scanning Electron Microscopy (SEM) studies. Batch isothermal equilibrium process was adopted at 308K to examine the efficiency of newly synthesized bio-sorbent for elimination of Pb⁺² from the aqueous solution. Experiments were allotted to check the effect of pH, adsorbent dosage, contact time and initial Pb⁺² concentration. The newly synthesized composite are proved to be excellent adsorbent which might be successfully used for removal of Pb⁺² from aqueous solution.

2. Materials and Method

2.1 Chemicals

The chemicals used within the research had been of analytical grade. Chitosan, lead nitrate Pb(NO₃)₂ (95%), potassium hydroxide pellets KOH (90%), and sodium hydroxide pellets NaOH (98%) were purchased from Merck (Mumbai, India). Hydrochloric acid HCl (~36%) and methanol (99.5%) have been received from Global Marketing, Nagpur (India). All reagents have been used as obtained with none in addition treatment. Deionized water become used at some stage in the experimental process.

2.2 Preparation of Activated Carbon from the bark of *Ziziphus mauritiana* (ZMAC)

The bark of *Ziziphus mauritiana* (Fig.A) was gathered from the native place. The bark was cut into small portions and washed with tap water to put off the sand debries after which dealt with formaldehyde to keep away from launch its colouration into aqueous solution. Then, it was washed numerous instances with deionized water and solar dried for 5 days. After drying, the bark changed into subjected to pyrolysis technique for carbonization the usage of Muffle Furness at 800-900^oC for 7-8 hrs in order that volatile constituents had been eliminated and residue was transferred right into a char. The char was then subjected to activation in microwave oven for 40 min. The ensuing activated carbon particles had been ground and sieved in 120-200 μ m size. This activated carbon was then washed with double distilled water and dried at 105^oC for 24 hrs and kept in air tight bottle.

2.3 Preparation of Chitosan Gel

50 g of chitosan become delivered into 900 ml of 10% oxalic acid with regular stirring. The mixture become warmed at 45 – 55^oC for homogenous mixing. The chitosan-oxalic acid mixture become formed as a whitish viscous gel.

2.4 Surface coating of ZMAC with Chitosan Gel

500 ml of Chitosan gel turned into double diluted with distilled water and warmed to 45 -50^oC. 200 g of ZMAC turned into slowly brought into diluted chitosan gel and shake using rotary shaker for 24 hr. The chitosan covered ZMAC (CCZMAC) (Fig.B) was then washed with deionized water and dried. The method was repeated 3-4 times to form thick coating of chitosan at the ZMAC surface. The coated chitosan turned into 30 to 35% by weight. Oxalic acid was quantitatively neutralized through 0.5% sodium Hydroxide solution. The solid form of CCZMAC was filtered, washed with deionized water, dried and kept in air tight container.

2.5 Characterization of CCZMAC

The structure of prepared composite became accomplished XRD. The morphology of the composite became tested with the aid of using SEM. For functional groups assessment Fourier Transform infrared (FTIR). The TGA analyses had been accomplished to screen the thermal stability of CCZMAC.

2.6 Batch Experiments of Pb(II) Adsorption onto CCZMAC

The batch experiments were performed using Flame Atomic Adsorption Spectrometry (AAS). Adsorption experiment was carried out by mixing a definite amount CCZMAC with 25 mL of Pb(II) solution in Erlenmeyer Flask. The pH of the

mixture was adjusted to the respective value of using 0.1M HCL and 0.1 M NaOH. The mixture was shaken at a definite temperature in a fixed time. The adsorbent-solution was filtered by using Whatman No.1 filter paper and the metal concentrations were analysed before and after adsorption using Atomic Absorption Spectrometer. The experiments were conducted to investigate effect of various parameters on Pb(II) adsorption onto CCZMAC namely, solution pH (2.0-9.0), contact time (10-180 min), initial Pb(II) concentration (10-100 mg/L) and adsorbent dosage (1-10 gm).

2.7 Theoretical Calculations

500 ppm solution of Pb^{2+} was prepared by dissolving the appropriate quantity of $Pb(NO_3)_2$ in deionized water. All operating solutions of the preferred concentrations have been obtained by dilution with deionized water. A calibrating curve was drawn using 5, 10, 15, 20, 25, 30, 35, 40,45 and 50 ppm solutions. Sample concentrations have been calculated in keeping with the Beer–Lambert law with reference to the standard curve.

The equilibrium adsorption potential and the percentage elimination of Pb^{2+} ions ($Re\%$) have been calculated use of Equations (1) and (2),

$$q_t = \frac{(C_0 - C_t)V}{W} \text{-----1}$$

$$R_e = \left(\frac{C_0 - C_e}{C_0} \right) \times 100 \text{-----2}$$

where q_t (mg/g) is the adsorption capacity of CCZMAC for Pb^{2+} at time t (min) and C_0 and C_e (mg/L) are the liquid phase concentrations of Pb^{2+} before and after adsorption, respectively. V (L) and W (g) are the volume of the adsorption solution and the weight of the dry adsorbent used, respectively.

2.8 Adsorption isotherms

There are numerous adsorption isotherms to be had in literature, namely: Langmuir, Freundlich, BET, Temkin, Dubinin-Radushkevitch, Hill, Redlich-Peterson and Sips [46]. But on this study, we hired handiest two, Langmuir (equation 3) and Freundlich (equation 5) isotherms as they may be the maximum typically used theoretical adsorption isotherm models. These isotherms display the impact of initial concentration of metal ions and temperature at the adsorption process. We computed the adsorption capacities at equilibrium (q_e) from Equation. (4) and (6) for Langmuir and Freundlich isotherms, respectively. To acquire this, we used 100 mL beakers to prepare 50 mL volume of Pb^{2+} ion solutions of changing concentrations, as much as the maximum initial concentration of 200 mg/L. The pH of the solution was adjusted to the maximum value of pH 6.0 with usage of 0.1 M nitric acid and sodium hydroxide solutions. We proceeded to add 10 gm of the adsorbent and dispersed it with the aid of magnetic stirring at 600 rpm for a time of 4 h. After equilibrium changed into attained, the samples had been then filtered to be able to separate the cake adsorbent from the filtrate. We went directly to decide the residual Pb^{2+} ion concentrations with the aid of using AAS in the filtrate. We then used the result generate to best fit both models as given by Equation (4) & (6) in addition to the equilibrium relationship, Eq. (7) [47]

Langmuir Isotherm equations

$$q_e = \frac{q_m b C_e}{1 + b C_e} \text{----- 3}$$

$$\frac{C_e}{q_e} = \frac{1}{q_m b} + \frac{C_e}{q_m} \text{-----4}$$

Freundlich Isotherm equations

$$q_e = K_f C_e^{1/n} \text{-----5}$$

$$\ln q_e = \ln K_f + \frac{1}{n} C_e \text{-----6}$$

Equilibrium relationship equation

$$q_e = \frac{(C_0 - C_e)V}{W} \text{----- 7}$$

In the equations(7), q_e represents the adsorbed metal ions per unit mass of adsorbent (mg/g); q_m represents the maximum adsorbed metal ions per unit mass of adsorbent (mg/g), and this is a characteristic Langmuir parameter; b represents the Langmuir adsorption equilibrium constant and is sometimes known as K_L the equilibrium constant (L/mg); K_F represents the adsorption capacity (L/mg); $1/n$ represents the adsorption intensity (g/L) which is the relative distribution of the energy and the non-homogeneity of the adsorbate sites (n is adsorption energetics).

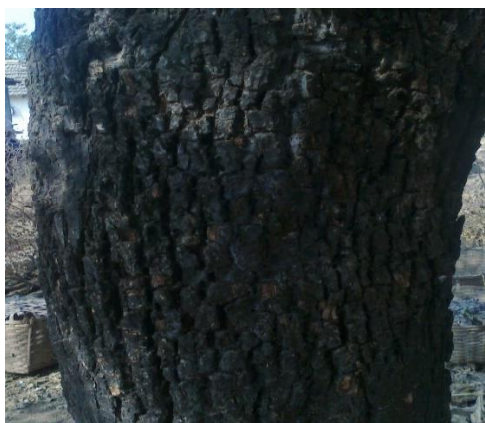


Fig. A . Bark of *Ziziphus mauritiana*



Fig. B. Chitosan Coated Activated Carbon (CCZMAC)

3 Result and Discussion

3.1 Characteristics of CCZMAC

3.1.1 The XRD Pattern of CCZMAC: Fig.1 suggest X-ray diffractographs of CCZMAC which has two diffraction peaks at 11° and 24° which suggest the crystalline nature of the material. A peak at $2\theta = 38^{\circ}$ to 39° once more proves the crystalline nature of the material. Pure chitosan additionally gives such function peak at $2\theta = 29^{\circ}$ to 30° that determine the functional properties and crystallinity of chitosan [46]. The peak area for the peak at $2\theta = 29^{\circ}$ to 30° within each the diffractogram is located to be very small.

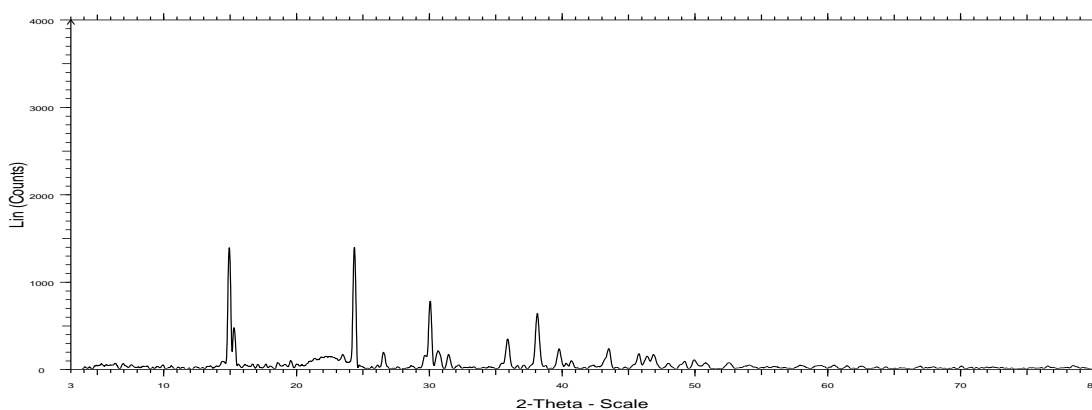


Fig. 1 X-Ray Diffraction Pattern of Chitosan Coated *Ziziphus mauritiana* Activated Carbon (CCZMAC)

3.1.2 FTIR Studies: Fig.2. FTIR spectrum of ZMAC is shown in Fig1. A band at 3442.21cm^{-1} is connected with $-\text{OH}$ stretching band. The $-\text{OH}$ groups are seem to be associated by means of hydrogen bonds, as the band for hydroxyl group not involved in hydrogen bonding usually appears as a sharp band located above 3500cm^{-1} . The band for $-\text{OH}$ stretching in the range below 3700cm^{-1} was assigned by Zawadzki. A band at 1633.75cm^{-1} is indicative of $\text{C}=\text{O}$ stretching in aldehyde or ketone (carbonyl group). The sufficiently lowering in the band position suggest that $\text{C}=\text{O}$ group may also involved hydrogen bonding. It is because of the reason that the intra-molecular hydrogen bonded structure is stabilized by the phenomenon of resonance. The peak at 1084.14cm^{-1} is suggestive of ortho- substitution. Low band at 565.20cm^{-1} is evidence of C-I stretching vibration.

3.1.3 SEM images of CCZMAC is given in Fig.3. SEM image has been obtained using an accelerating voltage of 20kV at X1500 magnification. High magnification SEM micrographs clearly reveal that the wide varieties of pores are present on the surface of Chitosan coated *Ziziphus mauritiana* activated carbon (CCZMAC) accompanied with fibrous structure. It can also be noticed that there are holes and cave type openings on the surface of the adsorbent, which would have created more surface area available for adsorption. The size of holes and caves was found to be in the range 1- $10\mu\text{m}$.

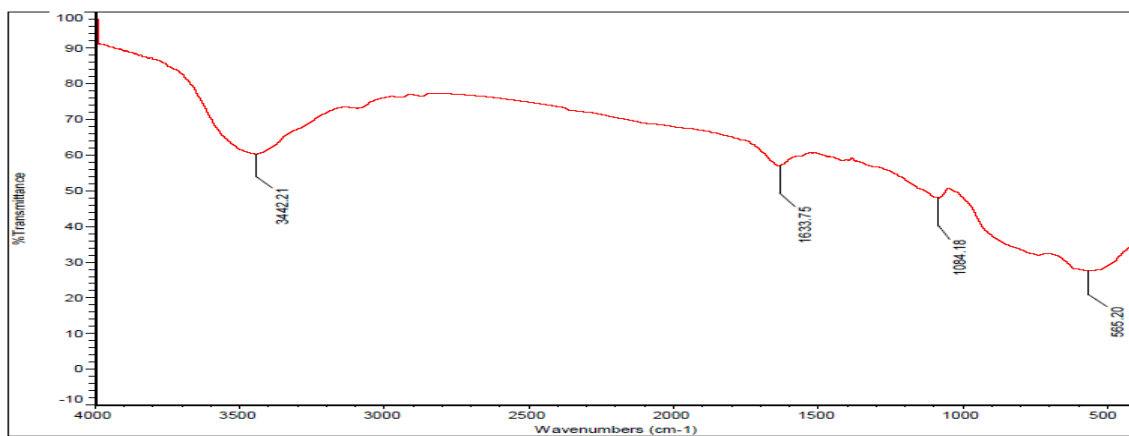


Fig.2. FTIR Spectrum of Chitosan Coated *Ziziphus Mauritiana* Activated Carbon (CCZMAC)

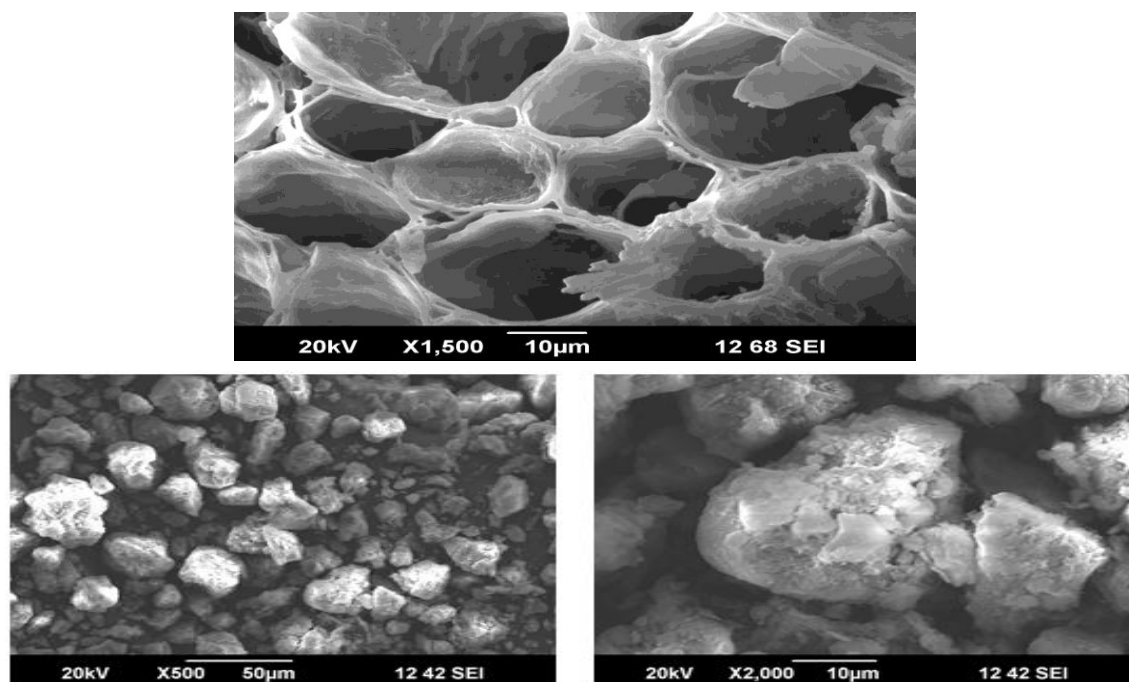


Fig. 3 SEM image of Chitosan Coated *Ziziphus Mauritiana* Activated Carbon (CCZMAC)

3.1.4 T.G curve of CCZMAC is represented in **fig. 4**. The first derivative peak is at very low temperature 62⁰C corresponding to the weight loss 5.90% of the material. This is may be the loss of water molecules loosely bounded on the surface of CCZMAC. The weight loss of 7.0% at 100⁰C represented the evaporation of moisture from the surface of the adsorbent. There is no weight loss between the temperature range of 100⁰C to 650⁰C shows the adsorbing material is thermally stable. But, at temperature 683.68⁰C, weight loss was found to be maximum i.e. 25% which is degradation of chitosan composite and other organic molecules.

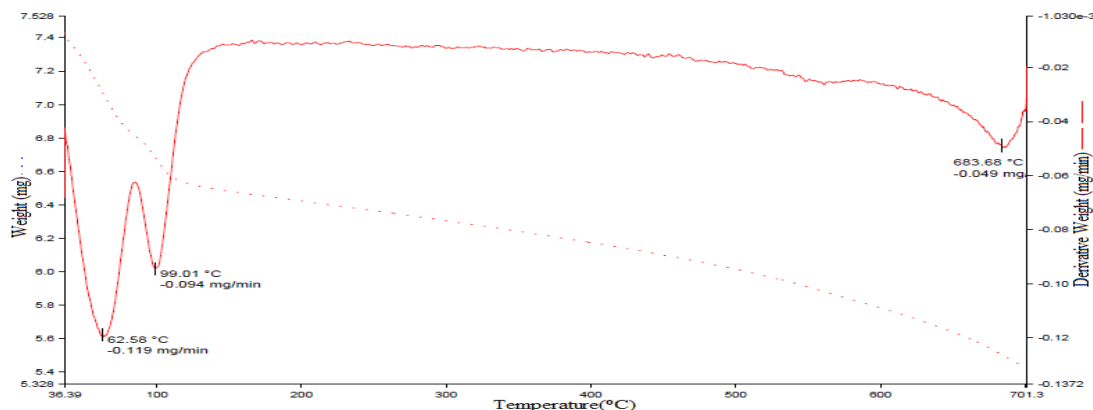


Fig.4. TG Curve of Chitosan Coated *Ziziphus Mauritiana* Activated Carbon (CCZMAC)

3.2 Adsorbent Dosage: Figure 5 shows the impact of adsorbent dose on the surface assimilation of CCZMAC for Pb²⁺ elimination. The proportion removal efficaciousness of Pb(II) by CCZMAC considerably will increases with the rise in dose of CCZMAC over the vary 1-12 g/L and therefore the maximum removal efficiency of Pb(II) ion i.e. 94.7% occurred at the adsorbent dose of 10 g/L. It might be explained as increasing CCZMAC dose, the active sites offered for biosorption of Pb(II) increased and consequently most removal of Pb(II) take place. An extra increase of dose over 10 g /L didn't result in associated degree considerable increase of removal efficiencies. This result might be explained that the overlapping or aggregation of active sites at higher dose and decreasing in total sorbent surface area. Therefore, the maximum CCZMAC dose was 10 g/L .

3.3 pH effect : The adsorption of any significant heavy metals is considerably plagued by the pH of the solution, since it determines adsorbent properties like surface charge likewise because of the adsorbate evolution and degree of ionization in aqueous solutions. The result of pH of the solution on the Pb(II) removal was observed with pH varying from 1 to 10 and are represented in Figure 6. The Pb(II) adsorption from aqueous solution could keen about the pH value. It's ascertained that a gradual rise in the percentage of removal potency came about with a rise in pH from 1.0 to 7.0 and decreased slightly at the pH > 6.0 . The maximum percentage removal efficiencies of CCZMAC occurred at pH 5.5 and reached 94.6 % . It was well known that at lower pH, concentration of H⁺ in the solution is extremely high and therefore the functional groups in adsorbent surface were protonated. Hence, Pb(II) ion adsorption was hindered due to the competition between H⁺ and Pb²⁺ for the adsorption sites on the surface of the adsorbent. At higher pH (> pH 6), the concentration of H⁺ in the solution low adsorption capability was decreased therefore the functional groups in adsorbent surface were deprotonated. Thus, additional Pb(II) ions were absorbable because of less competition between H⁺ and Pb²⁺. Thus adsorption capability was decreased. This is often principally because of the formation of hydroxyl radical metal complexes when Pb(II) began to precipitate.

3.4 Effect of contact time on Pb(II) removal : The Result of contact time on Pb(II) removal is allotted in fig.7 It's indicated that, the Pb(II) removal efficiencies of CCZMAC increased quickly with increasing the contact time and reached the utmost and equilibrium set at 130 min. Initially biosorption of Pb(II) by CCZMAC was very fast and 75% of Pb(II) ions were adsorbed within 80 min. The equilibrium sorption was established after 130 min where the Pb(II) removal efficiencies increased up to 94.60% for CCZMAC. It showed no vital sweetening of removal potency with increasing contact time (>120 min). Initially speedy uptake of Pb(II) ion due to the availability of unoccupied binding sites on the surface of adsorbent to interact with Pb(II)ion. As contact time extended, the sorption sites were majorly lined, decreasing the chance of Pb(II) ions to react with the functional groups on the adsorbent. Therefore equilibrium is reaching, the saturated binding sites didn't facilitate the Pb(II) adsorption associate degree virtually constant adsorption capability.

3.5 Effect of initial concentration: The initial metal ions concentrations Pb(II) in solution play a significant role as a good driving force in conquest mass transfer resistance of metal ions between the solution and adsorbent . As illustrated in Figure 8, that the percentage removal of Pb(II) attenuated from 94.60 to 69.4 for CCZMAC because the Pb(II) ion concentrations were raise from 5 to 275 mg/L . At lower Pb(II) concentration, most Pb(II) ions might bind on the adsorbent surface as there's an oversized magnitude relation of accessible surface assimilation site between Pb(II) present in the solution. As the initial Pb(II) concentration increased, the magnitude relation of unoccupied binding site is obtaining smaller whereas the lower removal of Pb(II) at high concentration could also be due to the dearth of accessible active sites on the surface of CCZMAC.

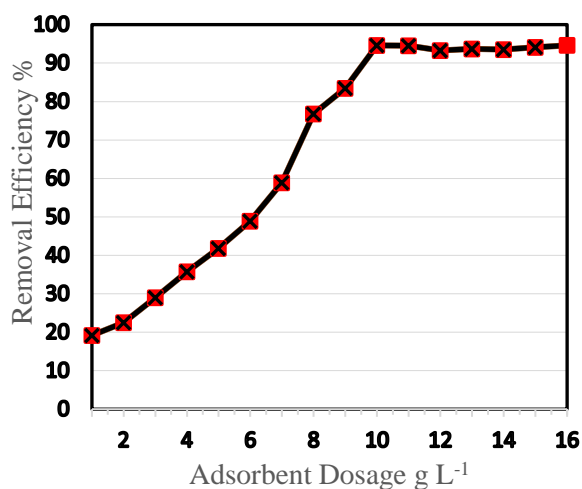


Figure 5 Effect of Adsorbent Dosage

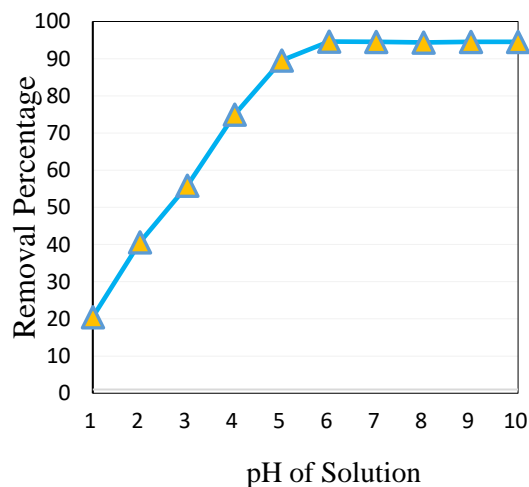


Figure 6 pH effect on Pb(II) adsorption

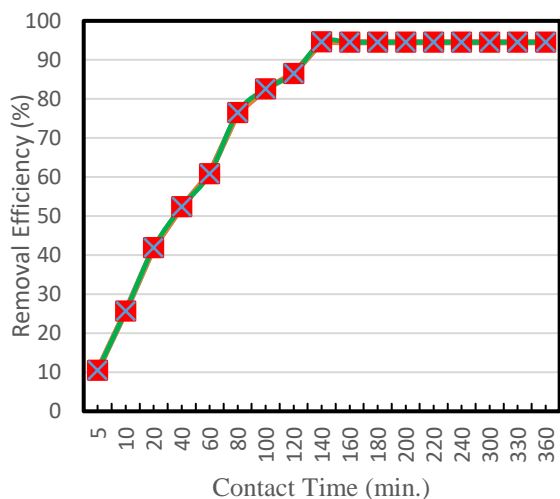


Fig. 7. Effect of Contact Time

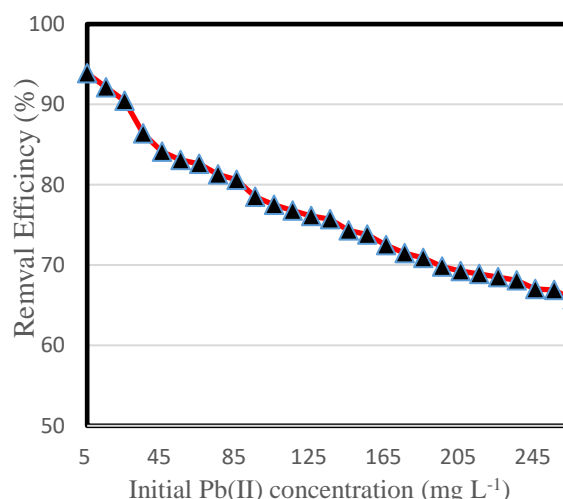


Fig. 8 Effect of concentration on Pb(II) adsorption

3.6 Adsorption Isotherm: Langmuir and Freundlich isotherms are used to explain the mechanism of adsorption and therefore the relationship between the number of adsorbed metal ion and also the concentration of metal ion remained in solution.

3.6.1 Freundlich Adsorption Isotherm: The Freundlich model proposes an adsorption process that happens in multiple layers on a heterogeneous surface, and it also assumes that the adsorption capacity depends on the concentration of the sorbate in solution. The sorption capacity increases because the concentration increases. In the present study, the Freundlich equation is utilized for the adsorption of Pb(II) on the adsorbents i.e. CCZMAC and equilibrium data were well fitted in the linear plots of $\log Q_e$ versus $\log C_e$ as shown in Figure 9. The values of adsorption capacity ' k_F ' and intensity of adsorption ' n ' were evaluated at 30°C for CCZMAC. The value of ' k_F ' for CCZMAC was found to be 3.110 mg/g. Quite higher values ' k_F ' suggestive of accumulation number of adsorbate molecules (liquid phase) found in larger surface area of adsorbent (solid phase). The values of ' n ' which provides idea about intensity of adsorption were found to be 2.15 for CCZMAC. The values of ' n ' obtained are in good agreement of the adsorption favourable. The square of the coefficient of correlation (R^2) values were found to 0.986 which means the most effective fitting of Freundlich isotherm for the adsorption system under investigation.

3.6.2 Langmuir Adsorption Isotherm:

Langmuir adsorption isotherm assumes that each one available adsorption active sites are similar, the adsorbable species doesn't interact, and a monolayer is created during adsorption. The linear style of the Langmuir isotherm was applied for calculation of the corresponding parameters, given in Table 1. The linear plots of C_e/Q_e versus C_e for the adsorbents suggests the relevancy of the Langmuir isotherms represented diagrammatically in Figure 10. The values of ' Q_m ' and ' K_L ' were determined from slope and also the intercept of the plots. The coefficient of correlation (R^2) values were found to be 0.991 which indicates the best fitting of Langmuir isotherm. The adsorption efficiency ' Q_m ' value was found to be 13.346 mg/g for CCZMAC. The value of adsorption energy ' K_L ' CCZMAC was found to be 0.5070. Hence, it is often concluded that the most adsorption corresponds to a saturated monolayer of adsorbate molecules on the adsorbent surface. The constant adsorption energy values suggest that there is no transmission of the adsorbate in the plane of adsorbent surface. The favourability of the adsorption process, the separation factor ' R_L ' values were calculated and was found in between 0 to 1 which suggest confirmation regarding favourable adsorption process. It was concluded that the two models were reasonably suitable for describing adsorption. However, the Freundlich equation provided an improved fit than the Langmuir equation. The value of K_F indicated moderate affinity for Pb^{2+} . Freundlich model is additionally characterized by the heterogeneity factor $1/n$ i.e. $0.1 < 1/n < 1.0$ indicates good adsorption of Pb(II) ions onto CCZMAC. From the isotherm data in Table 1, it implies that the Freundlich model well fit the adsorption, suggesting a chemical adsorption process, as indicated by the n value 2.15, the heterogeneity factor.

Table No.1 Langmuir and Freundlich isotherm parameters for Pb²⁺ adsorption on CCZMAC

Adsorbent	Freundlich				Langmuir			
	n	1/n	K_F (mg/g)	R^2	Q_m (mg/g)	K_L	R^2	R_L
CCZMAC	2.15	0.465	3.110	0.986	13.346	0.5070	0.991	0.197

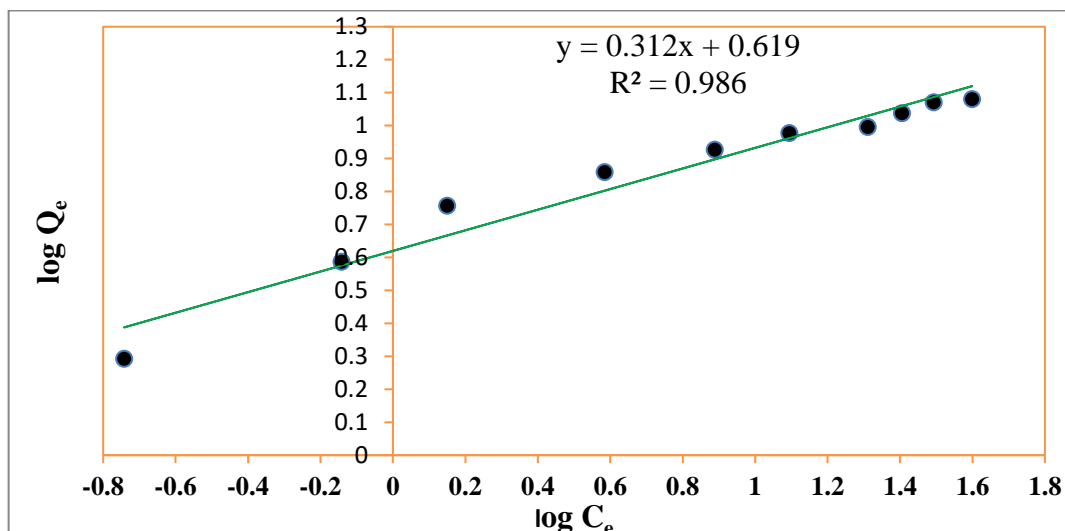


Fig.9 Freundlich Isotherm for the adsorption of Pb(II) on CCZMAC

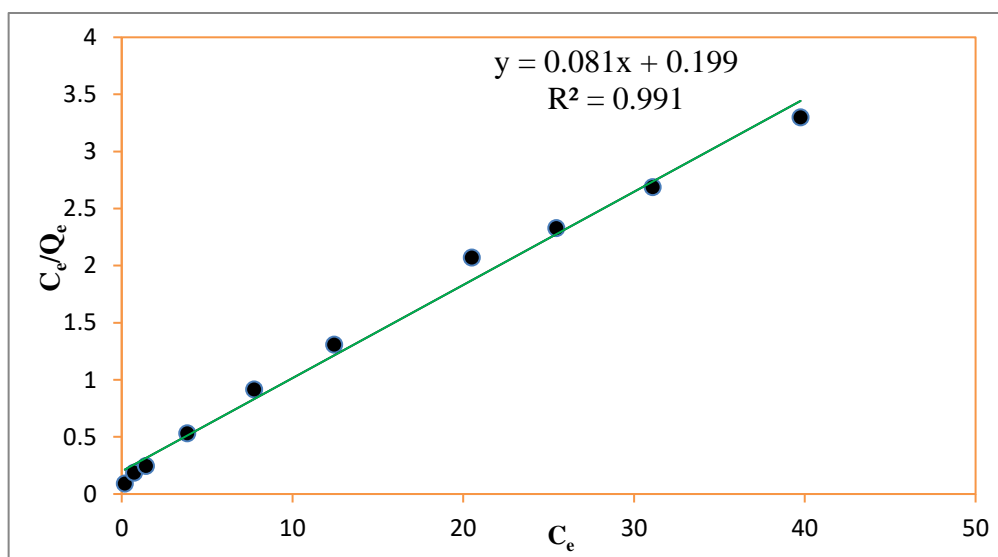


Fig.10 Langmuir Isotherm for the adsorption of Pb(II) on CCZMAC

Conclusion

The study indicate that the activated carbon successfully prepared from the bark of *Ziziphus mauritiana*.

- The Surface coating of recently prepared activated carbon with Chitosan was successfully done and will act as an effective and potentially low-cost adsorbent for lead removal from aqueous solution
- The CCZMAC were with success characterized by X-ray diffraction, Fourier-transform infrared, scanning electron microscopy and thermal analysis.
- Batch studies were carried out under different conditions like dose of adsorbent, pH of solution, initial Pb(II) concentration and contact time to judge the adsorption potency of Pb(II) ions on CCZMAC.
- The adsorption of Pb(II) on CCZMAC was found to be pH-dependent. The best removal potency 94.66% was obtained at pH 5.5. The initial concentration of the Pb(II) ion in solution was found to possess a pronounced result on the adsorption method.
- Kinetic experiments proved that the removal potency of Pb(II) ion from aqueous solutions was speedy and equilibrium was achieved at intervals 130 min
- The adsorption equilibrium of Pb²⁺ was satisfactorily described by both the Langmuir and Freundlich equations along the studied concentration range, with better correlation to the Freundlich isotherm. The most adsorption (qm) calculated from the Langmuir equation was 13.346 mg/g.

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Reference

- [1] J. Ocreto, C. I. Go, J. C. Chua, C. J. Apacible, and A. Vilando, "Competitive effects for the adsorption of copper, cadmium and lead ions using modified activated carbon from bamboo," *MATEC Web of Conferences*, vol. 268, Article ID 6021, 2019.
- [2] Minh T.D., Lee B.K., Ternary cross coupled nanohybrid for high efficiency 1H-benzo[d]imidazole, Chemisorption', *Env. Sci. & Pollution Res.*, vol.25 (22), pp.21901-21914, 2018
- [3] Minh T.D., Lee B.K., Linh P.H., 'Highly efficient removal of emerging organic compound 1,3 benzodiazole using novel triangular coordination of magnetic polymer nanohybrid [C₂H₅OH]-MNPs@Y-APTEs@GO', *Research on Chemical Intermediates*, vol.44 (11), pp.6515-6536, 2018
- [4] Minh T.D., Lee B.K., Nguyen M.T., 'Methanol dispersed of ternary Fe₃O₄@Y-APS/GO based nanohybrid for novel removal of benzotriazole from aqueous solution', *J. of Management*, vol.209, pp. 452-462, 2018
- [5] Minh T.D., Lee B.K., 'Effect of functionality and textural characteristics on the removal of Cd(II) by ammoniated and chlorinated nanoporous activated carbon', *Journal of Material Cycles and Waste Management*, vol.19(3), pp.1022-1037, 2017
- [6] Yang J., Hour B., Wang J., Tian B., Bi J., Wang N., 'Nanomaterials for the removal of heavy metals from waste water', *Nanomaterials*, 9, 424, 2019
- [7] Akcil A., Koldas S., 'Acid Mine Drainage (AMD): Causes, treatment and case studies, *J.Clean. Prod.*, 14, 1139-1145, 2006
- [8] Carolin C.F., Kumar P.S., Saravanan A., Joshiba G.J., Naushad M., 'Efficient technique for removal of toxic heavy metals from aquatic environment : A review', *J. Environ. Che. Eng.*, 5, 2782-99, 2017
- [9] Vardhan K.H., Kumar P.C., Panda R.C., 'A review on heavy metals pollution, toxicity and remedial measures: Current trends and future Perspective', *J. Mol. Liq.*, 290, 111-197, 2019
- [10] Visa M., Synthesis and Characterization of new zeolite materials obtained from fly ash for heavy metals removal in advanced waste water treatment, *Powder Technol.*, 294, 338-347, 2016
- [11] Malik A., Metal bioremediation through growing cell, *Environ. Int.*, 30, 261-278, 2004
- [12] Ziagova M., Dimitriadis G., Aslanidou D., Papaioannou X., Litopoulo U., Tzannetaki E., Liakopoulou- Kyriakides M., 'Comparative Study of Cd(II) and Cr(VI) biosorption on *Staphylococcus xylosum* and *Pseudomonas* sp. Single and binary mixture', *Bioresour. Technol.* Vol.98, pp. 2859-2865, 2007
- [13] E. Bernard, A. Jimoh, and J. Odigure, "Heavy metals removal from industrial wastewater by activated carbon prepared from coconut shell," *Research Journal of Chemical Sciences*, vol. 2231, p. 606x, 2013.
- [14] M. Sobh, M. A. Moussawi, W. Rammal et al., "Removal of lead (ii) ions from waste water by using lebanese cymbopogon citratus (lemon grass) stem as adsorbent," *American Journal of Phytomedicine and Clinical @erapeutics*, vol. 2, pp. 1070–1080, 2014.
- [15] Wongrod, S.; Simon, S.; Guibaud, G.; Lens, P.N.L.; Pechaud, Y.; Huguenot, D.; van Hullebusch, E.D. Lead sorption by biochar produced from digestates: Consequences of chemical modification and washing. *J. Environ. Manag.*, 219, 277–284, 2018
- [16] Seema, K.M.; Mamba, B.B.; Njuguna, J.; Bakhtizin, R.Z.; Mishra, A.K. Removal of lead (II) from aqueous waste using (CD-PCL-TiO₂) bio-nanocomposites. *Int. J. Biol. Macromol.*, 109, 136–142, 2018
- [17] Beltrame, K.K.; Cazetta, A.L.; de Souza, P.S.C.; Spessato, L.; Silva, T.L.; Almeida, V.C. Adsorption of caffeine on mesoporous activated carbon fibers prepared from pineapple plant leaves. *Ecotoxicol. Environ. Saf.*, 147, 64–71, 2018
- [18] Sone, H.; Fugetsu, B.; Tanaka, S. Selective elimination of lead(II) ions by alginate/polyurethane composite foams. *J. Hazard. Mater.*, 162, 423–429, 2009
- [19] Tanveer Mahamad Ali Shaikh, 'Adsorption of Pb(II) from wastewater by natural and synthetic adsorbents', *Biointerface Research in Applied Chemistry*, Volume 10, Issue 5, pp.6522 – 6539, 2020
- [20] Byambaa, M.; Dolgor, E.; Shimori, K.; Suzuki, Y. Removal and Recovery of Heavy Metals from Industrial Wastewater by Precipitation and Foam Separation Using Lime and Casein. *Journal of Environmental Science and Technology*, 11, 1-9, 2018
- [21] Eltarahony, M.; Zaki, S.; Abd-El-Haleem, D. Aerobic and anaerobic removal of lead and mercury via calcium carbonate precipitation mediated by statistically optimized nitrate reductases. *Scientific Report*, 10, 4029, 2020
- [22] Lai, Y.C.; Chang, Y.R.; Chen, M.L.; Lo, Y.K.; Lai, J.Y.; Lee, D.J. Poly(vinyl alcohol) and alginate crosslinked matrix with immobilized Prussian blue and ion exchange resin for cesium removal from waters. *Bioresource Technology*, 214, 192–198, 2016
- [23] Lalmi, A.; Bouhidel, K.A.; Sahraoui, B.; Anfif, C.H. Removal of lead from polluted waters using ion exchange resin with Ca(NO₃)₂ for elution. *Hydrometallurgy*, 178, 287-293, 2018
- [24] Novais, R.M.; Buruberri, L.H.; Seabra, M.P.; Labrincha, J.A. Novel porous fly-ash containing geopolymer monoliths for lead adsorption from wastewaters. *J. Hazard. Mater.*, 318, 631–640, 2016
- [25] Alghamdi, A.A.; Al-Odayni, A.B.; Saeed, W.S.; Al-Kahtani, A.; Alharthi, F.A.; Aouak, T. Efficient Adsorption of Lead(II) from Aqueous Phase Solutions Using Polypyrrole-Based Activated Carbon. *Materials*, 12, 2020, 2019

- [26] Landaburu-Aguirre, J.; Pongracz, E.; Peramaki, P.; Keiski, R.L. Micellar-enhanced ultrafiltration for the removal of cadmium and zinc: Use of response surface methodology to improve understanding of process performance and optimization. *J. Hazard. Mater.*, 180, 524–534, 2010
- [27] Rahmanian, B.; Pakizeh, M.; Esfandyari, M.; Heshmatnezhad, F.; Maskooki, A. Fuzzy modeling and simulation for lead removal using micellar-enhanced ultrafiltration (MEUF). *J. Hazard. Mater.*, 192, 585–592, 2011
- [28] Petrinic, I.; Korenak, J.; Povodnik, D.; Helix-Nielsen, C. A feasibility study of ultrafiltration/reverse osmosis (UF/RO)-based wastewater treatment and reuse in the metal finishing industry. *Journal of Clean Production*, 101, 292–300, 2015
- [29] Yoon, J.; Amy, G.; Chung, J.; Sohn, J.; Yoon, Y. Removal of toxic ions (chromate, arsenate, and perchlorate) using reverse osmosis, nanofiltration, and ultrafiltration membranes. *Chemosphere*, 77, 228–235, 2009
- [30] Lertlapwasin, R.; Bhawawet, N.; Imyim, A.; Fuangswasdi, S. Ionic liquid extraction of heavy metal ions by 2-aminothiophenol in 1-butyl-3-methylimidazolium hexafluorophosphate and their association constants. *Sep. Purif. Technol.*, 72, 70–76, 2010
- [31] Ferniza-García, F.; Amaya-Chávez, A.; Roa-Morales, G.; Barrera-Díaz, C.E. Removal of Pb, Cu, Cd, and Zn Present in Aqueous Solution Using Coupled Electrocoagulation-Phytoremediation Treatment. *International Journal of Electrochemistry* 2017, 2017,
- [32] Zhang, J.; Li, Y.; Xie, X.; Zhu, W.; Meng, X. Fate of adsorbed Pb(II) on graphene oxide under variable redox potential controlled by electrochemical method. *J. Haz. Mat.*, 367, 152-159, 2018
- [33] Mimouni I., Bouzuani A., Naciri Y., Boujnah M., El Beghiti M.A., El Azzouzi M., ‘Effect of heat treatment on photocatalytic activity of α -Fe₂O₃ nanoparticles toward diclofenac elimination’, *Envi. Sci.,Poll. Res.*, vol.29.pp.7984-7996,2021
- [34] Naciri Y., Hsini A., Bouziani A., Djellabi R., Ajaml Z., Laabd M., ‘Photocatalytic oxidation of pollutants in gas phase via Ag₃PO₃- based semiconductor catalyst: Recent Progress, new trends and future perspective’, *Crit. Rev. Environ. Sci. Technol.* 1-44, 2021
- [35] Abdic , S., Memic , M., Sabanovic , E., Sulejmanovic , J. & Begic , S., ‘Adsorptive removal of eight heavy metals from aqueous solution by unmodified and modified agricultural waste: tangerine peel’. *Int. J. Environ. Sci. Technol.* 15, pp. 2511–2518,2018
- [36] Jayakumar, V., Govindaradjane, S. & Rajasimman, M., ‘Efficient adsorptive removal of zinc by Green marine macro alga *Caulerpa scalpelliformis* – characterization, optimization, modelling, isotherm, kinetic, thermodynamic, desorption and regeneration studies’. *Surf. Interfaces* 22, 100798,2021
- [37] Turkmen Koc, S. N., Kipcak, A. S., Derun, E. M. & Tugrul, N. 2020 Removal of zinc from wastewater using orange, pineapple and pomegranate peels. *Int. J. Environ. Sci. Technol.* Available from: <https://link.springer.com/article/10.1007/s13762-020-03025-z>.
- [38] Feizi, M. & Jalali, M., ‘Removal of heavy metals from aqueous solutions using sunflower, potato, canola and walnut shell residues’. *J. Taiwan Inst. Chem. Eng.* 54, 125–136,2015
- [39] Coruh, S., Geyikci, F., Kılıç, E. & Coruh, U., ‘The use of NARX neural network for modelling of adsorption of zinc ions using activated almond shell as a potential bio sorbent’. *Bioresour. Technol.* 151, 406–410, 2014
- [40] Segovia-Sandoval, S. J., Ocampo-Pérez, R., Berber-Mendoza, M. S., Leyva-Ramos, R., Jacobo-Azuara, A. & Medellín-Castillo, N. A., ‘Walnut shell treated with citric acid and its application as biosorbent in the removal of Zinc(II)’. *J. Water Process. Eng.* 25, 45–53, 2018
- [41] Massimi, L., Giuliano, A., Astolfi, M. L., Congedo, R., Masotti, A. & Canepari, S., ‘Efficiency evaluation of food waste materials for the removal of metals and metalloids from complex multi-element solutions’. *Materials.* 11(3), 334, 1–15,2018
- [42] Santos, C. M., Dweck, J., Viotto, R. S., Rosa, A. H. & Morais, L. C., ‘Application of orange peel waste in the production of solid biofuels and biosorbents’. *Bioresour. Technol.* 196, 469–479, 2015
- [43] Kumar, C.S.; Bhattacharya, S., ‘Tamarind Seed: Properties, Processing and Utilization’. *Critical Reviews in Food Science and Nutrition.* 48, 1-20,2008
- [44] Mashile, G.P.; Mpupa, A.; Nqombolo, A.; Dimpe, K.M.; Nomngongo, P.N. Recyclable magnetic waste tyre activated carbonchitosan composite as an effective adsorbent rapid and simultaneous removal of methylparaben and propylparaben from aqueous solution and wastewater. *J. Water Process Eng.* 33, 101011,2020
- [45]Zhang, Y.; Xue, Q.; Li, F.; Dai J., Removal of heavy metal ions from wastewater by capacitive deionization using polypyrrole/chitosan composite electrode. *Adsorpt. Sci. Technol.* Vol.37 (3-4), pp.205-216, 2019.
- [46] Kegl T., Kosak A., Obnik A., Novak Z., Kovac Kralj A., Ban I., Adsorption Of rare earth metals from wastewater by Nanomaterials: A Review., *J. Hazard. Mater.*, vol. 386, 1211632, 2020
- [47] El AILA H.J., Elsousy K.M. Hartany K.A., Kinetics, Equilibrium and isotherms of the adsorption of cyanide by MDFSD, *Arab. J. Che.*, vol.9, pp S198-S203,2006
- [48]Trang S.T., Wah W.T., Nguyen T.Q., Chuen H.N., Wellem F.S., Functional Characteristics of Shrimp Chitosan and its membranes as affected by the degree of deacetylation, *Bioresources Technology*, 97,pp.659-663, 2006