DETERMINATION AND QUANTIFICATION OF HEAVY METAL IONS USING NATURAL WASTE AS ADSORBENT

M.Sc. Dissertation report by:

VEDA R. PEDNEKAR

SCHOOL OF CHEMICAL SCIENCES

GOA UNIVERSITY

GOA 403206

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DETERMINATION AND QUANTIFICATION OF HEAVY METAL ION USING NATURAL WASTE AS ADSORBENT

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By

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To the

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Goa 403206

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CERTIFICATE

This is to certify that the dissertation entitled **"DETERMINATION AND QUANTIFICATION OF HEAVY METAL IONS USING NATURAL WASTE AS AN ADSORBENT" is bonified work carried out by MISS VEDA RAGHUNATH PEDNEKAR of M.SC. (Analytical chemistry) under my supervision in partial fulfilment of the requirement for the award of degree of Masters of Science in Chemistry at School of Chemical Sciences, Goa University.**

Dr. Rupesh Patre
Guiding teacher,
School of chemical sciences,
Goa University.

Dr. V. Verenkar
Dean of SCS Goa University

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Abstract

The use of natural waste material as an adsorbent is encouraging due to their contribution in reduction of waste disposal costs.

Different techniques are used for trace analysis of inorganic metal ions. These techniques are atomic absorption spectroscopy, spark source, inductively coupled plasma, thermal ionization source. The natural waste material which we are using as an adsorbent is washed thoroughly with the water to remove dirt and impurity, then washed with the deionized water, then dry it and crushed to fine powder. This powder is then heated in oven at higher temperature to have the active sites on the adsorbent for adsorption. The commonly used procedure for removing metal ion from effluent include chemical precipitation, membrane filtration, coagulation, lime coagulation, ion exchange and solvent extraction. The ability of adsorbent to bind with heavy metal ion is depend on different mechanism which include chemisorption, complexation, adsorption complexation on surface and pore, ion exchange, surface adsorption. Adsorption efficiency depends on adsorbent concentration, temperature, pH, contact time initial concentration. The natural waste as a adsorbent, discussed in this literature survey are pomegranate peel, saw dust and neem bark, citrus lemon peel, meranti sawdust, olive mill waste, bagasse fly ash moringa olifera seed pods, rice husk, lignin, cassava root husk, date palm, Mango peel waste, chemically modified orange peel, wild herbs, persimmon leaf bio-waste, chili seed, palm kernel shell, banana peel tea waste and citrus sinensis peel.

INRODUCTION

[1]Adsorption is mass transfer process that involves accumulation of substances at interface of two phases or a separation technique from which target elements of liquid phase are shifted to solid surface.

[2]Heavy metal contamination into aqueous media and in industrial effluents is a major ecological problem due to their toxic nature and accumulation of these metal ions into the food chain. Heavy metals are not biodegradable and tend to accumulate in living organism, and many of them are known as carcinogenic. Toxic heavy metals of particular concern in treatment of industrial waste waters which include copper, nickel, mercury, cadmium, zinc, lead and chromium. The industrial sources of commonly encountered heavy metals are refineries, coal-fired power plants, and municipal waste water for mercury , mining operations, tanneries and electronics for copper , cadmium nickel batteries , phosphate fertilizers , pigments and stabilizers for cadmium. Etc. Among all of these metals' cadmium, arsenic and mercury are considered to be the most toxic "Big Three" category of heavy metals with the greatest potential hazard to humans and the environment. Hence these heavy metals can cause irreparable damage to natural environment and human health and further, these toxic effluents pose a major t[1]hreat to the surrounding ecosystem if left untreated.

[3]Removing heavy metals from waste water via adsorption method is an efficient process. Heavy metals are usually important toxic pollutants. In the adsorption process, activated carbon is commonly used adsorbent as it has a high capacity for adsorption. However, activated carbons are expensive and the industries begin to look for cost-efficient adsorbent. Various researcher has discovered and discussed the potential adsorbents produced from agriculture products and waste. Conventional technologies are generally complex and expensive, time consuming.

[4]When natural organic materials are used as adsorbents process is called biosorbents. Biosorbents are waste organic material. Lignocellulosic waste material are suitable adsorbents for removal of heavy metal ions from waste water or water as they are cheap and further treatment is simple and economic.

[5]The aim of our work was to investigate removal of some heavy metal ions from aqueous solution using different kinds of natural waste. The technique as gain attention for treatment of industrial waste water mainly owing to low cost, bulk availability of bio-adsorbents, metal selectivity, easy metal recovery, higher heavy metal uptake and reuse.

A Techniques for removing heavy metals using natural waste as adsorbent

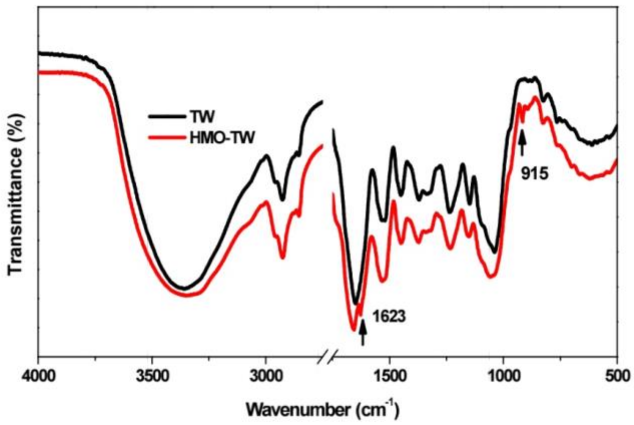
1. Pomegranate peel

[6]Musaab K. Rashed, Wissam Tayh (2020) studied the use of pomegranate peel as the adsorbent to remove the metal ions such as Cu(ll), Cd(ll) and Zn(ll). Pomegranate peel was washed to remove the impurity and dirt, then was dried and crushed to form powder. This powder was then heated at higher temperature to provide the active site for adsorption. pomegranate peel was proven to be effective adsorbent and a dose of 30g/L has efficiency in removing Cu, Zn and Cd ion at room temperature 25°C and pH 5 to 6. Cu ion also has similar trend in removal despite of reduction of adsorbent dosage from 30g/L to 20g/L removal percentage was low for Cd (13%) and Zn (16%) when adsorbent dose was manipulated. Removal efficiency increase by increasing adsorbent dose. This increase is attributed to increase in surface area and increase in interaction. Pomegranate peels is inexpensive adsorbent used for removing heavy metal ion Cu>Cd>Zn. Percentage of removal obtained was 80% for Cu^{+2}, 50.5% for Cd^{+2} and 32.5% for Zn^{+2} by using 30g/L adsorbent dose in 1000 ppm. Solution concentration under acidic pH was (5-6) at room temperature 25°C.Optimum contact time was 1 hr for both single and mixed ion solution. As the number of mixed ions increase, percentage of ion removal was decrease. Removal percentage of mixed ions were relatively low, resulting from competition and interaction between the ions.

2. Tea waste

[7]V. Online, N. Qu, M. Wang et al. (2015) studied the use of tea waste by modifying with hydrated manganese oxide for the removal of Pb(ll), Cd(ll), Cu(ll) and Zn(ll). Tea waste was modified by deposition of hydrated manganese oxide onto it through in situ precipitation. Successful deposition of hydrated manganese oxide on tea waste was confirmed by transmission electron microscope and fourier transform infrared spectroscopy. Metal ion concentration was determined by flame atom adsorption spectroscopy and adsorption of all the samples were tested in triplicate. An atom fluorescence spectrophotometer was used to determine metal ion concentration. FT-IR spectra of hydrated manganese oxide tea waste was taken before and after metal adsorption and results indicate that adsorption of hydrated manganese oxide was done on tea waste. SEM images indicate that pore on tea waste was wide and spread before loading of hydrated manganese oxide and loading the pores became tiny and dense. The loaded hydrated manganese oxide amount was 4.82(w/w)% in Mn mass, while no Mn was found in supporting tea waste. The maximum adsorption occurs at pH 2-7. The sorption process reached equilibrium within 200 minutes. The maximum adsorption capacity of Pb(ll), Cd(ll) , Cu(ll) and Zn(ll) were 174.3, 78.38, 54.38 and 37.5mg/g respectively. Hydrated manganese oxide provide better selectivity for heavy metal ions against competing metal ions present in water such as Ca(ll) and Mg(ll). The adsorption selectivity order was Pb(ll)> Cd(ll)> Zn(ll). The presence of co-ion in solution decrease the removal efficiency <25% of Pb(ll) and Cu(ll) whereas for Cd(ll) and Zn(ll) decrease by 60%.

The adsorption capacity of Cu(ll) is higher than Cd(ll) and Zn(ll) ,as Cu(ll) has highest hydration energy and lowest ionic radius which suggest lowest ion exchange and and weakest hydrated manganese oxide -Cu interaction. The tea waste without modification selectivity for adsorption is not so strong with modification gives better results. Pb(ll) , Cd(ll) and Zn(ll) sorption capacity of unit mass Mn for hydrated manganese oxide-tea waste were 3616.2, 1626.1 and 778 mg/g resp. And for pure hydrated manganese oxide was 710.1, 304.1 and 117.7mg/g resp. Improvement of Mn utilization efficiency can be attributed to dispersion of hydrated manganese oxide on tea waste which increased the binding sites of hydrated manganese oxide.



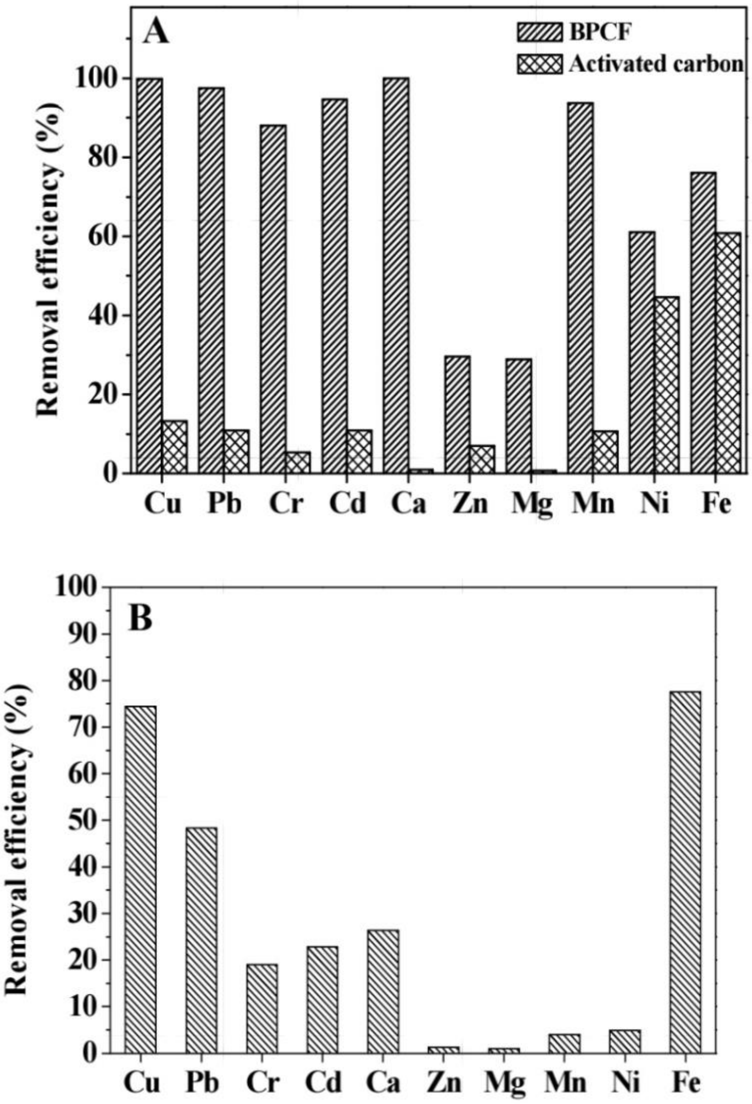
(b)

FT-IR spectrum of Tea waste (TW) and hydrated manganese oxide on tea waste (HMO)

3. Banana peel

[8]V. Online. J. Liu, H. Tang, et al. (2016) studied the banana peel carbon foam for removal of Cu(ll) ,Pb(ll), Cd(ll) and Cr(vl)ions. Banana peel was processed by simple calcination treatment and foam like carbon material was obtained.SEM studies show that material has porous structure EDS results suggest that mechanism involve was ion exchange process. FTIR result indicate that O-H and C-O groups are present. Banana peel carbon foam has more number of hydroxyl and carboxyl group which imply that banana peel carbon foam has capacity of sorbing great amount of heavy metal than the commercial carbon. Equilibrium time to remove Cu(ll), Pb(ll), Cd(ll) and Cr(vl)ions using adsorbent was 5 minutes. At pH 2 the minimum adsorption was seen for Cr(vl). Then adsorption increased from pH 2 -4 . The maximum adsorption was seen at this pH range. There are a 3 hydrate form of Cr(vl) which are existing in aqueous solution when pH value was lower than 6.8 including chromate, dichromate and hydrogenchromate. These 3 ions are negatively charged which is unfavourable to bind with deprotonated carboxyl and hydroxyl groups in banana peel carbon foam owing to electrostatic repulsion.The size of Cr(vl) hydrate is larger than that of free

metal ions and therefore they have difficulty in getting through the pores. Thesefact will reduce the adsorption of banana peel carbon foam toward Cr(vl). At adsorption equilibrium at concentration of 5mg/L the removal ratio for Cu(ll), Pb(ll), Cd(ll) and Cr(ll)ions are 92.05%, 9.35%, 91.89% and 82.88% resp. The removal ratio of above 4 metals using banana peel carbon foam was 98% at contact time of 1hr. The maximum adsorption capacity for Cu(ll) ,Pb(ll), Cd(ll) and Cr(ll)ions were found to be 49.5, 45.6 30.7 and 25.2 mg/g resp. Which are higher than other adsorbents derived from banana peel which are mentioned in literature. The efficiency of 98% using the banana peel carbon foam was determine at the contact time of 1hr.The removal efficiency for 10 types of metal ions are 1.3 to 98.6 times higher then those by using commercial activated carbon. Among these removal efficiency for Cu(ll) ,Pb(ll), Cd(ll) and Cr(ll)ions in this research is 7.5 , 8.9 , 8.7 and 16.6 times higher than that of commercial activated carbon respectively.



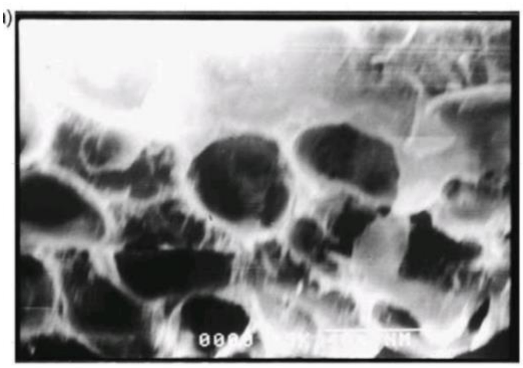
(A) The comparison of banana peel carbon foam and commercial activated carbon for metal ion removal.

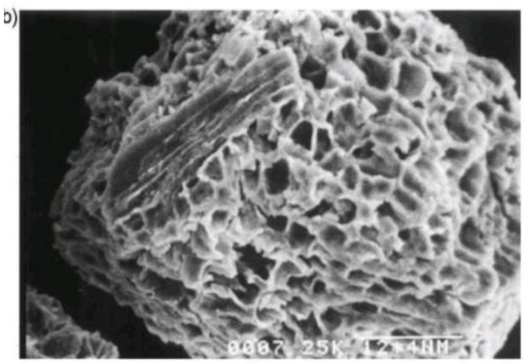
(B) The adsorption behavior of banana peel carbon foam for metal ions under the coexistence of various metal ions.

4. Saw dust and Neem bark

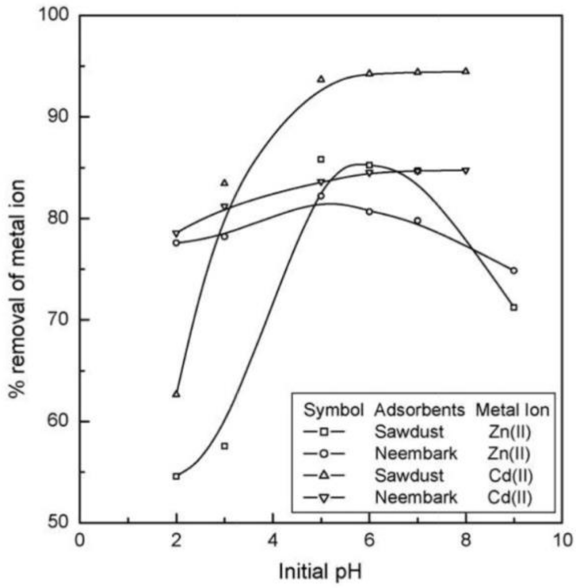
[9]S. Das (2008) had studied saw dust and neem bark as a adsorbent to remove Zn(ll) and Cd(ll) from aqueous solution. SEM studies indicate that adsorbent has a irregular and porous surface. Saw dust and neem bark are cellulose-based material which contain tannin and lignin based organic compound. Fourier transform infrared spectroscopic studies were done at 4000-400 nm range, which suggest saw dust and neem bark has several functional group such as carboxylic acid, amine, amide and sulphonate groups and these are responsible for binding process. At low pH due to high positive charge density on the surface sites, electrostatic repulsion between metal ion and H+ ion will be high during the uptake of metal ion which results in lower removal efficiency. Whereas with increase in pH electrostatic repulsion decreases due to reduction of positive charge density of proton on the sorption sites which results in an enhancement of metal adsorption. The optimum pH value for adsorption of Zn(ll) was 5 and Cd (ll) was 6 by saw dust and neem bark. The removal percentage efficiency was 85.8% and 94.25% for Zn (ll) and Cd (ll) by saw dust. Whereas in case of neem bark the removal percentage efficiency was 82.2% for Zn(ll)

And 84.5% or Cd(ll) adsorption while maintaining the pH values. The maximum removal efficiency was achieved at an adsorbent dose of 10g/L for both the metal ions , which then consider as a optimum adsorbent dose level. With increase in adsorbent dose more surface area is available for adsorption that is due to increase in active sites on adsorbent. The Removal of Zn(ll) was 85.76% and 81.6% for saw dust and neem bark resp. while maintaining the optimum adsorbent dose that is 10g/L, whereas for Cd(ll) it was 94.5% and 84.5% for saw dust and neem bark resp. For saw dust equilibrium time was 3hr for both Zn(ll) and Cd(ll) adsorption. In case of neem bark time required for equilibrium is 3 hr for Zn(ll) and 4 hr for Cd(ll).





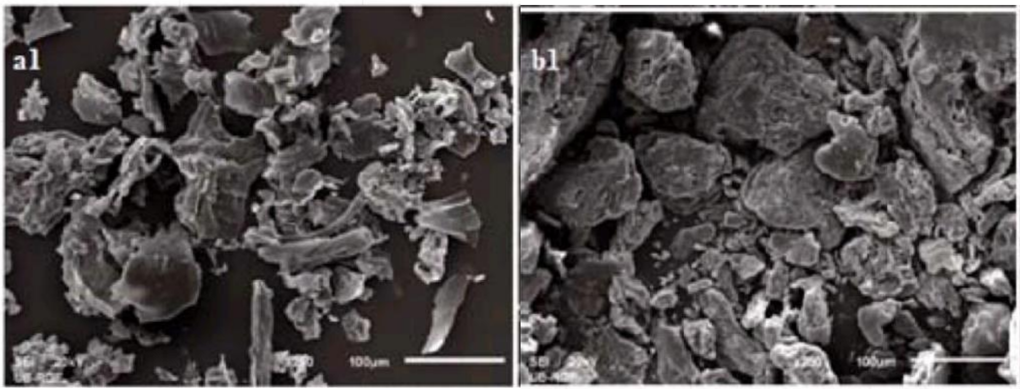
SEM micrograph of Saw dust SEM micrograph of Neem bark



Effect of pH on adsorption of Zn(ll) and Cd(ll). Experimental conditions were contact time 5hr, adsorbent dose10mg/L , initial concentration. For Cd(ll) 10mg/L, Zn(ll) 25mg/L.

5. Citrus lemon peel

[10]E. Sabanovi, M. Mermi, J. Sulrjmanovi et al.(2020) studied the lemon peel as a adsorbent to remove heavy metal from waste water. New lemon peelbased bio-massed material was prepared and was characterized by infrared spectroscopy with Fourier transformation (FTIR), scanning electron microscopy, electron dispersive spectroscopy. Quantification was done by atomic absorption spectroscopy.To enhance the biosorption characteristic of lemon peel different modification were applied.The modification made the material more alkaline and negatively charged which make better affinity to bind with positively charged metal ion. From FTIR it was concluded that metal ions were incorparated with the modified lemon peel vi interaction with COO^- and OH^-.SEM-EDS analysis shows that modification results in removal of smaller particles of native material, thereby making the surface of biosorbent the functional group active for binding of ions. At pH 5 the main group responsible for metal sorption which was seen from FTIR of lemon peel are protonated due to high concentration of H^+ species. Above pH 5 was not tested in the risk precipitation or hydrolysis. At pH 5 it show highest removal efficiency for all the ions Cd(ll), is 36.40 % , Co(ll) is 12.24%, Cr (lll) is 68.46%, Cu(ll) 81.73%, Mn (ll) is 12.40%, Ni(ll) is 17.35% and Pb(ll) is 87.45.The optimal contact time was 60 minutes at room temperature with 300mg/5mL. The adsorption capacity obtained was 46.77mg/g. High removal efficiency was seen at initial minutes followed by a gradual stabilization.



SEM images of lemon peel a1) modified b10 modified sorbent loaded with metals

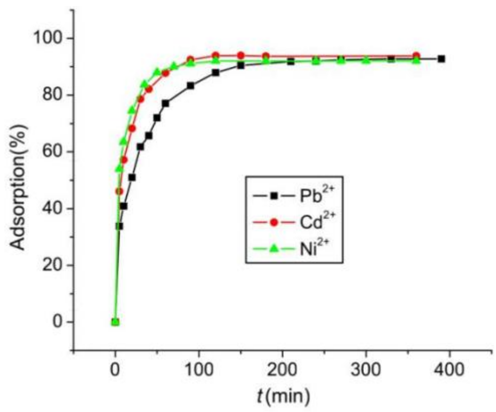
6. Meranti sawdust

[11]M. Rafatullah , O. Sulaiman , R. Hashim, A. Ahmad. (2012) studied the use of Meranti sawdust for adsorption of Cu (ll), Ni (ll), Cr(ll)and Pb (ll) ions from aqueous solution. Removal of different metal ions occurred in 20 minutes and no appreciable changes in terms of removal were noticed after 120 minutes. The adsorption rates were initially high which is probably due to availability of larger surface area of sawdust for adsorption of these ions. As surface adsorption sites become exhausted, rate of uptake is controlled by rate of transport from exterior to interior sites of adsorbent particles.The uptake of Cu(ll),Cr(ll), Ni(ll) and Pb(ll) ions depends on pH, it increase with increase in pH reaching maximum adsorption at pH 6 . On higher pH values slight decrease of adsorption for Cu(ll) , Cr (ll), Ni(ll) and Pb(ll) ions was observed. Ion exchange and hydrogen bonding may be the principal mechanism for removal of heavy metal. At pH value lower than 3, adsorption capacities were found to be low due to competitive adsorption of Ho_3^+ ions and metal ions for same active adsorption site.At higher pH value than 6 metal precipitation appeared and adsorbent was deteriorated with accumulation of metal ions , therefore pH 6 was selected to optimum pH . The adsorption of Cu (ll) by Meranti sawdust increase 65% to 89% ,C(ll) increase from76% to 94% ,Ni (ll) increase from 73% to 97% and Pb(ll) increase from 76% to 96% respectively, by increase sawdust dosage from 2 to 10 g/L under equilibrium condition. Increase in adsorption percentage is due to increase in adsorbent and thus making easy penetration of metal ions to sorption sites. It can be concluded that Meranti sawdust is a suitable adsorbent for removal of Cu(ll) , Cr (ll), Ni(ll) and Pb(ll) ions from aqueous solutions in terms of low cost, natural and abundant availability.

7. Chemically modified orange peel

[12]N. Feng, X. Guo, S. Liang et al.(2011) studied orange peel and co-polymerization modified orange peel to remove Pb(ll) ,, Cd(ll) and Ni (ll) ions from waste water.The orange peel contain high content of cellulose , pectin ,hemicellulose and lignin. Modification is done to enhance adsorption capacity and adsorbent stability of the component present in biomass. As

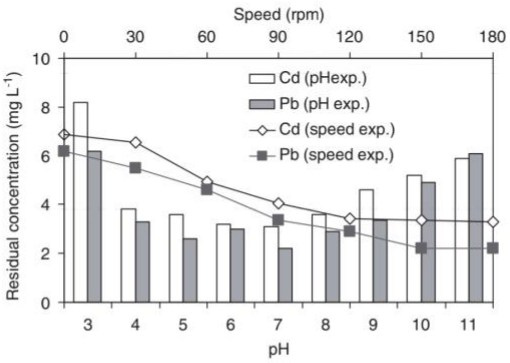
the adsorption of metal ions takes place only on the biomass surface , increasing the active sites on the surface would increase the adsorption capacity.By introducing the functional group on the biomass surface by grafting of long polymer chain onto biomass surface via direct grafting or polymerization of monomer would increase the adsorption capacity. co-polymerization modified orange peel as a biosorbent is prepared from orange peel by means of hydrolysis of grafted copolymer, which was then synthesized by interacting methyl acrylate with cross-linking orange peel. This modification was done to check if it is able to remove the metal ions. The minimum biosorption occurred at pH 2 due to fact that high concentration and high mobility of H^+ ion, H^+ ions are adsorbed rather than metal ions. At high pH values low concentration of H^+ ions and greater number of ligand with negative charge are present which results in greater metal ion biosorption. The amount of biosorption sharply increase with increase in contact time. At first from 0-30 minutes there is a sharp increase and after that there is a gradual increase to reach a equilibrium value that is 150 minutes. The shaking time was fixed that was 3 hr. The recovery of co-polymerization modified orange peel was made with the help of 25 mL of 0.05 mol/L HCl . co-polymerization modified orange peel can be used three times without any loss in biosorption capacity for Pb(ll) , Cd(ll) and Ni(ll) ions. FTIR spectrum of co-polymerization modified orange peel indicate that carboxyl and hydroxyl groups were present in abundance. FTIR spectra also indicate that peaks are shifted due to Pb(ll) , Cd(ll) and Ni (ll) ions biosorption. These shifts are attributed to changes in counter ions associated with carboxylate and hydroxylate anion suggesting that acidic, carboxyl and hydroxyl are predominent contributors in metal ion uptake.The maximum uptake capacities for Pb(ll) , Cd(ll) and Ni (ll) ions were 476.1, 293.3 and 162.6 mg/g. Removal of Pb(ll) , Cd(ll) and Ni (ll) ions from aqueous solution by co-polymerization modified orange peel was found to be effective compared to the unmodified orange peel . compared to the unmodified orange peel biosorption capacity of modified orange peel increased 4.2, 4.6 and 16.5 fold for Pb(ll) , Cd(ll) and Ni (ll) ions resp.That was due to superior ion exchange capacity and chelating capacity of co-polymerization modified orange peel because of increase in number of carboxyl group after grafting compared to unmodified orange peel .So co-polymerization modified orange peel is more efficient compared to unmodified orange peel for removing metal ions.



Biosorption of Pb(ll), Cd(ll) and Ni(ll) ions

8. Olive mill waste

[13]G. Martinez-Garcia, Robert Th. Bachmann. Ceri J. Williams, Andrea Burgoyne, Robert G.J. Edyvean (2006) studied the use of olive mill waste from two-decanter olive oil production system for removal of metal ions by biosorption. Olive mill waste can be use in repeated generation cycles for adsorption of heavy metals from aqueous solution. Uptake from single metal ion solution of initial concentration of 10mg/L . Lead was the most effectively adsorbed with about 75% removed whereas aluminium showed poorest adsorption. Molar adsorption capacity increase with the atomic weight of element. Olive mill waste have the affinity in terms of metal uptake from solution in the following order: Pd>Cd>Cu>Hg>Fe>Al. Metal ion adsorption performance olive mill waste does not seems to be good for Cd and Cu. The optimum pH value is between pH 4 and 7. Most of particle have average size that varies from 50 to 200 micrometer. Even with no agitation biosoption still occurred. Increasing speed of agitation enhanced degree of biosorption. About 60rpm was sufficient for mixing. In case of Pb no further removal was found after 150 rpm. In case Cd solution agitation at 120 rpm was found to be optimal. For satisfactory metal ion removal biomass should be agitated at 120 rpm or greater. The maximum uptake for lead solution takes place at pH 7 in 10mg/L of lead solution and for cadmium it is pH 6 in 10mg/L of cadmium solution. Below pH 3 it is too acidic for biosorption to take place.When there are more than one metal in the solution adsorption capacity decrease. Olive mill waste did not perform well compared to other biomass still removal Cd and Pb reached acceptable levels of around 80% and 75%, resp.



The effect of agitation speed and pH on the adsorption of Pb and Cd from 10mg/L initial solution concentration.

9. Moringa olifera seed pods

[14]Irene Wangari Maina , Veronica Obuseng, Florence Nareetsile (2017) studied the use of powdered Moringa olifera seed pods as a adsorbent to remove Pb, Cu, Cd, Zn and Fe ions from waste water. Scanning electron microscopy provide the information of sample surface topography and composition. SEM results showed that high metal removal due to available

binding cavities for the metal ions.The efficiency of sorbent mainly depend on number of pores , pore size and surface area.Fourier transform infrared spectroscopy gives the information that OH, C-H of alkenes ,C=C alkenes and C-O from carboxylic acids are responsible for metal removal in Moringa olifera seed pods. The particle with higher surface area and having many pores is expected to be more efficient for metal ion removal. The percentage efficiency of Moringa olifera seed pods increased with time and subsequently reached a constant value at the optimal time where no more ions were adsorbed from the solution. By keeping all other factors (time ,temperature , metal concentration , sorbent dose and particle size) constant there is increase in pH increased the percentage removal of the selected metal ions using Moringa olifera seed pods . pH 8 was taken as optimum pH. At lower concentration , percentage removal was higher due to larger surface area of adsorbent being available for adsorption.When the concentration of ions increase , percentage removal decrease due to decrease in available sites for adsorption which is as the result of saturation of adsorption sites. The adsorption capacity of large particle is low whereas the adsorption capacity of small particle is greater as a higher surface area.100 micrometer was taken to be optimal particle size. 35°C is used as optimum temperature, 60 minutes is optimum contact time and1g is optimum biomass dosage.The removal efficiency trend was Pb>Fe>Cu>Cd>Zn under optimized parameter.The percentage removal efficiency of Fe, Cu, Cd ,Zn and Pb ions using Moringa olifera seed pods was found to be 99,98.7 ,72.5, 65.9 and 99.6 resp. Quantification of the extracted metal ions was done using flame atomic adsorption spectroscopy (FAAS).

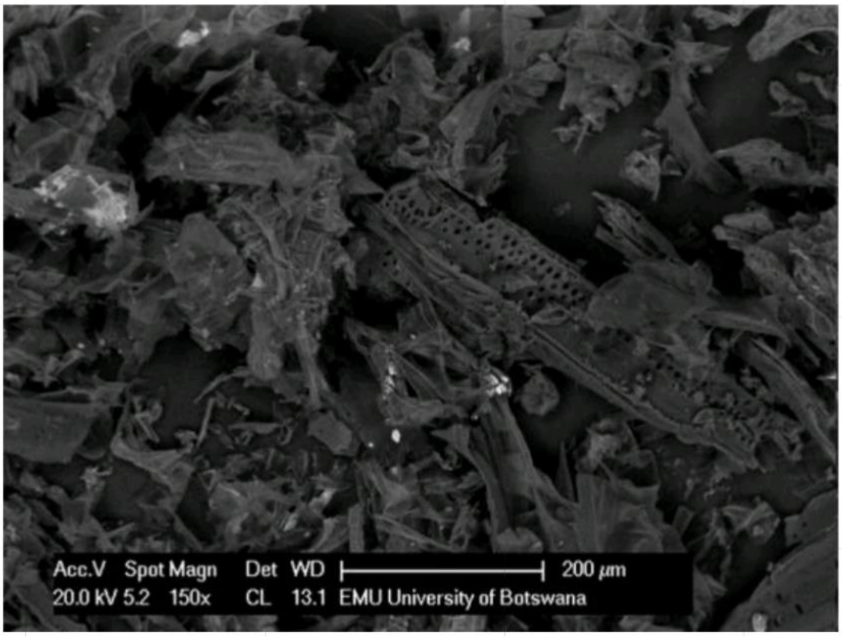


Fig. 1: SEM image of Moringa Oleifera seed pods (MOSP)

10. Lignin

[4]Xueyan Guo , Shuzhen Zhang, Xiao-quan Shan(2008)studied the adsorption heavy metal ions Pb(ll), Cu(ll),Cd(ll), Zn(ll) and Ni(ll) on a lignin isolated from black liquor , a waste product of he paper industry. Lignin has affinity with metal ions in the following order : Pb(ll)> Cu(ll)>Cd(ll)> Zn(ll) >Ni(ll).Lignin surface contain two main types of acid sites attributed to carboxylic - and phenolic- type surface groups and phenolic sites have a higher affinity for metal ions than the carboxylic sites. The cation exchange capacity of lignin was 23.9cmol/kg . The average pore diameter was 147.6 A° and the specific surface area of lignin was 21.7m^2/g as measured by the N_2-BET method.The surface was not high as expected ,probably due to BET measurement method we use which has been demonstrated not to quantitatively detect inner surface area of some sorbent, resulting in lower specific surface area values. The difference in physical and chemical properties of lignin from different origins and extraction or isolation technology used may also contributed to lower specific surface area to some extent.The FT-IR spectrum of lignin indicate that signal assigned to carboxyl groups showed low intensity, but high intensities were observed at 1217 and 1514 cm^{-1} , indicating the phenolic units were more abundant then carboxyl groups in the lignin. The adsorption equilibrium is reached with minimum contact time of 20 minutes. The maximum equilibrium adsorption capacity was obtained found for Pb(ll), (0.432mmol/g), which decrease to 0.360mmol/g for Cu (ll), 0.226mmol/g for Cd(ll) , 0.172mmol/g for Zn(ll) and 0.102mmol/g for Ni(ll). Metal adsorption was strongly pH dependent and increased with increased in pH. At pH 4 over 81% of Pb(ll) and 65% of Cu(ll) were absorbed, while less than 27% of Cd(ll) , Zn (ll) and Ni(ll) were adsorbed. When the pH was higher than 6 more than 85% of the metal ions were adsorbed on the surface efficiently.Precipitation may also occur at higher pH. Increasing the ionic strength from 0.01 to 0.1 led to significant decrease in Cu(ll) adsorption. Similar effect were observed for other metal ions.

11. Cassava root husk

[15]P. Tho, H. Van, H. Nguyen et al (2021) studied the modification of cassava root husk-derived biochar (CRHB) with ZnO nanoparticles (ZnO-NPs) for simultaneous adsorption of As(lll), Cd(ll), Pb(ll) and Cr(vl). By conducting batch-mode experiments, it was conducted that 3% w/w was the best impregnation ratio for the modification of CRHB using ZnO-NOs and was denoted as CRHB-ZnO3 in the study.The optimal conditions for heavy metal adsorption were obtained at a pH of 6-7, contact time of 60 min, and initial metal concentration of 80mg/L. The heavy metal adsorption capacities onto CRHB-ZnO3 showed the following tendency: Pb(ll)>Cd(ll)>As(lll)>Cr(vl). The total optimal adsorption capacity achieved in the adsorption of 4 above mention metals reached 115.11 and 154.21mg/g for CRHB and CRHB-ZnO3, respectively. For each Pb(ll), Cd(ll), As(lll), Cr(vl) metal the maximum adsorption capacities of CRHB-ZnO3 were 44.27, 42.05, 39.52 and 28.37mg/g, respectively, and those of CRHB were 34.47, 32.33, 26.42 and 21.89mg/g, resp. The FTIR and EDS analysis confirmed the important role of oxygen containing surface groups, which

significantly contributed to removal of heavy metals with extremely high adsorption capacities. This study was successfully developed a highly effective, cheap and eco-friendly adsorption material with combination between agricultural by-product derived-biochar and ZnO nanoparticles. The study was only limited at lab scale with tests on simulated waste water .

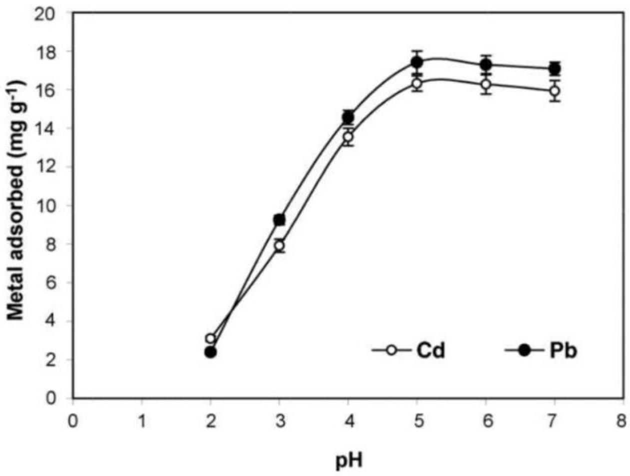
12. Date palm

[16]M. Shafiq , A. Alazba, . Amin (2018) studied the used of date palm to remove heavy, metal like Cu. Using date palm studies show that equilibrium time was approximately 2hr, with acidic pH values of 5-6, which indicated the interference of H^+ ions with metal ions at low pH values.Raw date palm trunk fiber was first tested with initial particle size of 75-251 micrometer and adsorbent dose was in range of 0.4 -5 g/L.The best adsorption efficiency was obtained with the smallest particle size with the maximum concentration. With the use of different initial concentration of cu(ll) ion there is decrease in metal removal by 10% but, the adsorption capacity increase three-fold times with an initial concentration of 20-100mg/L. The higher removal efficiency was achieved of Cu^{+2} using the modified date palm waste than with raw trunk fiber while maintaining all the parameters.In date palm fibers , the elemental composition consist of 62% of carbon which is generally associated with lower polarity and hence a greater potential for adsorption. The efficient adsorption takes place at pH 6 with minimum contact time , with adsorbent dose of 5g/L. Small size of adsorbent give better results as with the larger molecule it may be too large to enter the small pore.The removal capacity of date palm was higher than that of other natural waste material as it contain high carbon percentage.

13. Mango peel waste

[2]R. Lakshmipat (2008) studies were done using mango peel as adsorbent to remove Pd(ll) and Cd(ll) from waste water.Elemental composition of mango peel waste was done by atomic absorption spectroscopy. FTIR spectrum of mango peel waste indicate that hydroxyl and carboxyl groups were present in abundance, which are responsible for sorption of Cd(ll) and Pb(ll). Chemical modification of mango peel waste for blocking of carboxyl and hydroxyl groups showed that 72.48% and76.26% removal of Cd(ll)and Pb(ll) respectively was due to involvement of carboxylic group whereas the 26.64% and 23.74% was due to hydroxyl group. EDX analysis of mango peel waste was done before and after metal sorption and release of cations Ca(ll), M(ll) , Na(l) and K(l) and proton H^+ from mango peel waste with the corresponding uptake of Cd(ll)and Pb(ll).EDX analysis suggest that mechanism involved in sorption was ion exchange.The regeneration experiment suggest that mango peel waste can be reuse for 5 cycles without any loss in sorption capacity. As the amount of adsorbent increase availability of sorption sites eased resulting in greater percentage removal of both the metal ions. This increase at higher dosage than 2.5 g/L may attributed to presence of excess of

metal binding sites on adsorbent than the available metal ions present in solution at fixed concentration of 50mg/L. At pH 2 low metal adsorption take place (15.5% Cd(ll) , 11.99% Pb(ll)).In the range of pH 2-5 continuous increase in adsorption take place (81.6% Cd(ll), 87.05% Pb(ll) at pH 5). The maximum adsorption by mango peel waste was observed at pH 5 for both metal ions.



Effect of pH on the sorption of Cd(ll) and Pb(ll)from 50mg/L solution by 2.5g/L mango peel waste during orbital shaking at 100rpm at 25°C.

14. Wild herbs

[17]G. Al-senani, F. Al-fawzan (2018) studied the use of wild herbs to remove Co , Li and Cd ions from aqueous solution. FTIR studies indicate the presence of O-H , N-H and -C00H functional group and these group have significant effect on adsorption and efficiency of adsorbing metal ion via ion exchange. There is increase in adsorption percentage with increase in adsorbent as there is increase in surface area at higher concentration. Studies suggest that there is decrease in adsorption with increase in adsorbent particle size. Adsorption equilibria is less than 2 hr as after 2 hr there is decrease in number of active sites. Adsorption was maximum with 0.5 g of adsorbent and with 50 microgram of particle size. Temperature has slight effect on adsorption in the range of 25-60°C. At higher temperature there is a increase in active sites because of bond rupture at high temperature.The percent of adsorption of Cd was increased with increase in pH from3 to 5 , then was stabilized till pH 9 , and then adsorption increase to 98%. That was due to presence of carboxyl, hydroxyl and amine group on the surface of adsorbents which are involved in binding mechanism.With increase in pH adsorption percentage of Li was not increased, this was due to stability of Li adsorption ratio with increase in pH due to decrease of electronegativity and increase of ionic radius.

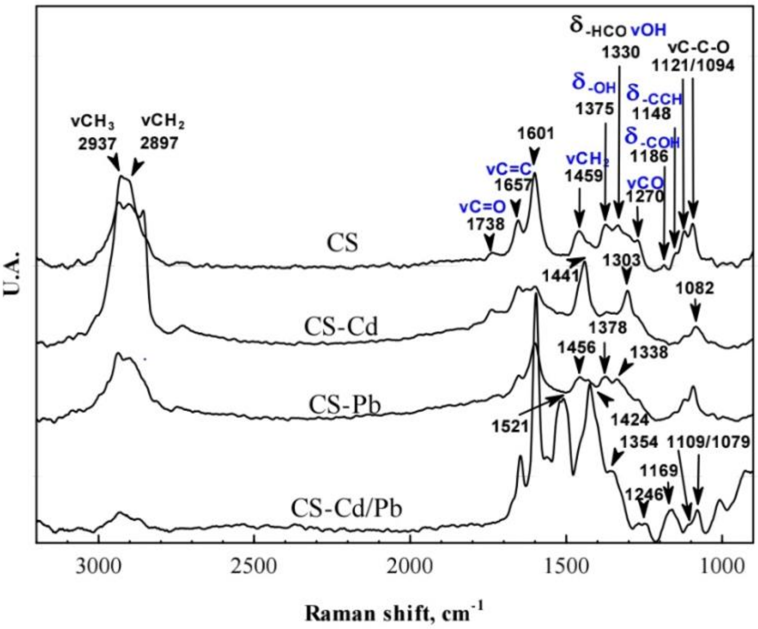
15. Persimmon leaf bio-waste

[18]S. Lee, H. Choi.(2018) have investigated the possibility of remove Pb , Cu and Cd in aqueous solution by using raw persimmon leaves and dried persimmon leaves. The persimmon leaf contain high quantities of tannin and catechin. The FTIR analysis suggest that raw persimmon leaves and dried persimmon leaves had a structure which facilitates the adsorption of heavy metal because of presence of carboxylic group, C=O carbonyl group, CH stretching , O-H carboxylic acid, and bonded -OH groups. SEM studies suggest that surface of leaf is very irregular and porous which are helpful for adsorbing heavy metal ions. The surface of leaf composed of many layers of thin films which are also helpful to adsorb heavy metals.When raw persimmon leaves was used removal efficiency was more than 90% at a concentration below 2mg/L and when dried persimmon leaves was used removal efficiency was more than 90% at a concentration of up to 4mg/L of metal ions. That is because of dried persimmon leaves have large surface area compared to raw persimmon leaves. When the concentration increased adsorption removal rate decreased. The removal of heavy metal by raw persimmon leaves and dried persimmon leaves indicate that dried persimmon leaves had a 10-15% higher removal than raw persimmon leaves. The decrease of removal efficiency as the concentration of heavy metal increased was less in dried persimmon leaves than in raw persimmon leaves.The order of removal efficiency was found to be Pb>Cu>Cd. The removal efficiency of Pb, Cu and Cd was 20-45% at pH 2-3. Removal efficiency of Pb was similar in both, but the removal efficiency of dried persimmon leaves for Cu and Cd was about 10% higher than that of raw persimmon leaves. Pb, Cu and Cd show the high metal removal efficiency at pH above 6. The optimum amount of adsorbent required was 4g/L for raw persimmon leaves and 3g/L for dried persimmon leaves.As the temperature increase adsorption improves. Using persimmon leaves as a adosrbent is a eco-friendly method as it remove metal without using chemical.

16. Chili seed

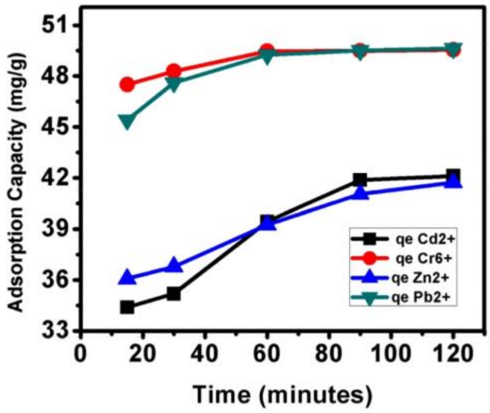
[5]N. Medellin-castillo,E. Padilla ortega, M. Regules-martinez et al.(2017) invastigated the chili seed (capsicum annuum) as a adsorbent to remove Pb(ll) and Cd(ll) from aqueous solution. The chili seed composed of cellulose and hemicellulose. SEM studies show that surface of chili seed is nonporous. The nature of surface of chili seed is acidic .The concentration of Cd(ll) and Pb (ll) was determined by atomic absorption spectroscopy.Raman spectrum indicate that hydroxyl group from lignin are involve in adsorption of Cd(ll) and Pb(ll) on chili seed and π-cation interaction between the aromatic ring of lignin and Cd(ll) and Pb(ll) occurred during adsorption.

The maximum adsorption capacity of chili seed towards Cd(ll) was 0.08, 0.12 , 0.18 and 0.23meq/g at pH of 2, 3, 5 and 7resp and towards Pb(ll) was 0.072, 0.096 and 0.21meq/g at pH value 2, 3 and 5 resp. The adsorption capacity increase 2.9 times by varying pH from 2 -7 for Cd(ll) and for Pb(ll) 3 times by varying pH from 2-5. The single adsorption capacity of chili seed depends on pH because of electrostatic interaction and ion exchange mechanism. In competitive adsorption of Cd(ll) and Pb(ll) , Pb(ll) exhibit strong opposition in competitive adsorption of Cd(ll) whereas Cd(ll) is unaffected by presence of Pb(ll).On competitive adsorption studies for Cd(ll)-Pb(ll) implies that affinity of Pb(ll) for chili seed was more than 5 times higher than that of Cd(ll).



17. Palm kernel shell

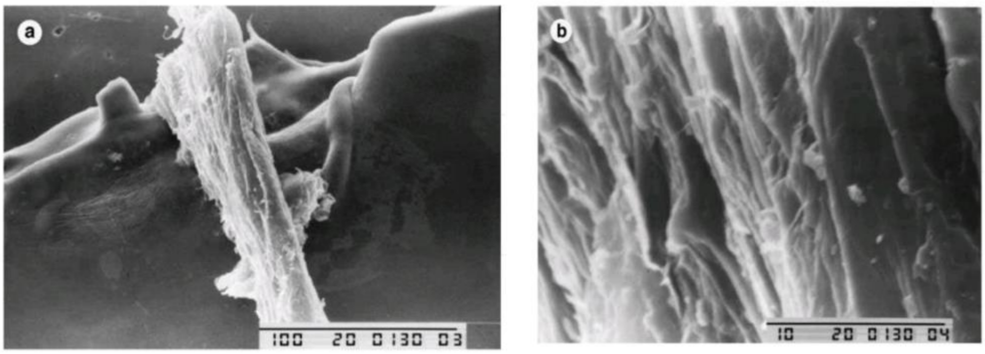
[19]R. Bab, B. Sa, M. Zobir(2019) studied the use of palm kernel shell as a adsorbent to remove Cr(vl), Cd(ll), Pb(ll) and Zn(ll) from waste water. Palm kernel shell was washed first with tap water followed by deionized water then dried in the oven for 24 hours at 70°C .After that adsorbent was crushed to fine powder and then it was use for further studies. Fourier transform infrared spectroscopy suggest that hydroxyl and carbonyl groups were present and they have been shifted to higher value than expected which suggest that adsorption of metal ions had take place on adsorbent. Field emission scanning electron microscopy indicate that surface of palm kernel shell before adsorption was rough with layers, stacking on the top of one another.And after adsorption the surface has been change slightly to smoother surface. The changes on surface is due the adsorption via electrostatic, chelation surface adsorption and biosortion. In basic condition formation of precipitation of metal ion occurs . Therefore maximum adsorption was seen in acidic condition .Pb(ll) ion show maximum adsorption of about 95.20% at pH 4 . Whereas the Cr(vl), Cd(ll) and Zn(ll) show maximum adsorption of 90.20%, 75.50% and 67.30% at pH 6 resp. As the metal ion concentration increases, adsorption decreased, due to the saturation of active sites for adsorption.Cr(vl) and Pb(ll) ions took 60 min to reach the equilibrium with the adsorption capacity of 98%. Cd(ll) ions took 90 min to reach equilibrium of 84% whereas the Zn(ll) took 120 min to reach equilibrium of 83%. By following the optimized condition 99% of Cr(vl) and Pb(ll) ions and more than 835 of Cd(ll) and Zn(ll) ions were removed. The adsorption capacity of palm kernel shell as a adsorbent was 49.55, 49.64, 43.12and 41.72 mg/g for Cr(vl), Pb(ll) , Cd(ll) and Zn(ll) resp. Palm kernel shell was used as adsorbent without any pretreatment with the chemicals.



Adsorption capacity of palm kernel shell at different time interval for the adsorption of metal ions, Cr^{+6},Pb^{+2}, Cd^{+2} and Zn^{+2}

18. Rice husk

[18]D Campang (2003) studied the use of rice husk to remove Cd and Pd from waste water. The material which is considered a by-product obtained from rice milling was then investigated as a potential decontaminant of toxic metals present in industrial effluents. The physical Characterization of rice husks pointed out some properties such as the presence of functional groups (carboxyl, silanol, etc) which make adsorption possible .Studies using glass colums were carried out at a room temperature employing 100 ml of synthetic solution containing Cd(ll) and Pd(ll) at 100mg/l in order to study. Under optimized condition that is pH 4 , flow rate of 8ml/min and <354 micrometer rice husk particle size,30 g of rice husks were necessary to release. Larger particles with spherical shapes in general , present higher external mass transfer than smaller particle.



Scanning electron microscope of rice husk (<355micrometer)

a. 500 and b. 5000 magnification. The bars indicate magnification , represented by the first number . Other number indicate the acceleration voltage (kV), date (day $month^{-1}$) and number of micrograph, respectively.

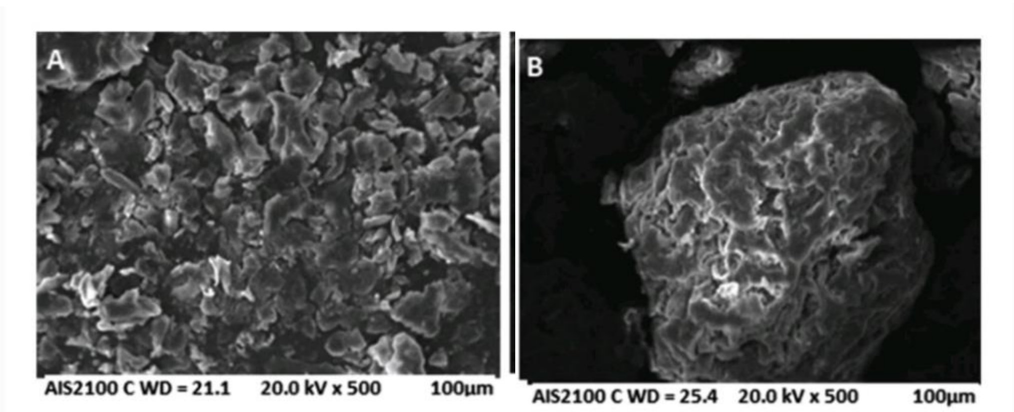
19. Bagasse fly ash

[20]Vinod K. Gupta, C. K. Jain, I mran Ali, M. Sharma , V. K. Saini(2003) studied the use of bagasse fly ash, an industrial solid waste of sugar industry, for the removal of Ni and Cd from waste water.As much as 90% removal of Cd and Ni is possible in about 60 to 80 minutes under the batch test condition. The total metal ion adsorbed increase sharply in the beginning and then slowly towards the end of run. The adsorption of cadmium increased from 1 to14 mg/l and that of Nickel from 1 to 12 mg/l , and then become constant indicating that maximum adsorption occurred at 14 and 12mg/l for cadmium and nickel , resp. The maximum uptake of Cd and Ni occurred at pH 6 and 6.5, resp. The adsorption increased from 0.70mg/g at pH 2 to 1.20mg/g at pH 6 in case of cadmium and from 0.24mg/g at pH 2 to about1mg/g at pH 6.5 in case of nickel and then started to decrease in both cases. The adsorption increased from 0.64 to 1.18mg/g for Cd and 0.40 to 0.96mg/g in case of nickel with increase in adsorbent dose from 2 to10 g/l . The dose of 10g/l is sufficient for optimum removal of both metal ions. The adsorption followed the order of 30°C>40°C>50°C for both metal ions.

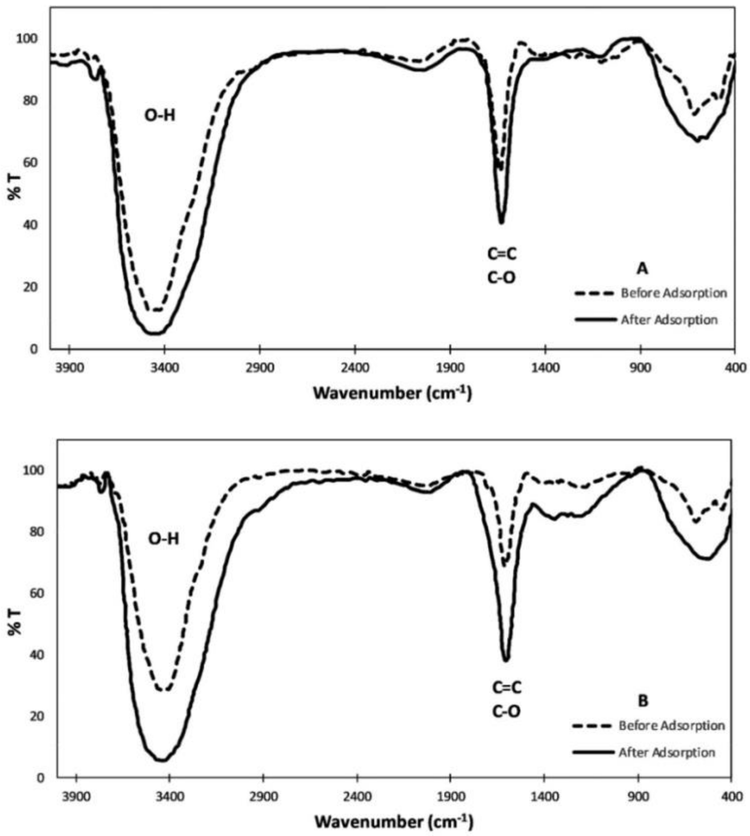
20. Citrus Sinensis Peel

[10]W. Malti, A. Hijari, .A. Khalil. Et al. (2022) studied the use of citrus sinensis peel and its activated carbon to remove heavy metal ions from waste water. The citrus sinensis activated carbon was prepared by pyrllysis in a furnace at 300°C for 2 hours. The resulting biochar was washed with deionized water and dried at 100°C for 24 hours. The chemical activation was done by adding H_2O_2 to a 50g biochar sample and stirring at 25°C for 24 hours. The resulting powder was filtered and dried for 24 hours at 100°C . The particle size of adsorbent was 88 microgram. Scanning electron microscopic imagies suggest that adsorbent have irregular shape with rough surface and many pores are present which can improve the adsorption The Citrus sinensis and its activated carbon was were inspected using Brunner-Emmett-Teller technique . The results obtained by N2 adsorption desorption technique suggest that surface area, total pore volume and average pore size were higher after calcination and H2O2 activtion . Energy -dispersive X-ray analysis indicate that adsorbent contain high amount of carbon content specially in citrus sinensis . Presence of compartively low amount in activated carbon is due to high content of polypheonol component in citrus peel which are volatilized during pyrolysis process. FTIR suggest that both citrus sinensis and activated carbon have similar functional group before and after adsorption of heavy metals. The functional group present in the adsorbents are hydroxyl, carbonyl and carboxyl . The optimum contact time was 2 hours with using 0.25 g of adsorbent and 400mg/L of metal ions. The maximum adsorption capacity was obtained t pH 5 where 71.7mg/g of Cd(ll), and 33.3mg/g of Cu(ll) was adsorbed on citrus peel .Slightly lower maximum adsorption capacity was obtained at pH 5 by activated carbon particles for Cd(ll) and Cu(ll). At lower pH low adsorption capacity because of higher protonation present at adsorbent surface. At higher pH insoluble Cd(ll) and Cu(ll) hydroxide salt will begin to precipitate. The adsorption capacity decrease with

increase in mass of adsorbent powder. The adsorption capacity of citrus peel slightly increase with increasing the temperature until it reaches a maximum value of 40.1mg/g at 75°C this increase is due to increase in number of functional group on biomass surface resulting from higher hydrolysis rate . Temperature rise dose not affect the Cd(ll) ion on citrus peel .2 reuse cycles are recommended for Cd(ll) and Cu(ll) on for activated carbon as there is a adsorbent loss from 41 to 75% . for citrus peel loses almost 13 to 9% for Cd(ll) and Cd(ll) ions after3 cycles. Citrus peel showed a better adsorption capacity compared to activated carbon.



SEM imagies of A)citrus peel B)Activated carbon



FT-IR spectra of A)Citrus peel B) Activated carbon before and after adsorption of heavy metal ions

CONCLUSION

The heavy metal ions which are discussed in these literature report are Cd(ll), Zn(ll), Cr(vl), Pb(ll), Ni(ll), Cu(ll), As(ll) and Fe(ll). The adsorption capacity depends on temperature, surface area of particle , size of particles, pH ,agitation speed , contact time, initial concentration.Presence of functional groups like hydroxyl , carbonyl , carboxyl make adsorption better. Smaller size particle give better adsorption as larger surface area are present for adsorption which provide more sites for adsorption.

Citrus peel showed a better adsorption capacity compared to activated carbon for Cd(ll) and Zn(ll). Palm kernel shell was used as adsorbent without any pretreatment with the chemicals . Affinity of Pb(ll) for chili seed was more than 5 times higher than that of Cd(ll). Using persimmon leaves as a adsorbent is a eco-friendly method as it remove metal without using chemical. Cassava root husk studies developed a low cost , eco-friendly , effective adsorbent material in combination between agricultural by-product derived-biochar and ZnO nanoparticles but the study was only limited at lab scale with tests on simulated waste water .The removal capacity of date palm as a adsorbent was higher then that of other natural waste material as it contain high amount of carbon. Mango peel waste as a adsorbent can be reuse for 5 cycles without any loss in sorption capacity. The removal percentage of olive mill waste was comparatively low as compared to other biomass. Co-polymerization modified orange peel is more efficient compared to unmodified orange peel for removing metal ions. Meranti sawdust was a suitable adsorbent for removal of Cu(ll) , Cr (ll), Ni(ll) and Pb(ll) ions from aqueous solutions in terms of low cost, natural and abundant availability. Biosorption using citrus lemon peel could make simultaneous metal recovery economically feasible in places where pollution control is insufficient due to high cost. The removal efficiency of banana peel for 10 types of metal ions are 1.3 to 98.6 times higher than those by using commercial activated carbon. Among the removal efficiency for Cu(ll) ,Pb(ll), Cd(ll) and Cr(ll)ions in the research is 7.5 , 8.9 , 8.7 and 16.6 times higher than that of commercial activated carbon respectively. The tea waste as a adsorbent without modification the selectivity for adsorption is not so strong with modification gives better results. Pb(ll) , Cd(ll) and Zn(ll) sorption capacity of unit mass Mn for hydrated manganese oxide-tea waste were 3616.2, 1626.1 and 778 mg/g resp. And for pure hydrated manganese oxide was 710.1, 304.1 and 117.7mg/g resp. Improvement of Mn utilization efficiency can be attributed to dispersion of hydrated manganese oxide on tea waste which increased the binding sites of hydrated manganese oxide. Using pomegranate removal percentage of mixed ions were relatively low, because of competition and interaction between the ions. Using natural waste as a adsorbent is a low cost, effective , eco-friendly method which reduce the waste disposal as well as it purify the contaminated water from heavy metals.

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