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EVALUATION OF THE POTENTIAL OF ONION PEEL COMPOSITE AS AN ADSORBENT FOR THE REMOVAL OF CATIONS IN FISH POND WASTEWATER

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ABSTRACT

Toxic metals in wastewater when discharge in to the environment can accumulate in vital organs when ingested, and get concentrated through the food chain causing poisonous effects to living organisms. Alumina modified onion peel composite was used in this study as an adsorbent for the removal of lead, nickel, chromium, copper and zinc ions from Fish pond wastewater via adsorption process. Batch adsorption experiments were conducted to examine the effect of adsorbent dosage, pH, adsorbate concentration, and contact time on the adsorption of the cations. The optimum adsorbent dosage was 0.3g, pH was 2, contact time was 60 mins and initial concentration was found to be 10 mg/l. The concentration of metal ions present were analyzed using Atomic Absorption Spectrophotometer. The characterization by Fourier Transform Infrared (FTIR) showed absorbance peaks that correspond to hydroxyl, aldehyde, alkyl, amide and carboxylic acid functional groups. These functional groups helped in enhancing the adsorption of the metal ions. Scanning Electron microscope (SEM) analysis was carried out for the morphological characteristics of the adsorbent, before and after adsorption. The experimental isotherm data were analyzed using linear form of Langmuir and Freundlich isotherm models. The Langmuir isotherm provided the best fit for the sorption of Zn^{2+}, Cu^{2+}, Cr^{3+} and Pb^{2+} ions with the correlation coefficient (R^2) as 0.981, 0.994, 0.9192 and 0.9478 respectively while the Freundlich isotherm had a best fit for the sorption of Ni^{2+} with the correlation coefficient (R^2) of 0.9574. The maximum monolayer adsorption (q_m) for copper was found to be the highest with 28.2 mg/g while nickel had the lowest qm value of 1.15 mg/g. The results of these study indicated that onion peel composite as a low cost adsorbent can be utilized to minimize the amount of metal ions in Fish pond wastewater before being discharged

Keywords: Adsorbent, Adsorption, Alumina, Composite, Isotherm

INTRODUCTION

Due to increase in industries, urbanization and population growth, there has been increase in water utilization and poor waste water management that is gradually wading to water crisis (Selivanovskaya and Latypova, 2003). However poor water management has led more waste water generation. Hence the quality of water for human consumption requires modern remediation technology (Fakayode, 2005). Various treatment processes such as chemical precipitation, adsorption, ion exchange, nanofiltration and membrane filtration have been developed over the years to remove the heavy metals dissolved in wastewaters (Singh et al., 2020).

The major advantages of adsorption technology are its effectiveness in reducing the concentration of ions to very low levels and the use of inexpensive adsorbent materials (Cafer et al., 2011). However, most of these techniques have some disadvantages, such as complicated treatment process, high cost and energy consumption.

Biosorbent are solid materials from biological origin, which have the properties of attracting soluble analytes species in solution and attaches them to its surface by removing them from solution (Surchi, 2011).Different types of agricultural biosorbents such as waste tea leaves, sugarcane bagasse, wheat bran, rice husk, orange peel, coffee beans, apple peel, banana peel, coconut shells, maize corn cob, cotton stalks etc., have been tried by various researchers for the removal various heavy metals (Faizan and Sadaf, 2020). Agricultural waste are rich in organic content which have various functional groups such as phenolic, carbonyl, hydroxyl, carboxylic groups and consist of lignocellulosic materials with lignin as the major structural components (Singh et al., 2020). These properties help bind heavy metal, organic or inorganic contaminants to the surface of the adsorbent. The major advantage of agricultural waste material over other conventional adsorbent is its high affinity and selectivity towards contaminants due to availability of binding groups, can easily be processes, applied and recycled without posing any threat to the environment (Kwikima et al., 2021).

Onion peel has not been studied extensively as other biosorbents. Onions are locally available, used globally and their peels are left as waste. This has resulted to disposal problem hence an approach that seeks to use onion peel as adsorbents will be utilizing onion peels waste generated. Onion peel contains flavanol compounds which contain polyphenolics groups. Due to this, they are able to bind metals towards themselves hence can be used in remediation of water containing heavy metals. (Babel and Kurniawar, 2002). The purpose of this research work is to determine the efficiency of alumina modified onion peel composite as a biosorbent in the removal of some selected cations from Fish pond wastewater using batch adsorption experiments, and to determine its adsorption capacity using Langmuir and Freundlich adsorption isotherms.

MATERIALS

Experimental Procedures

Analytical grade chemical reagents of all the metal salt which include, Lead (II) Nitrate, Nickel (II) sulphate, Copper Nitrate, Zinc metal, Potassium dichromate at concentration 1000 mg/l. For modification of adsorbent, Aluminium Nitrate and Ammonium hydroxide was used. For varying of adsorbate concentration synthetic waste water was prepared. This was done so as to observe the adsorbate concentration most favourable for adsorption of ions using modified onion peel composite. For adjustment of pH, NaOH (percentage purity 98 %, MW 40 g) and HCl (percentage purity 36.5%, specific gravity 1.18).

Sampling

Onion peels were collected randomly from a local market (Kawo Market), in Kaduna metropolis. Agricultural waste water sample from fish pond was collected in Happier Valley, Nigerian Air Force Base Mando, Kaduna. Several samples were collected to form a composite wastewater sample so as to have a representation of the overall water quality. The composite sample was stored in a clean dry polyethylene bottle after it was acidified to pH of 2.0 with few drops of nitric acid. This was done to minimize precipitation of cations (Mojeed et al., 2020).

Preparation of adsorbent

The collected onion peel was washed with tap water several times to remove dust, rinsed with distilled water and then dried overnight using an oven at 110 ^{c}C.. The dried sample was ground to a fine powder and sieved through 220 µm mesh sizes and placed in an air tight container for further use, (Yusuff et al, 2019).

Metal Quantification in fish pond waste water sample

Acid preserved fish pond waste water sample was transferred into a beaker to which 10ml of conc HNO_3 was added. The sample was boiled slowly and then evaporated on a hot plate to the lowest volume possible of 15 ml. Heating was continued with the addition of concentrated nitric acid till digestion was completed indicating a light clear solution. Care was taken not to let sample get dried during the digestion. The beaker wall was washed with deionized water and the content was transferred into 100 ml volumetric flask and made to mark with deionized water, (APHA, 2017). Atomic Absorption Spectrophotometer was used in determining the amount of the five selected cations (Cu, Zn, Ni, Cr and Pb) present in the fish pond waste water sample that was digested.

Modification of onion peel

The preparation of synthesized alumina modified onion peel composite was done following the procedure reported by (Yusuff et al, 2019). About 100 g of onion peel powder was added into 250 mL of 0.5M $Al(NO_3)_3$, and the resulting mixture was stirred at 150 rpm using a magnetic stirrer while 1.5 M NH_4OH was added dropwise until the mixture becomes basic at pH 10. The reaction between $(Al (NO_3)_3$ and (NH_4OH) produced an amorphous $Al (OH)_3$, which occurs in the activated onion peel pores. Furthermore, the precipitate obtained was washed with distilled water and then filtered. The composite was calcined at 600^{o} C for 2.5 hours in a muffle furnace and product was labeled and stored for further analysis.

Characterization of Adsorbent

Scanning electron microscope (SEM) micrographs of onion peel composite before adsorption and after adsorption at 200 µm magnification was taken, to show the variation in surface morphology of the adsorbent before and after adsorption. Fourier transform infrared spectroscopy (FTIR) of the adsorbent before and after modification was done by using Shimatzu Fourier Transform Spectrometer at a wave number range of 4000 to 400 cm^{-1} region with a resolution of 4 cm^{-1}.

Adsorption Experiments

Batch Adsorption Experiments

The experiments were carried out using the method of (Beatrice et al., 2016). Four different sets of batch experiments were carried out to investigate the removal of the selected cations from the water sample using modified onion peel composite. The experiments were repeated at pH from 2-12, contact time of 30-150mins, adsorbent dosage ranging from 0.1-0.5g and concentration of cations from 10-50 mg/l.

Effect of pH

The preserved waste water was adjusted to the various pH (2, 4, 7, 9 and 12) using 0.1M HCl and 0.1M NaOH .Exactly 30ml of each of the adjusted wastewater sample was then added to different beakers containing 0.3g of the adsorbent (composite).The mixtures were agitated for 1 hour in a shaker at a speed of 200 revolutions per minute (rpm),allowed to stand and then filtered using a filter paper into a labelled sample bottle The metal ions in the filtrate were determined using AAS, and the optimum pH for the sorption was established.

Effect of Adsorbent Dosage

Different dosages of the adsorbents within the range of 0.1, 0.2, 0.3, 0.4, and 0.5g were added in different conical flasks containing 30 ml fish pond wastewater sample solution at optimum pH of 2. Water sample solutions were corked and agitated in a shaker for 1 hour at a speed of 200 revolutions per minute (rpm), allowed to stand at room temperature. The content of each flask was then filtered and analyzed using AAS.

Effect of Contact Time

The effect of contact time on the biosorption process was evaluated over a period of 30, 60, 90, 120 and 150 minutes. This was done by weighing 0.3 g of the adsorbents into a conical flask containing 30 ml of fish pond wastewater solutions at a pH of 2 and the flask was agitated in a shaker at 200 rpm at 30mins, allowed to stand at room temperature. The content of the flask was then filtered using a filter paper into a sample bottle and analyzed using AAS. The above procedure was repeated at contact time of 60, 90, 120 and 150 mins.

Effect of adsorbate Concentration

The effect of initial concentration on the biosorption process was evaluated by varying concentrations at (10, 20, 30, 40 and 50) mg/l. Exactly 30 ml of 10 mg/l of synthetic waste water sample solution was mixed with the adsorbent dosage of 0.3 g, at pH of 2, agitated at 200 rpm over 60 mins. The resulting mixture was allowed to stand and then filtered using a filter paper into a labelled sample bottle and analyzed using AAS. The above procedure was repeated at initial concentration 20, 30, 40 and 50 mg/l.

Analysis of the Filtrate

The labelled filtrate samples were analyzed for the concentration of the selected cations using Atomic Absorption Spectrometry (AAS). The amounts of metal ions adsorbed per unit mass by the modified onion peel, during the batch investigation was calculated as:

$$qe = \frac{(C_o - C_e)v}{w}$$

where: *qe*= Amount of metal ion removed at equilibrium, Co = Initial concentration of sorbate (mg/L) *Ce*= Concentration of sorbate at equilibrium (mg/L), W= mass of adsorbent used (g), V = volume of solution used (ml)

The equation that gives percentage of ion removal by the onion peel adsorbent is given by:

$$\% \text{ Adsorbed} = \left(\frac{Co - Ce}{Co} \right) \times 100$$

Co is the initial concentration of the metal ion before the adsorption process, Ce is the equilibrium concentration of the metal ion in the filtrate after adsorption process.

Adsorption Isotherm

Several models have been used to describe experimental data for adsorption isotherms. However, among these, the Langmuir and Freundlich isotherms are the most common models used by several researchers.

According to the Langmuir isotherm, adsorption occurs at homogeneous sites and forms a monolayer.

The linear forms of the Langmuir isotherm equation is given as (Boukhiar *et al*., 2008):

$$\frac{Ce}{q_e} = \frac{1}{q_m K_L} + \frac{Ce}{q_m}$$

Where; *qe* is the amount of solute adsorbed (mg/g), where Ce is concentration of adsorbate at equilibrium (mg/g). K_L is Langmuir constant related to adsorption capacity (mg /g). The experimental data will be applied to the equation above and a plot of Ce/qe against Ce plotted.

The Freundlich isotherm gives the relationship between equilibrium liquid and solid phase capacity based on the multilayer adsorption properties consisting of heterogeneous surface of the adsorbent. The linear forms of the Freundlich isotherm is (Ayawie *et al*., 2017):

$$\text{Log}q_e = \log K_F + 1/n \log Ce$$

where; qe is the amount of solute adsorbed (mg/g), Ce the equilibrium concentration of the solute in the bulk solution (mg/L) K_F constant, is an indicative of the relative adsorption capacity of the adsorbent (mg/g), while 1/n is the function of the strength of adsorption in the adsorption process, (Freitas et al., 2008). A plot of log *qe* versus log *Ce* with a good linear correlation implies that the sorption fits the Freundlich model.

RESULTS AND DISCUSSION

Table 1 Metal ion Concentrations in Fish Pond wastewater

Metal ions	Mean/Standard deviation
Zinc	0.0065 ± 0.007
Nickel	0.357 ± 0.05
Chromium	0.091 ± 0.002
Copper	0.487 ± 0.05
Lead	1.404 ± 0.03

The results of the mean initial concentration of metal ions present in fish pond waste water are presented in table 1 above.

Characterization of Adsorbent

Fourier Transform Infrared

The FTIR technique, serves as an important tool in identifying the functional groups present in an adsorbent material, which are important for the adsorption of cations. The FTIR spectra obtained for unmodified activated onion peel and modified alumina activated onion peel composite samples are shown in Fig1 and 2 respectively.

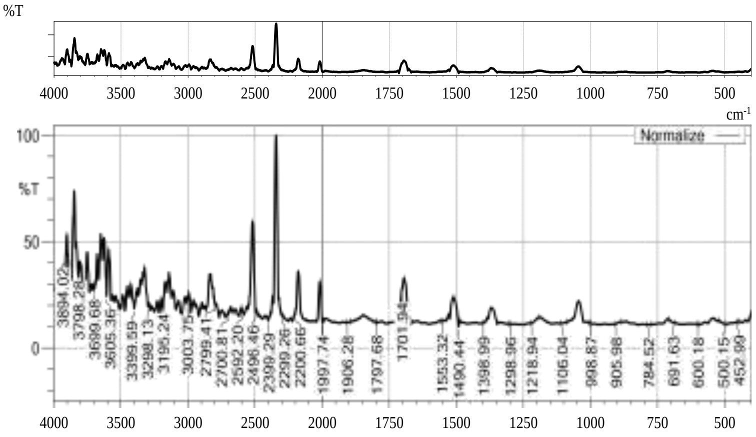

Fig. 1 FTIR Spectra of Unmodified Onion Peel

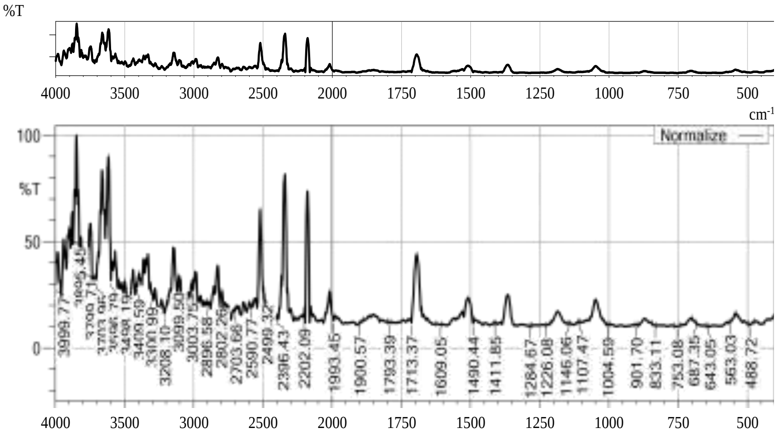

Fig. 2 FTIR Spectra of modified Onion Peel

The spectra shows the peak at the range of 3640 cm^{-1} – 3530 cm^{-1} assigned to O-H stretching due to inter and intra- molecular hydrogen bonding of polymeric compounds such as alcohol, phenols and carboxylic acids (Mahdi *et al*., 2018), while at 2830-2720 $cm^{-1,}$ C-H stretching bond for alkane functional group. A strong narrow peak at The spectra for modified onion peel composite shows that there are similar chemical functional groups with that of unmodified onion peel, however some new bands occurred. The low intensity peak at 3400cm^{-1} corresponds to the N-H stretching of amine groups. The peaks at 3200-3000 $cm^{-1}$and 1411.85 cm^{-1} represent, aromatic C-H stretch and C-H bend respectively. The peaks between 1490 to 1500 cm^{-1}revealed the 2200.66 cm^{-1} was observed to be associated with C≡C stretching of alkyne group (Abel et al., 2020). The medium intense adsorption peak at 1997.74 cm^{-1} may be due to C-H bending for an aromatic compound. The peak at 1701 cm-^{1} represents a simple carbonyl compound and at 1553.22 cm^{-1} is the vibration of C=C stretch (Nandiyato et al, 2019). presence of C=C stretching of aromatic benzene ring group (Abel et al., 2020). The finger print region at 1107 cm^{-1} shows C-O stretch which could be the reason for the successful anchoring of Alumina, C-O-R^{+} where, R^{+} is Al^{3+} (Hariani et al, 2015), but absent in unmodified onion peel.

Scanning Electron Microscopy (SEM)

The morphological structures of onion peel composite before adsorption and after adsorption were provided by SEM studies in Fig a and b above. The surface morphology after adsorption is different from that of before adsorption as the adsorption process significantly altered the physicochemical properties and porosity of the adsorbent material. Before adsorption surface of Alumina activated onion peel composite is heterogeneous, rough with fibres which are randomly arranged and pores which did not have regular fixed shape and sizes there by providing a large surface area for the adsorption of cations.

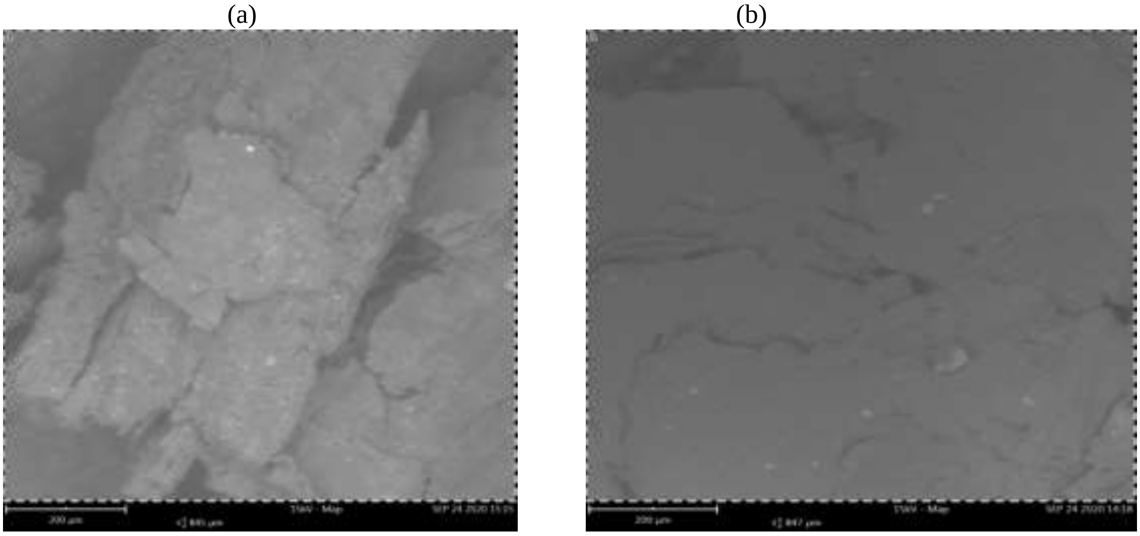

Fig a and b: SEM image of Alumina Activated Onion Peel Before Adsorption (a) and After Adsorption (b)

Adsorption Experiments

Effect of pH on the Adsorption of The Cations

The effect of pH on adsorption of Cu, Zn, Ni, Pb, and Cr was investigated at pH range (2, 4, 7, 9 and 12), the result is shown in Fig 3. pH is one of the most important parameters that affects the adsorption of metal ions by influencing the surface properties of the adsorbents and the ionic forms of the cations. More adsorption at acidic pH indicates that the increase in H$^+$ ions on the adsorbents surface results in electrostatic attraction between positively charged Alumina activated onion peel and the cations (Yusuff et al, 2019). The H$^+$ ions are higher and they preferentially bind to the adsorbent by electrostatic adsorption as both H$^+$ and oxygen (in the functional groups of the adsorbents already mentioned in the FTIR study) have a strong affinity for each other to occupy sites (Zada et al., 2020).

At high pH there is a decrease in adsorption, this might be because at a high pH there are more hydroxyl ions (OH$^-$) in the solution which react with the cations to form their insoluble hydroxides (Huang et al., 2017) thus, precipitation takes place which reduces the rate of adsorption.

The Effect of Adsorbent Dosages

The effect of adsorbent dosage on the amount of cations adsorbed was carried out at a fixed time (60 mins), adsorbate concentration (10mg/l) and pH (2). The experiments were carried out by varying adsorbent doses in the range 0.1g – 0.5g as illustrated in Fig 4. The percent removals of metal ions were found to increase as mass of the adsorbent increases. At lower dosage of adsorbent, there are insufficient active sites that the adsorbate can easily occupy.

However, at higher dosage, active sorption sites are sufficiently available for the adsorbate to occupy, thereby increasing adsorption capacity. Similar results have been reported by other researchers (Beatrice et al., 2016; Soreta et al., 2015; Zada et al., 2020).

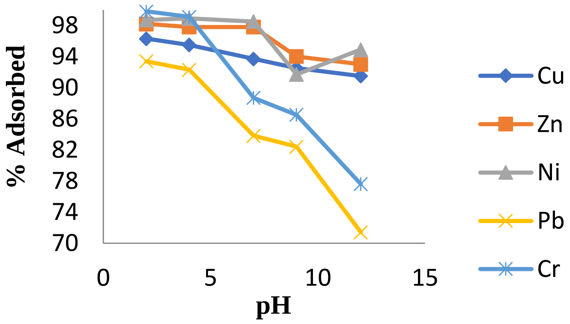

Fig. 3 Effect of pH in Percent Removal of Cations.

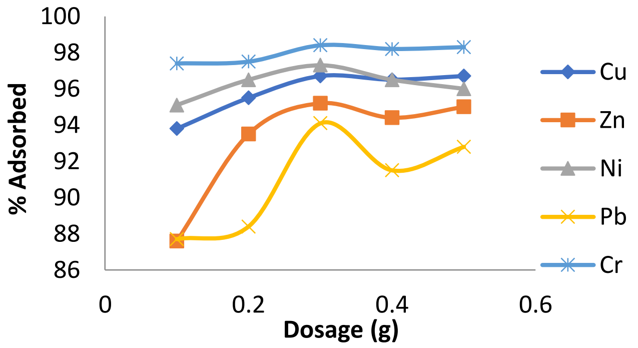

Fig. 4 Effect of Adsorbent Dosage on removal of Cations.

The Effect of Contact time

The effect of contact time on the amount of cations adsorbed was carried out at a fixed adsorbate concentration, adsorbent q3dosage and pH. The experiment was carried out by varying contact time in the range 30-150 mins as shown in Fig 5. rapid adsorption was seen in the first 60 minutes, following which the rate of percentage removal of metals remained near constant. The rise in rate of metal removal was negligible beyond the 60 minutes

Therefore, 60 minutes was found to be the optimum time period for attainment of equilibrium. A decrease in adsorption was observed as the contact time increases to 150 minutes. This could be because during the initial stage of sorption, a large number of vacant surface sites were available for adsorption. After lapse of time, the remaining vacant surface sites becomes difficult to occupy, due to repulsive forces between the solute molecules on the adsorbent surface and the bulk phase (Soreta et al, 2015). This phenomenon has also been proven by (Evbuomwan and Opute , 2018 ; Abel et al ., 2020).

Effect of adsorbate Concentration

The effect of adsorbate concentration on adsorption efficiency of Alumina modified onion peel waste is shown in Fig 6. The adsorbate concentration was varied at the range 10, 20, 30, 40 and 50 mg/l. It was observed that there is a decrease of the removal percentage with increase in adsorbate concentration for Zn, Cu, Ni and Pb. These results may be explained on the basis that at higher concentration there is an increase in the number of ions competing for the available binding sites so more cations would be left unadsorbed in solution while at lower concentration more active sites on the adsorbent would be available to adsorb the cations. These results are consistent with other reports (Beatrice et al., 2016; Soreta et al 2015)

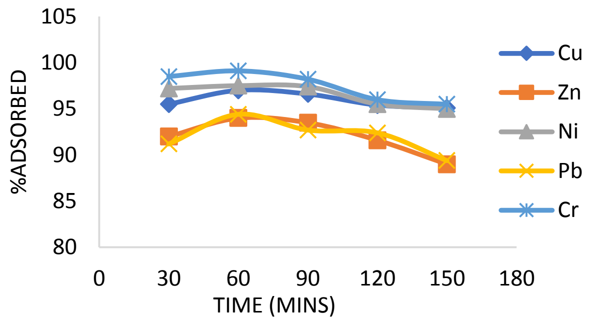

Fig 5 Effect of Contact time on Removal of Cations

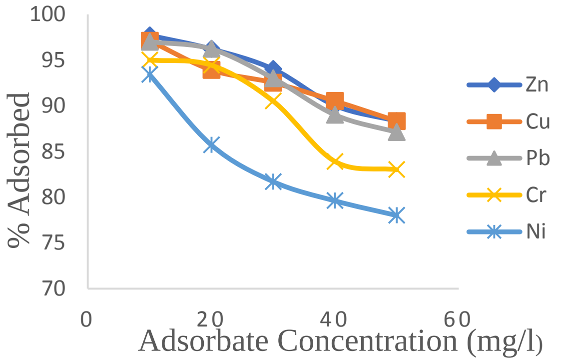

Fig 6 Effect of Adsorbate concentration on Removal of Cations

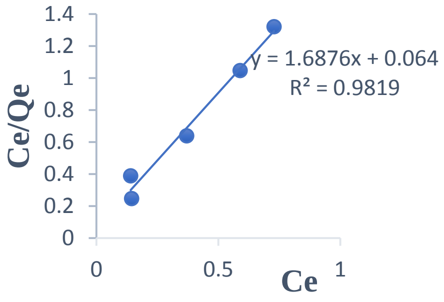

Fig. 7 Langmuir Adsorption Isotherm for Zn^{2+}

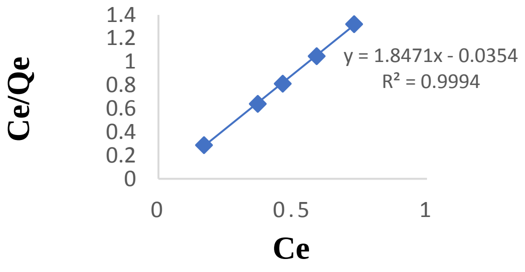

Fig. 8 Langmuir Adsorption Isotherm for Cu^{2+}

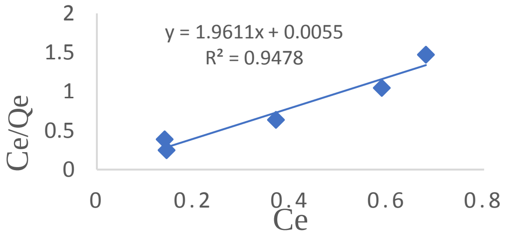

Fig. 9 Langmuir Adsorption Isotherm for Pb^{2+}

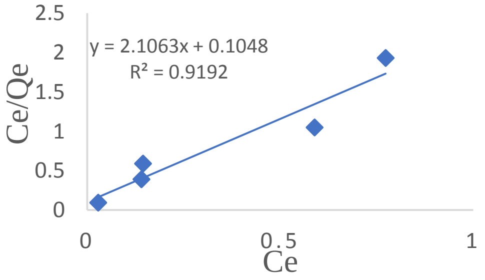

Fig. 10 Langmuir Adsorption Isotherm for Cr^{3+}

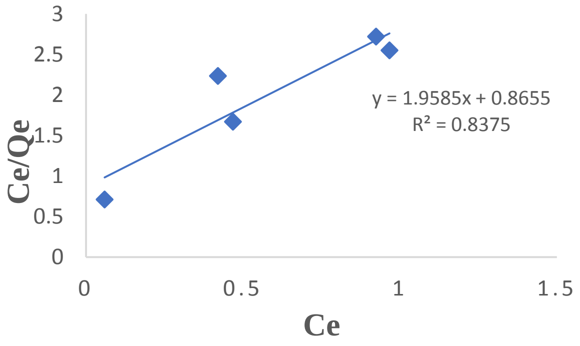

Fig. 11 Langmuir Adsorption Isotherm for Ni^{2+}

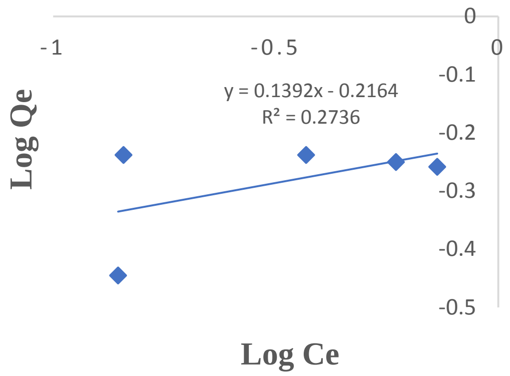

Fig. 12 Freundlich Adsorption Isotherm for Zn^{2+}

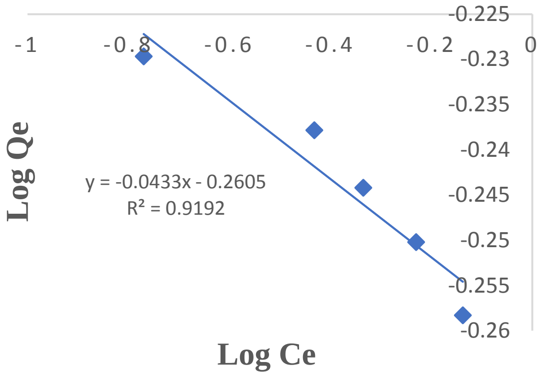

Fig .13 Freundlich Adsorption Isotherm for Cu^{2+}

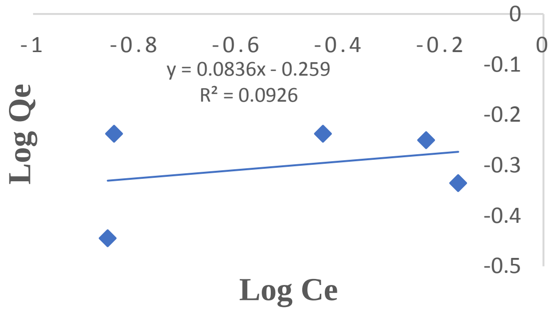

Fig. 14 Freundlich Adsorption Isotherm for Pb^{2+}

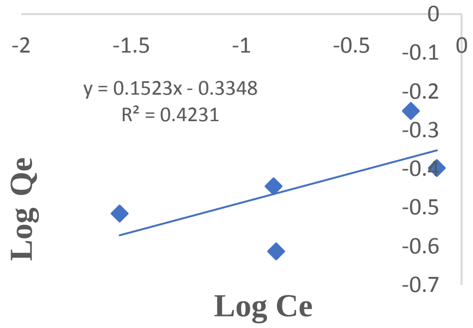

Fig .15 Freundlich Adsorption Isotherm for Cr^{3+}

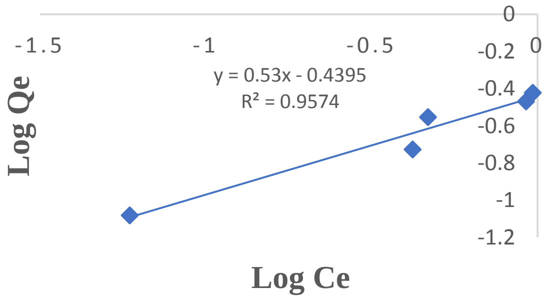

Fig. 16 Freundlich Adsorption Isotherm for Ni^{2+}

Table 2 Langmuir and Freundlich Isotherm constant and correlation coefficient R^2 for the Absorption of all Selected Cations

Metals	Langmuir Constant			Freundlich Constant		
	qmax (mg/g)	K_L(dm^3/mg)	R^2	1/n	Kf	R^2
Copper	28.24	0.0192	0.994	0.0433	0.5489	0.9192
Chromium	9.541	0.049	0.9192	0.1523	0.4626	0.4231
Zinc	15.625	0.0309	0.9819	0.1392	0.6076	0.2730
Nickel	1.155	0.4419	0.8375	0.530	0.3635	0.9574
Lead	18.181	0.0280	0.9478	0.0836	0.5508	0.0926

The Langmuir, and Freundlich isotherms models were employed to describe the uptake of cations by activated onion peel. Fig 7 to 11 and Fig 12 to 16 showed graphical presentation of Langmuir and Freundlich equilibrium data for adsorption isotherm respectively. The values of Adsorption constant K_L and Maximum monolayer adsorption capacity q_m in the Langmuir equation was calculated from the slopes and intercepts of the linear graph similarly, the values of freundlich constant (K_f) and intensity of the adsorption (1/n) in the freundlich equation were calculated from the slopes and intercept of the linear graph as shown in Table 2.

The Langmuir isotherm has R^2 values of 0.9940 for Cu^{2+} , 0.9819 for Zn^{2+},0.9478 for Pb^{2+},0.91292 for Cr $^{3+}$ and 0.8375 for Ni $^{2+}$, which indicated adsorption behavior was homogenously distributed (Horsefall et al., 2003). Cu^{2+} has the highest q$_m$ value of 28.2 mg/g which means it has the highest maximum monolayer adsorption capacity of selected cations while Ni^{3+} has the lowest q$_m$ value of 1.15 mg/g in the order Cu > Pb > Zn > Cr > Ni. Langmuir adsorption constant K$_L$ shows the degree of adsorbate- adsorbent interaction. The value of K$_L$ (dm^3/mg) were 0.0192 in copper, 0.0379 in zinc ,0.0280 in lead, 0.0490 in nickel and 0.442 in chromium. Higher K$_L$ value indicates strong adsorbate-adsorbent interaction while smaller K$_L$ value indicates weak interaction between adsorbate molecule and adsorbent surface (Beatrice et al., 2016; Hossain et al., 2012; Nandiyanto and Ragadhita , 2021).

The observed correlation coefficient for the Freundlich isotherms were 0.9192 ,0.2736, 0.0926, 0.4231 and 0.9574 for Cu^{2+}, Zn^{2+}, Pb^{2+}, Cr $^{3+}$ and Ni^{2+} respectively. The freundlich constant K$_f$ indicates greater adsorption capacity y, 1/n is the intensity of the adsorption or surface heterogeneity indicating the energy relative distribution adsorbate sites heterogeneity. When 1/n is greater than zero ($0< 1/n < 1$) the adsorption is favourable, when 1/n is greater than 1, the adsorption process is unfavourable, and it is irreversible when $1/n = 1$ (Ayawei et al., 2017; Cheragi et al., 2015; Al- Ghouti and Da'ana., 2020). The values of 1/n in Table 2 of all the cations falls within 0 to 1 which implied favorable adsorption metal ions by the adsorbent.

CONCLUSIONS

According to the results obtained in this investigation it was observed that Alumina activated onion peel presents a great capacity for the adsorption of cations in fish pond waste water. The Scanning Electron Microscope (SEM) image of the onion peel composite before and after adsorption showed that the porous structure of the adsorbent before adsorption could improve the adsorption capacity. The FTIR analysis confirmed the presence of the various functional groups that acted as the binding sites for the adsorption of the cations. Adsorption of the cations depends on optimum pH, contact time, adsorbate concentration and adsorbent dosage for high rate of sorption. The Langmuir isotherm were demonstrated to provide the best correlation coefficient (R^2) for the biosorption of Zn, Cu, Cr, and Pb ions while Freundlich isotherm provided the best correlation coefficient for Ni ions. It can be concluded that since onion peel is a locally available waste and has a considerable high biosorption capacity, it can be modified and used as a good adsorbent for the treatment of fishpond wastewater containing Cu, Pb, Zn, Ni, and Cr ions.

Declarations

The authors declare no conflict of interest.

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