Biosorption of nickel and cadmium from spent battery in aqueous solution using Animal waste as bio sorbent in a packed column

Divya K. and Abraham Jayanthi*
Microbial Biotechnology Laboratory, School of Biosciences and Technology, VIT University, Vellore, Tamil Nadu, INDIA
*jayanthi.abraham@gmail.com

Abstract
A promising technique for eliminating heavy metals from the environment and industrial effluents is biosorption. Toxic metals can be entirely removed from waste water by using organic molecules in the absorption process, but this requires a physiochemical mechanism. There are several approaches including the economical and environmentally beneficial method of bio adsorption, to remove heavy metals from contaminated water. Animal wastes including crab shells, fish scales and egg shells were used in research to determine whether they might play as an efficient adsorbent to remove heavy metals from wastewater. It has been reviewed that instead of using traditional ways to remove heavy metals from waste water, unused animal parts could be used as an adsorbent.

The possibility and mechanism, as well as the variables influencing favourable conditions that promote heavy metal adsorption, are examined in this study. It has been demonstrated that the study supports the high metal adsorption capacity of animal wastes, materials such as scales and shells and that the rate of adsorption is dependent on time, pH, the initial concentration of metals and the concentration of the adsorbent during suspension. With R^2 values ranging from 0.9275 to 0.9894, isotherm modelling investigations showed that the experimental data best suited the Freundlich and Langmuir models respectively. Using the removal efficiency formula, the amount of adsorption of each metal with various animal wastes material scales and shells was determined.

Keywords: Bio absorption, Nickel, Cadmium, Crab shells, Fish scales, Egg shells, FTIR, SEM-EDAX, AAS, XRD.

Introduction
A subset of trash electrical and electronic equipment is called electronic waste. Primary non-rechargeable batteries and secondary rechargeable batteries are divided into two groups based on their capacity to be charged, according to WHO[50]. Man is dependent on batteries in day to day activities[46]. Cadmium was once thought to be a hazardous element that might harm both people and animals and cause cancer in a variety of tissues. It triggers cell division, which prevents apoptosis and DNA repair[44]. The maximum amount of cadmium that can be found in water is 0.003 mg/l. Ionic versions of nickel are naturally occurring elements with minimal absorption. Minor amounts of nickel are necessary for the normal growth and reproduction of animals, plants and microbes.

Nickel compounds and salts are typically very soluble in water[2]. According to Wani et al[52], there is a 0.2 mg/l tolerance for nickel. When disposed of in large amounts, the biowaste from the seafood industry, which is abundant in crab shells, has a significant impact. The fact that crab shells are efficient bio sorbents, suggests that they have strong structures and mechanical resistance. Additionally, their surface has a distinct functional group that aids in the absorption of certain heavy metals[41].

In a bio adsorption investigation, fish scale was employed[30]. According to Kumar et al[30] and other studies, the surface area of the fish scale has certain functional groups such as carbonyl, nitro and amine groups with metal ions connected on the fish scale and porous layer generating a good surface for metal ions to be adsorbed on its surface. The membrane of an egg shell is composed of ceramic components that are arranged in three layers: the cuticle on the outside, a spongy layer in the middle and a lamellar layer on the inside[30,31,33,35].

Fish scales have a nanocrystalline hydroxyapatite and collagen fiber structure that offers a potent interaction with heavy metals [14]. Nitro compounds containing carbonyl and amine groups are present on the surface of fish scales which allow metal particles to stick to the metal ions and be adsorbed there. This work uses animal wastes such as crab shells, fish scales and egg shells, which are easily obtained in large quantities to adsorb nickel and cadmium from aqueous solutions.

Material and Methods
Nickel sulfate and cadmium sulphate were dissolved in filtered water to create the stock solution of nickel and cadmium at various concentrations such as 100, 200 and 300 mg/l. During the adsorption procedure, the solutions were kept at room temperature. To keep the pH at the necessary level, 0.1M sodium hydroxide and 0.1M hydrochloric acid were added. Crab shells, fish scales and egg shells were gathered from a Vellore local market in order to make porous powder. After removing contaminants with distilled water, the samples were dried at 100˚C for 24 hrs. To conduct the experiment, the samples were ground into a fine powder and dried for 24 hrs at 50˚C in an oven.

Adsorption experiments: A packed column with a diameter of 10 cm and a length of 25 cm was used for the experiment. Temperature and pH levels were monitored. Glass beads were layered 2cm deep within the column to provide a consistent flow of fluid. Atomic adsorption spectroscopy was used to analyse the metal concentrations in the samples which were collected at regular intervals and filtered via Whatmann filter paper [4].

Adsorption isotherm: The purpose of this investigation was to ascertain the equilibrium maximum adsorption capacity [9]. By increasing the metal ion concentrations from 100 to 300 mg/l, the absorption isotherm was computed. Validation of the adsorption on bio sorbents was done using Langmuir and Freundlich model. The relationship between the concentration of the solute in the liquid phase and the amount of solute adsorbed can be used to describe this process [9]. This study is used to determine the maximum adsorption capacity at equilibrium.

Langmuir equation is:

$$\text{qe} = \frac{qmax}{1 + K_l C_e}$$

where C_e denotes the equilibrium concentration of metal ions (mg/l), max is a required amount of metal ions to form monolayer on adsorbent surface (mg/g) and K_L stands the Langmuir equilibrium constant.

Freundlich equilibrium equation:

$$lnqe = lnKF + \frac{1}{Ce} \ln Ce$$

where KF is Freundlich equilibrium constant and n is exponent.

Desorption and reuse of the bio sorbent: Centrifugation was used to prepare the biomass which was then cleaned in a packed column for 20 mins using both acidic and alkaline eluents. After being separated from pollutants using 0.45µm Whatmann filter paper, the biomass was examined for the presence of metals. The amount of metal ions adsorbed on biomass and the final concentration of metal ions on the biosorption medium were used to calculate the efficiency of desorption.

Desorption equation is:

$$\text{Metal desorption percentage} = \frac{C0 - Ci}{C0} \times 100$$

NaOH treatment: Gharieb et al[23] stated that animal waste materials were treated with dialysis membrane and then cleaned with distilled water until the pH approached neutral. Sodium hydroxide was utilized as an alkaline elutant. After being dried at 60˚C, the biomass both treated and untreated was pulverized and kept for further use.

IR spectra of bio adsorption: To determine whether there were any efficient groups in the adsorbent, FTIR analysis was used. Before and after the intake of metals, the changes in bonding that occurred during biosorption, were noted and compared. Potassium bromide was used to prepare the samples[16].

Surface morphology: Scanning electron microscopy was used to examine the surface morphology of the bio adsorption both before and after the adsorption. After the samples were cleaned of contaminants using ethanol at varying concentrations, they were allowed to air dry. In 2002, Ramage et al[39] in order to stop the samples from charging applied gold palladium sputter on the samples before analysis (Ultra 55 model, Zeiss, EVO 18, Germany).

X-Ray diffraction: Using powder X-ray diffraction, the biomass of treated and untreated samples was utilized to ascertain the crystalline phase composition of crab shells, fish scales and egg shells on nickel-cadmium spent batteries. X-ray diffraction was measured using the dried samples at $3°min^{-1}$ and an angle of 2φ in the range of 10° to 90°. Using version 5.2.2 Profex,[27] the diffractions were analysed and the crystalline phase was identified. The peaks were then compared to JCPDS data from version 3.15[17] software to ensure that they matched.

Heavy metal biosorption: Utilizing Varian Spectra A240, Atomic Absorption Spectrometry (AAS) was employed to determine the nickel and cadmium concentrations on biomass. The sample's pH was measured and kept within the intended range. AAS analysis was performed on the filtrate obtained from the experiments and the results were compared to the concentration of heavy metals in the solutions before experimental trial.

Crab shells, fish scales and egg shells were used as the bio adsorbents for their study. For the purpose of a column study, the samples were gathered, dried and powdered. A column with a diameter of 10 cm and a height of 25 cm was utilized to hold powdered shells as a biosorbent. Different concentrations of nickel and cadmium ions were created as a stock solution. Atomic absorbance spectroscopy was used to determine the absorbance of the samples after they had been treated on a column with various shells for both nickel and cadmium[13].

Results and Discussion

Both cadmium and nickel exhibit a better fit according to the regression coefficients, or R^2, for the Freundlich and Langmuir isotherms. The experimental data, as can be shown, more closely matches the Freundlich model. Similar studies on bio adsorption have been conducted by other researchers[7]. They used fish scales (*Cyrinus carpio*) as bio-adsorbents for the removal of Cd (II) ions from an aqueous solution and discovered that the fish scales had an adsorption capacity of 68.6 mg/g. They suggested that the fish scales are a good adsorbent material for cadmium. Similarly, Norzila et al[36] studied on *Oreochromis niloticus*, also known as Tilapia fish bone scales, as adsorbent material to remove nickel ions from wastewater and it removed 74.6% of nickel.

According to Yeddou and Bensmaili's[53] study results, the eggshell membrane removes 90.9% of the metal ions from wastewater by acting as an adsorbent of Ni and Ag. Crab and egg shells were used in research by Wani et al[52] as a bioadsorbent Whereas crab shells removed 1.619 mg/l of cadmium and egg shells removed 2.935 mg/l of cadmium. According to our studies, the absorbance rate of nickel sulfate in the presence of crab shells was 0.656 mg/l, for fish scale it was 0.662 mg/l and for egg shells, it was 0.786 mg/l. Crab shells absorbed at a rate of 0.577 mg/l, fish scales at a rate of 0.543 mg/l and eggshells at a rate of 0.812 mg/l when tested for cadmium sulphate.

Effect of the adsorption: Figure 1 illustrates the adsorption of nickel and cadmium using a Langmuir isotherm. The removal efficiency improvements for Ni and Cd ions have been determined to be 84% to 97% for nickel and 79% to 92% for cadmium in crab shells; for fish scales, the percentage of absorption was 87% to 93% for nickel and 83 to 96% for cadmium; and for egg shells, the percentages were 73 to 81% and 65 to 88%.

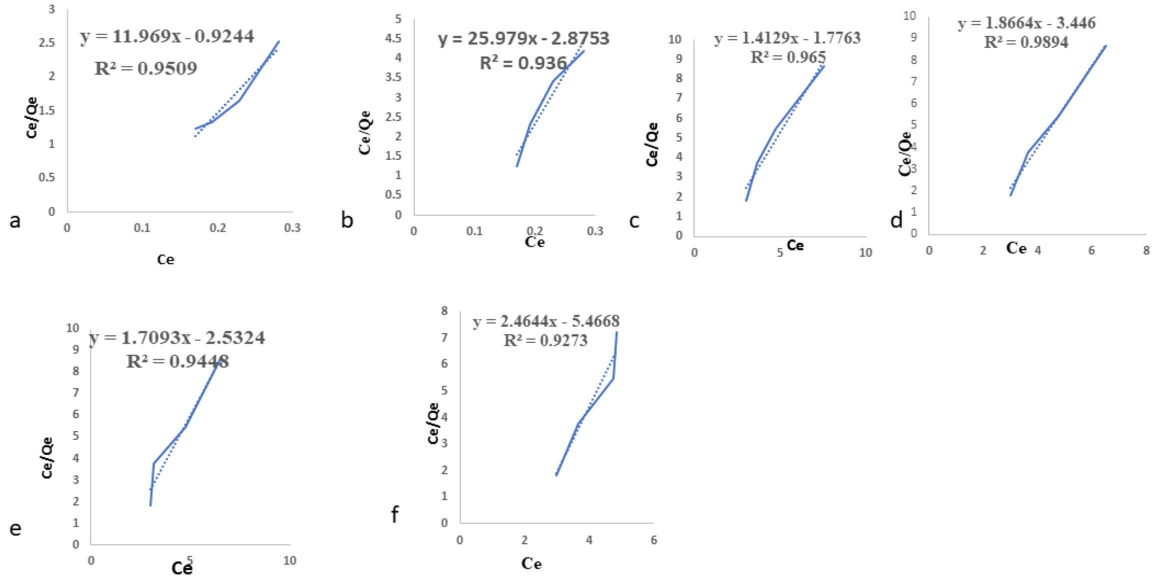

Fig. 1: Langmuir isotherm of bio adsorption by crab shells (a) nickel, (b) cadmium; fish scales (c) nickel, (d) cadmium; eggshells (e) nickel, (f) cadmium

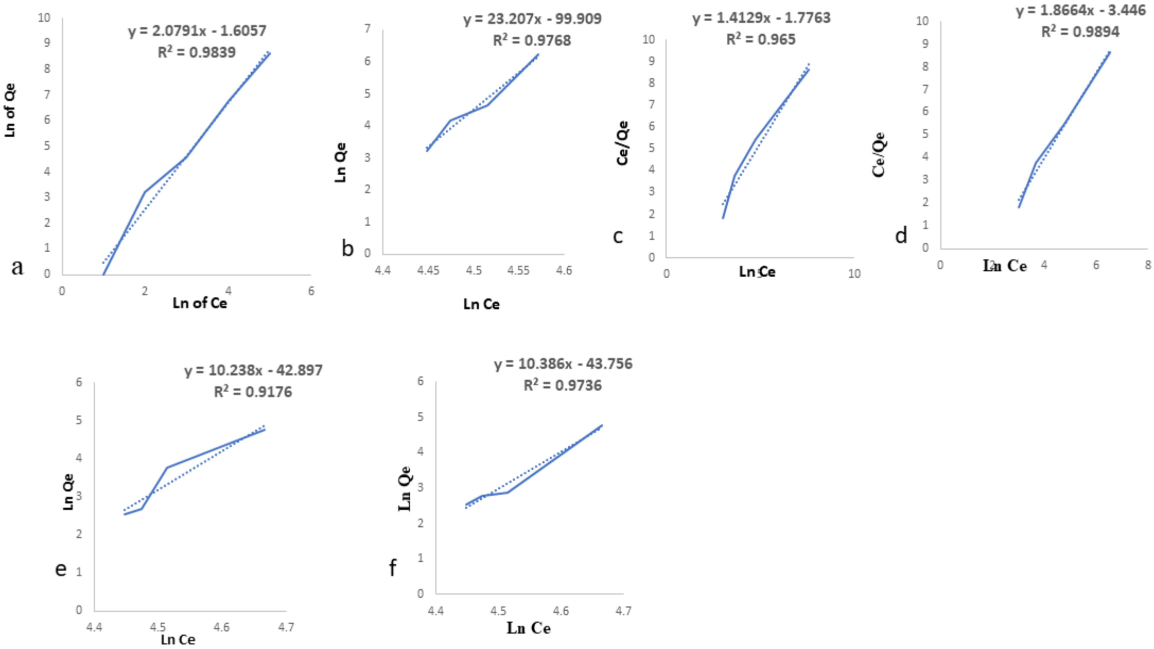

Fig. 2: Freundlich isotherm of bio adsorption by crab shells (a) nickel, (b) cadmium, fish scales (c) nickel, (d) cadmium, egg shells (e) nickel, (f)cadmium

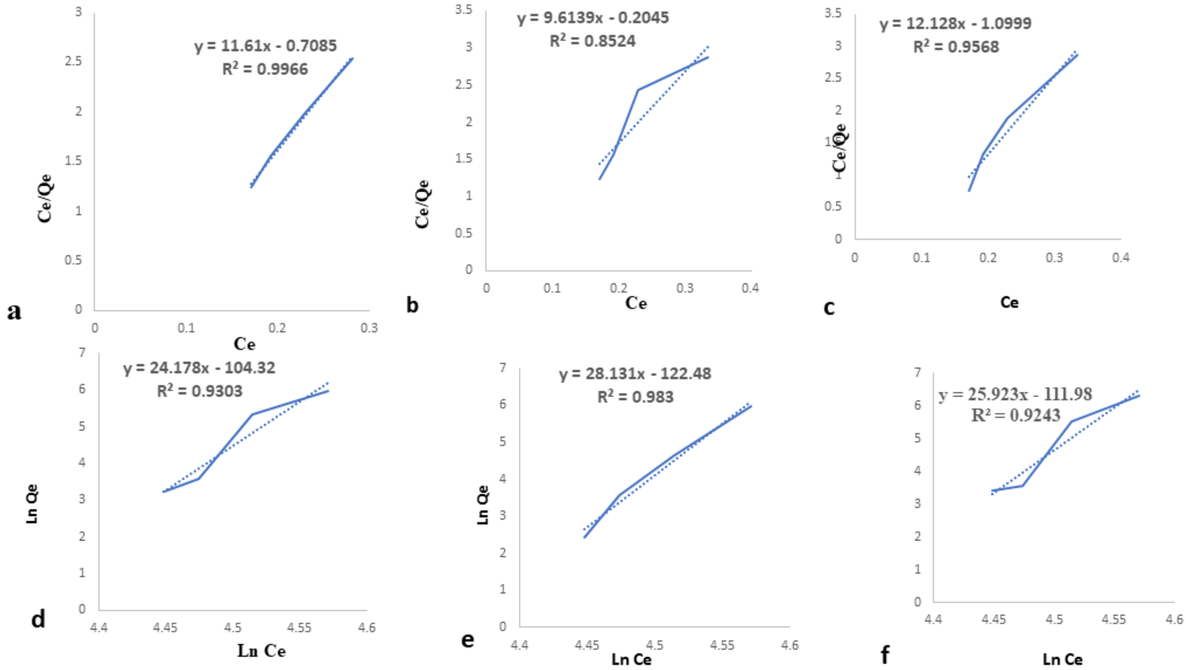

Fig. 3: Langmuir isotherm of spent nickel-cadmium battery (a) crab shells, (b) fish scales, (c) egg shells. Freundlich isotherm of spent nickel-cadmium battery (d) crab shells, (e) fish scales, (f) egg shells

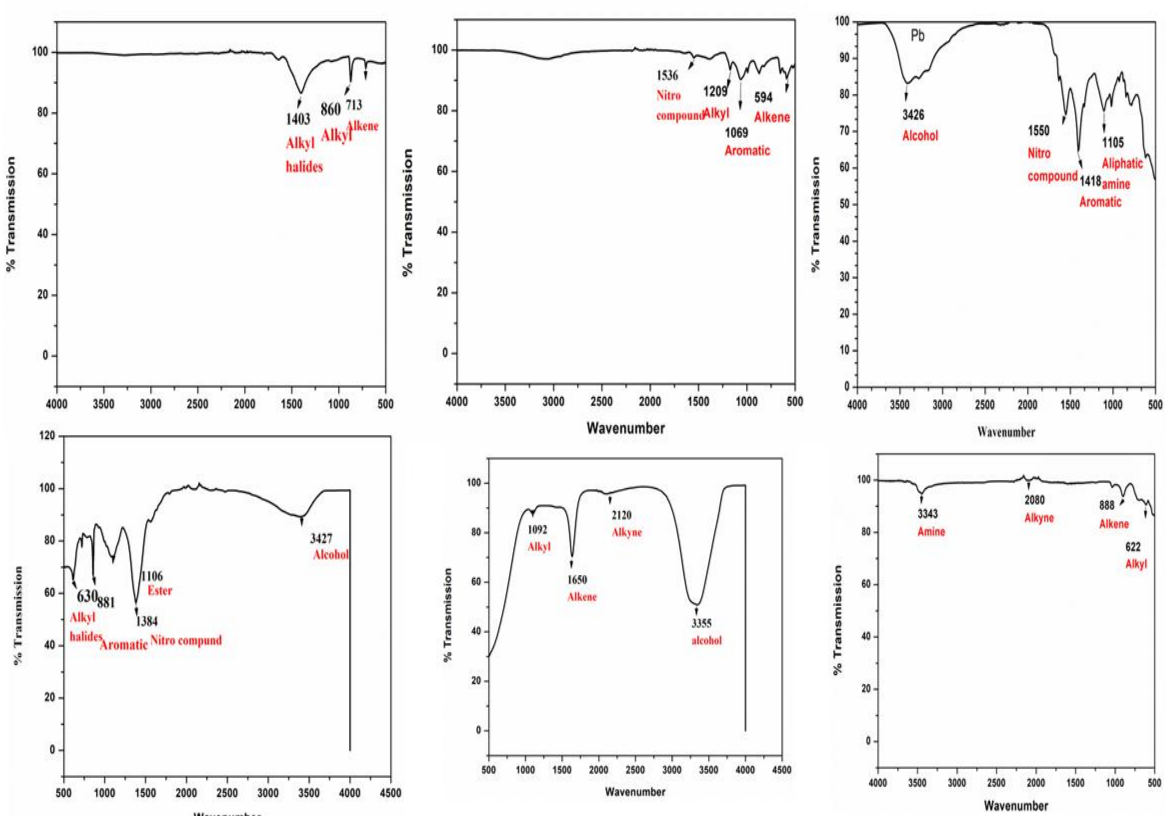

Fig. 4: FTIR spectrum of nickel ions on crab shells, fish scales and egg shells and cadmium ions on crab shells, fish scales and egg shells.

Plotting the Langmuir isotherm between Ce/Qe vs Ce yielded a straight line, as seen in fig. 1. Slope and intercept values were used to derive specification standards. As shown in fig. 1, the adsorption fits the Langmuir isotherm well, as evidenced by the correlation coefficients for nickel (0.9509) and cadmium (0.936). The equation indicates that the adsorbate has single layer coverage, which is equivalent to the adsorbent surface and the experimental data provided a perfect fit. Cadmium and nickel RL values of initial concentration were computed and tabulated. The adsorption of cadmium was validated by the regression values ranging from 0 to 1.

Freundlich isotherm: Plotting of the Freundlich graph was done between the logs of Qe and Ce. Slope and intercept were used to estimate the values. When it comes to determining the strength of adsorption bonds, the Freundlich isotherm is ideal because of the values of n. Higher values of n indicate that the adsorption occurred at higher intensities[4]. For nickel and cadmium when treated with the crab shells, the Freundlich isotherm's regression coefficient (R^2) value was 0.9839 for nickel and 0.9763 for cadmium. For fish scales, the R^2 value was 0.965 for nickel and 0.9894 for cadmium. For treated egg shells, the regression coefficient was 0.9176 for nickel and 0.9736 for cadmium.

Using isotherm modelling, the correlation coefficient of the adsorption isotherm was determined. The data for the nickel, cadmium and nickel-cadmium spent battery's Langmuir and Freundlich isotherms are presented in table 1. For crab shells, fish scales and egg shells, the regression coefficient for the Langmuir isotherm on the adsorption of used nickel-cadmium batteries was determined to be 0.9966, 0.8524 and 0.9568 respectively. For crab shells, fish scales and egg shells, the regression coefficient of the Freundlich isotherm on adsorption was 0.9303, 0.983 and 0.9243 respectively. According to Espinosa et al[20], metallic cadmium powder was created using nickel cadmium batteries on cadmium distillation, while metallic nickel was produced by melting nickel in a furnace.

FTIR Analysis: The IR spectra were used to determine the functional groups present on the surface of biosorbents of treated and untreated samples. The position of absorbance peaks of corresponding functional groups is represented in figure 5.

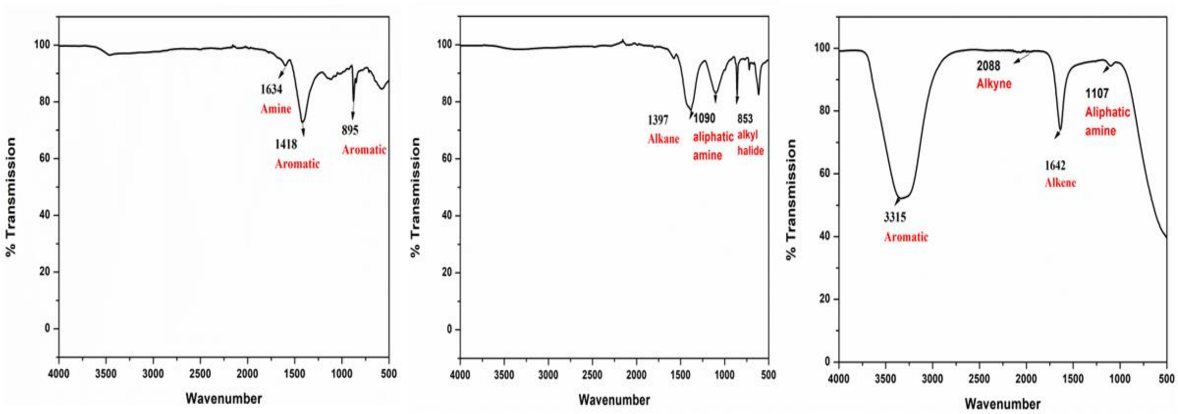

Fig. 5: FTIR spectrum of nickel-cadmium on spent battery treated with crab shells, fish scale and egg shells.

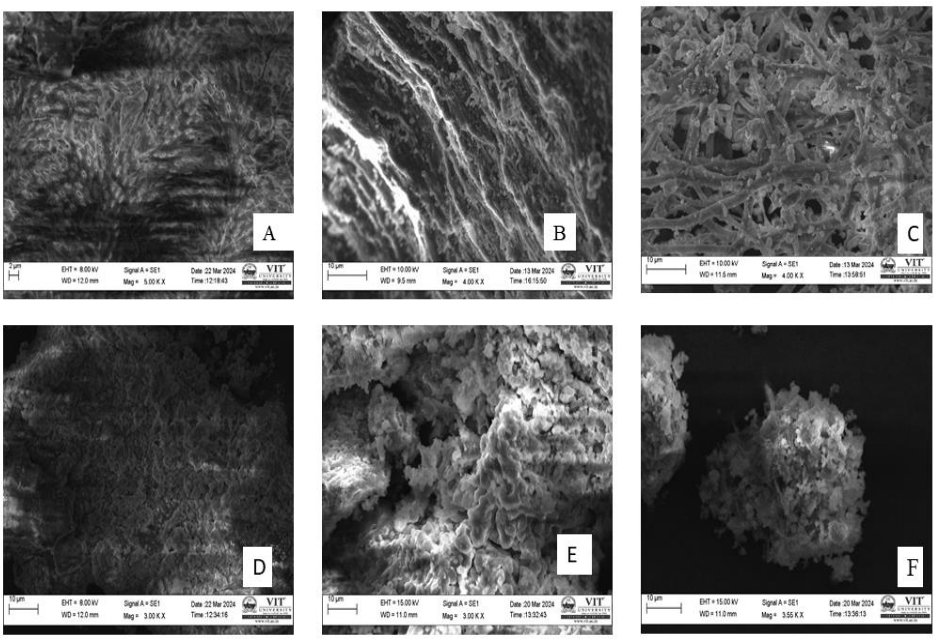

Fig. 6: Surface morphology of nickel ions (a) crab shells, (b)fish scales, (c) egg shells, morphology structure on cadmium ions (d) crab shells, (e) fish scales (f) egg shells.

Table 1
Isotherm parameters obtained during biosorption of heavy metals on animal waste for nickel, cadmium and nickel-cadmium spent battery ions.

S.N.	Heavy metals	Plant waste	Isotherm models					
			Langmuir model			Freundlich model		
	Nickel		Q max	K_L	R^2	K_F	n	R^2
1		Crab shells	0.92445	0.0772	0.9509	2.2877	44.374	0.9839
2		Fish scales	1.7762	0.0955	0.965	1.7887	14.372	0.9803
3		Egg shells	2.5324	4.3358	0.9448	1.6324	10.238	0.9176
4	Cadmium	Crab shells	2.8753	0.1106	0.936	1.9996	23.207	0.9768
5		Fish scales	3.4459	1.8462	0.9894	1.0803	2.1192	0.9685
6		Egg shells	5.4668	2.2183	0.9273	1.6410	10.385	0.9736
7	Ni-Cd spent battery	Crab shells	0.7084	0.0610	0.9966	2.0183	24.177	0.9303
8		Fish scale	0.2044	0.0212	0.8524	2.088	28.131	0.983
9		Egg shells	1.0998	0.0906	0.9568	2.049	25.923	0.9243

Table 2
Percentage removal of heavy metals from animal waste.

Concentration mg/l	Plant waste	Nickel	Cadmium	Ni-Cd spent battery
100	Crab shells	73%	65%	79%
200	Fish scales	87%	82%	84%
300	Egg shells	84%	79%	92%

Table 3
Desorption study of heavy metals using 0.1N (HCL and NaOH)

S.N.	Bio adsorbent	Quantity of heavy metals recovered from 0.1N (HCl) (mg/L)		Quantity of heavy metals recovered from0.1(NaOH) (mg/L)	
		Nickel	Cadmium	Nickel	Cadmium
1	Crab shells	345	488.2	378.8	376.8
2	Fish scales	126.4	166.4	254	298
3	Egg shells	433	454	465	476
4	Ni-Cd spent battery	424	421	476	532

The sample taken both before and after adsorption with each of the three adsorbates was compared to the FTIR spectra of various animal waste shells. Using an IR laser lamp, the infrared spectra were examined between 4000 and 500 cm^{-1}. The existence of efficient functional groups on bio sorbents is necessary for the heavy metal ion absorption; this is demonstrated by the sharp peak at 1642 and 1395 cm^{-1} which was present in the control spectrum and indicated the presence of sulfonyl chloride and alkene. S=O and C=C stretches are evident in the bands at 1403,860 cm^{-1} when nickel is treated with crab shells as an adsorbate. A prominent peak at 3426 cm^{-1} on egg shells is indicative of the presence of the main amine group. A new peak is detected at 1550 and 1196 cm^{-1} indicating the existence of sulfonate group and nitro compound.

After being exposed to cadmium ions, the biosorbent of crab shells produced a spectrum at 3343, 2080 and 888 cm^{-1} which showed the existence of halo compounds, isothiocyanate and aliphatic primary amine. A peak is observed at 3355 cm^{-1} and 2120 cm^{-1} on the surface of fish scales, indicating the presence of amine, azide and alcohol groups. A sharp peak at 3427 cm^{-1} and 1384 cm^{-1} at the wavelengths of N-H and C-H is observed when eggshells have been used on cadmium ions, showing the presence of amine and aldehyde group. A sharp peak is formed at 3427 cm^{-1} and 1384 cm^{-1} at the wavelengths of N-H and C-H when eggshells have been used on cadmium ions, showing the presence of amine and aldehyde group.

The study used crab shells, fish scales and egg shells to examine spent nickel cadmium battery powder. The existence of an amine and an alcohol group is shown by the control peaks, which are located at spectra of 3460, 2335 and 1066 cm^{-1}. A spectrum showing the presence of amine, carboxylic and alkene was found at 1634, 1418 and 895 cm^{-1} when battery powder was bioabsorbed using crab shells. On treated fish scale, a peak was raised at 1397, 1090 and 1107 cm^{-1}, indicating the presence of alkene and secondary alcohol and on egg shells. A peak raised at 3315, 1642 and 1107 cm^{-1}, indicated the presence of amine, oximine and secondary alcohol group.

SEM: Using Scanning electron microscopy, the morphology, structure and physical characteristics of the adsorbent were examined. The SEM images demonstrate the biosorbents' porous properties. To verify that heavy metals were bonded to the biosorbents, the SEM images of the bio sorbents were examined both before and after they were exposed to metals and during the biosorption process. The images that appear in figures 6(a) and (d) show how the bio adsorbents numerous pores, uneven surface actively participates in the adsorption of heavy metal ions from aqueous solution. It is also possible to see the alterations in the shape of the bio adsorbent molecules and the porosity of the absorbent surface filled with metal pollutants[37].

The surface of the fish scales in figures 6(b) and (e) has uneven white and dark areas. Dark areas are rich in protein, rich in carbon and oxygen, while white colour indicates an inorganic material with high calcium and phosphorus content[41]. Fibrous structures are present on eggshells after being treated with nickel and cadmium. It also contained calcium carbonate[27].

X-Ray diffraction: Calcium carbonate, which can be found in crab shells, has been determined to be present in Fig. 7(a). 9.05% of trace elements, including phosphorus, magnesium, sodium and potassium, are found in crab shells[30]. Proteins and 58.235 mg of organic material had been found to be present on chitin by X-ray diffraction. 52.1% of nickel was found to have biosorbent based on ignition damage. After treating the fish scales with spent batteries, fig. 7(b) XRD examination demonstrates the absence of lead oxide and ferric oxide in the biosorbent preparation. In order to maximize its efficiency, it has undergone a variety of chemical pre-treatments[11].

With a percentage of 63.8%, oxides were the most abundant on the bioabsorbent and their presence suggests that heavy metals on fish scales may be adsorbed. The presence of calcite on eggshell is indicated by the existence of a peak on fig. 7(c) at an angle of 2φ, 29.7° and a smaller peak in the range of 23.4 to 65°. At room temperature, calcite is composed of calcium carbonate. According to Gopinath et al[22], the rhomboid structure and reflecting hardness of egg shells verify that the compound is pure and crystalline. Employing XRD analysis meant for the advancement of bioleaching, the phase of battery powder before and after bioleaching was examined. Some peaks in the eggshell adsorbate were discovered to have an amorphous nature.

Conclusion

With respect to utilized batteries, the bioaccumulation and biosorption of heavy metals from electronic wastes have been thoroughly investigated. Effective adsorbents for removing nickel and cadmium from aqueous solutions included crab shells, fish scales and egg shells. It was found that the fixed-bed adsorption system worked better when the inflow concentration of nickel and cadmium ions was lower. Fish scales and powdered eggshells are inexpensive adsorbents for the biosorption of metal ions. Moreover, acidic conditions enhanced the adsorption capability of Ni and Cd ions on crab shells, fish scales and egg shell powder, which might be used for large-scale metal removal from its wastes.

The Langmuir and Freundlich models, both suit all three absorbents well, used to monitor the isotherm investigations while the absorption study was conducted for both the initial and final concentrations. Most of the absorbency values were found to be high, at 200 mg/l for two metals, when the elimination efficiency was calculated using the equation.

To investigate the changes that happened during the treatment with animal waste material, the SEM-EDAX and FTIR were used during bioaccumulation and biosorption. Studies involving bioleaching were conducted to remove metal while gradually lowering the pH of the spent battery. SEM-EDAX and XRD examination confirmed the alterations that took place during the bioleaching of the spent battery. In conclusion, it has been confirmed that possessing animal waste materials can be used as biosorbents adsorption/desorption characteristics.

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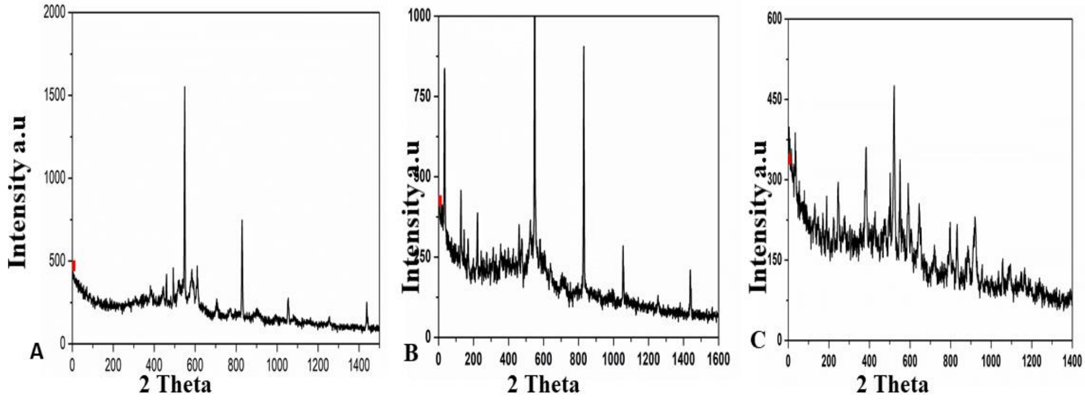

Fig. 7: X-ray diffraction of Ni-Cd ions on spent battery with crab shells, fish scales and egg shells.

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