DESORPTION STUDIES OF Pb, Cd, AND Fe (III) IONS FROM UNMODIFIED RAPHIA PALM FRUIT (RAPHIA HOOKERI)

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*Abstract***:** Batch desorption experiments were carried out on four raphia palm (*Raphia hookeri*) fruit biomasses sorbed with Pb, Cd, and Fe(III) ions, using HCl and NaOH as desorbing solutions. Results showed that for both acid and alkaline desorption, Pb^{2+} proved to be the most desorbed among the three metal ions considered. Maximum percent desorption was 98.35% on the UEN biomass. On a general consideration, MEP biomass appeared to be the best by which the metal ions could be desorbed. The modified biomasses were more generally desorbed than the unmodified. There was a general pattern of dependence for all the metal ions considered, such that desorption decreased with increase in concentration loaded on the biomasses.

Introduction

Solid-liquid interaction such as adsorption is an equilibrium process. Adsorbate mobility from bulk solution and subsequent attachment to the adsorbent surface is at some point balanced by a detachment from the surface and reentry into the bulk. The latter process is desorption. While adsorption is useful for adsorbate removal, desorption is an important regeneration step or process for the adsorbent after adsorption. The concern over metal pollution of the aqueous environment has been the main drive for the search for methods for removal of pollutants such as metal ions in the aqueous phase. Removal materials and methods are available for metal ions and other aqueous phase pollutants. By reasons of availability, low cost and regenerative benefit, removal of aqueous pollutant molecules or ions have been approached via phytofiltration or biosorption. Biosorption is a chemical technique of removing soluble solutes by the use of biological or agricultural or vegetable materials. Biosorbents have been proven to have high capacities for aqueous metal ions removal due to their metal sequestering properties and can significantly reduce the concentration of heavy metals in solution[1] [2]. They have been found to be effective, of low cost and eco-friendly above conventional methods [3],[4]**,**[5] and[6]. Studies have shown that plant biomass can effectively bind metals and thus remove them from solutions [7]. For these reasons, it is important to consider a reciprocal process as desorption to evaluate the reuse potentials of biosorbents. Some adsorption works have been followed up with desorption [8], [9],**[10]**. Pb and Cd ions were desorbed from *Amanita rubescens* and colemanite ore waste (CW) using both 1 M HCl and 1 M

HNO$_3$. The recovery for both metal ions was found to be higher than 90 % for *Amanita rubescens* and 95% for colemanite ore waste (CW) [11]. The effects of acidic, basic and neutral reagents on the recovery of Pb^{2+} and Cd^{2+} from metal-laden biomass of wild cocoyam(*C.bicolor*) was investigated by [12]. Acidic media recovery for Pb^{2+} was over 90%, and Cd^{2+} was 80.52%. Basic media recovery for Pb^{2+} and Cd^{2+} were 12.11% and 23.44% respectively. [13] put the HCl recovery from unmodified *Solanum elaeagnifolium* biomass at about 100% for Pb^{2+} and 53.8% for Cd^{2+}. The reuse potential of raphia palm (*Raphia hookeri*) fruit after adsorption is here investigated using two desorbing solutions.

Material and Methods

Batch adsorption experiments were first carried out to load the raphia palm (*Raphia hookeri*) fruit biomass with metal ions separately. In the loading, 0.2g of 600 μm of UEN, UEP, MEN, and MEP were separately weighed out into 15 mL glass tubes. The biomasses were equilibrated by shaking at 325 rpm with 10 mL of metal ion solutions with initial concentrations of 20, 40, 60, 80 and 100 mg/L respectively for one hour at room temperature. The reaction bottles were filtered, and the filtrates were analysed for metal ion concentrations using the atomic absorption spectrophotometer(AAS).

The same mass of metal ion- loaded residue of the previous filtration was placed in each tube containing 10 mL of 0.01 M HCl or 0.01 M NaOH as desorbing solutions. The tubes were shaken in a variable shaker at 325rpm at room temperature for one hour. After one hour, the mixtures were respectively filtered, and the filtrates were analysed for metal ion concentration by atomic absorption spectrometry (AAS). The amounts of metal ions in the filtrate showed the amounts of metal ions desorbed by the desorbing solutions.

Results and Discussion

The results of the desorption studies are presented in the plots of relevant variables in Figures 1 to 14.
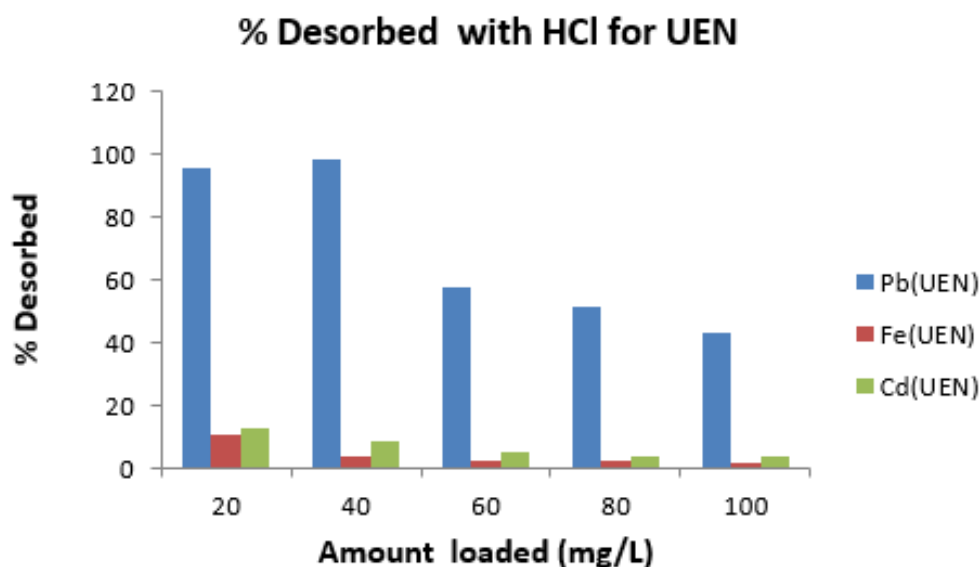

Figure 1: Percentage desorbed with HCl against the amount loaded for the desorption of Pb, Fe(III) and Cd ions using unmodified raphia palm fruit endocarp(UEN).
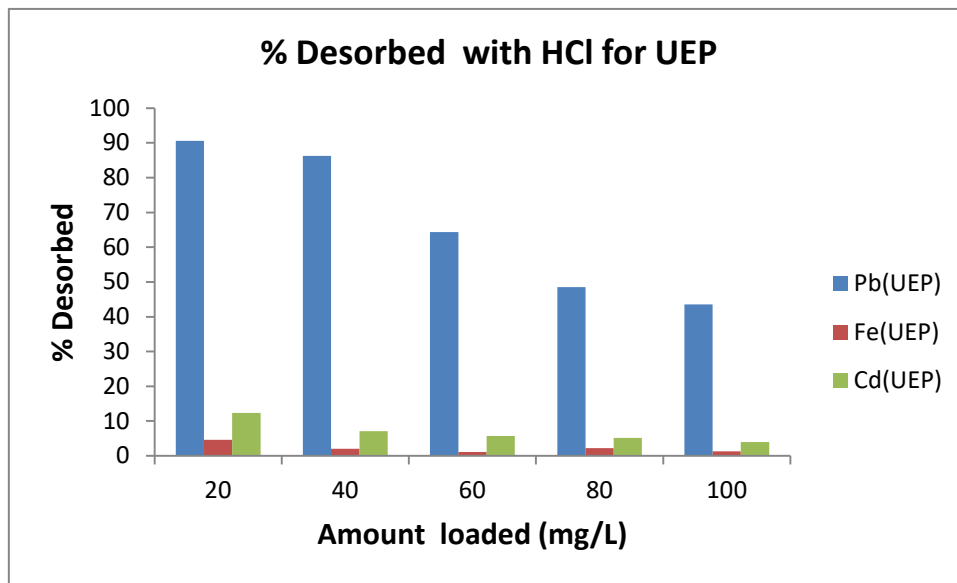
Figure 2: Percentage desorbed with HCl against the amount loaded for the desorption of Pb, Fe(III) and Cd ions using unmodified raphia palm fruit epicarp(UEP).
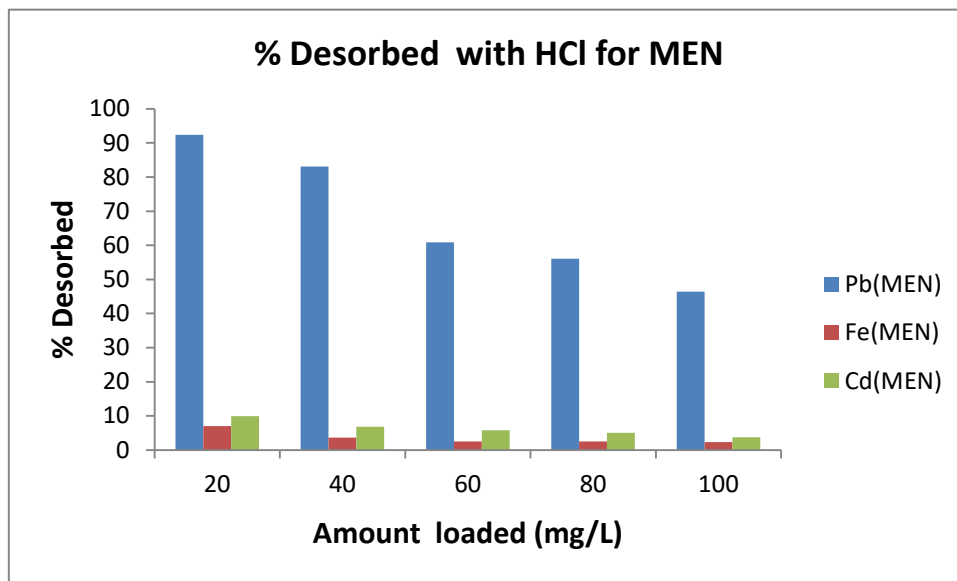

Figure 3: Percentage desorbed with HCl against the amount loaded for the desorption of Pb, Fe(III) and Cd ions using modified raphia palm fruit endocarp(MEN).
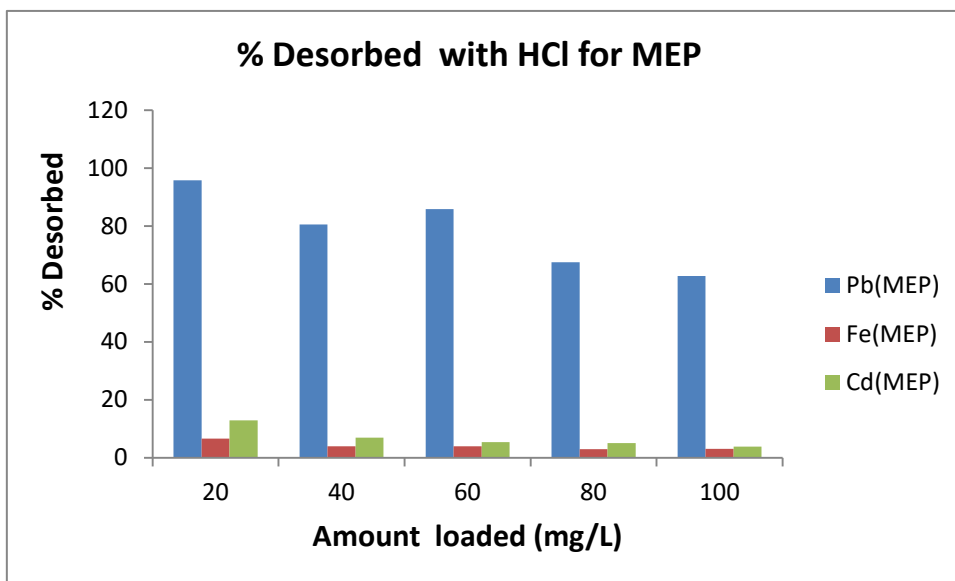
Figure 4: Percentage desorbed with HCl against the amount loaded for the desorption of Pb, Fe(III) and Cd ions using modified raphia palm fruit epicarp(MEP).
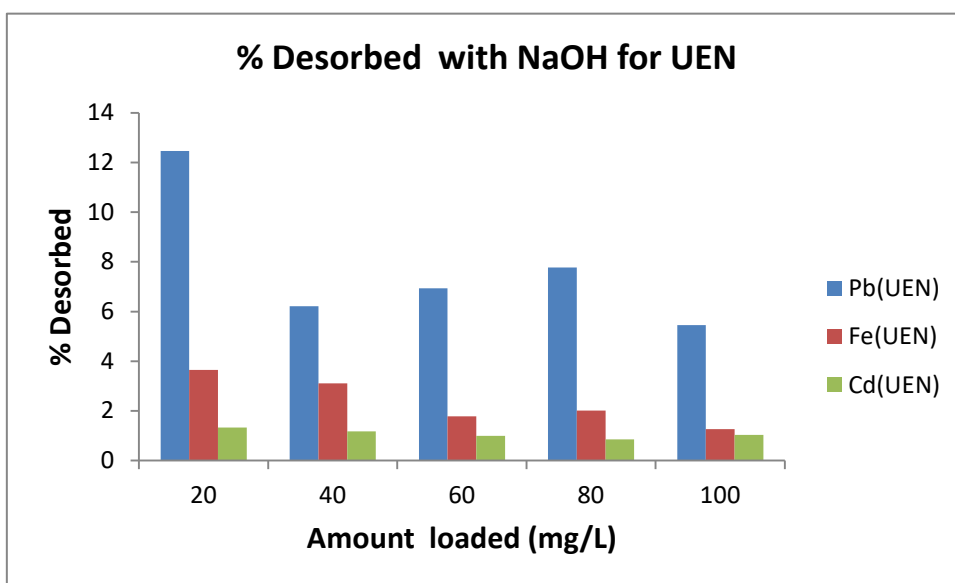

Figure 5: Percentage desorbed with NaOH against the amount loaded for the desorption of Pb, Fe(III) and Cd ions using unmodified raphia palm fruit endocarp(UEN).
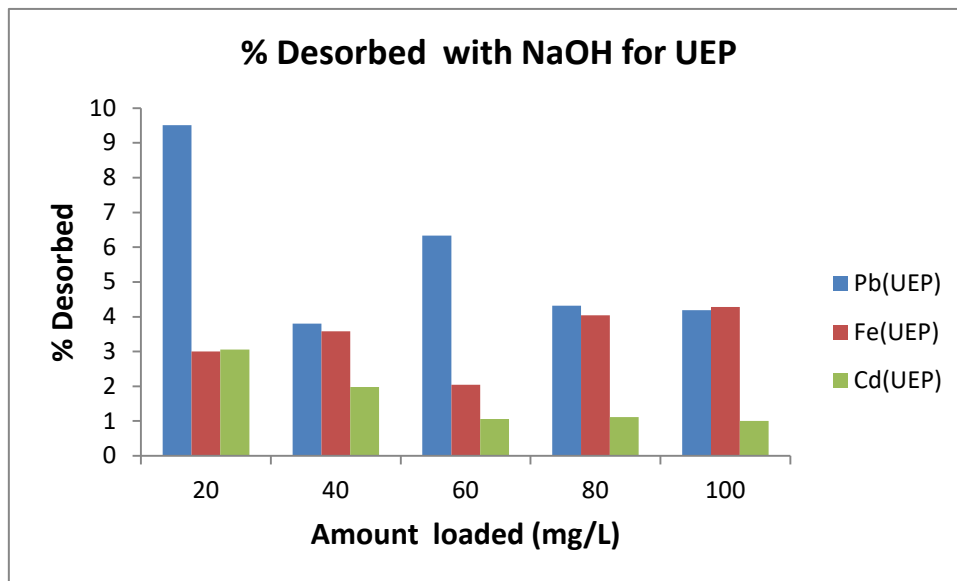
Figure 6: Percentage desorbed with NaOH against the amount loaded for the desorption of Pb, Fe(III) and Cd ions using unmodified raphia palm fruit epicarp(UEP).

Figure 7: Percentage desorbed with NaOH against the amount loaded for the desorption of Pb, Fe(III) and Cd ions using modified raphia palm fruit endocarp (MEN).

Figure 8: Percentage desorbed with NaOH against the amount loaded for the desorption of Pb, Fe(III) and Cd ions using modified raphia palm fruit epicarp(MEP).
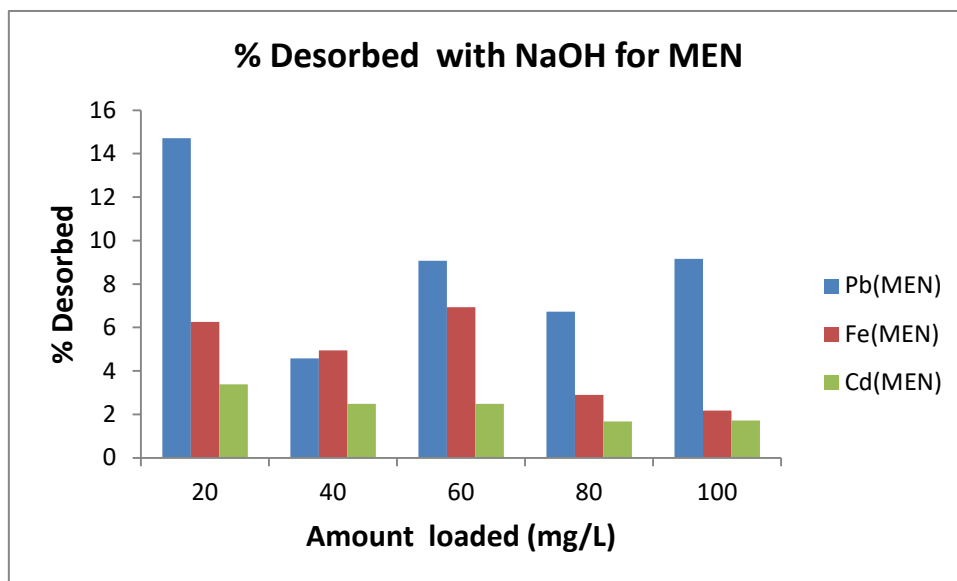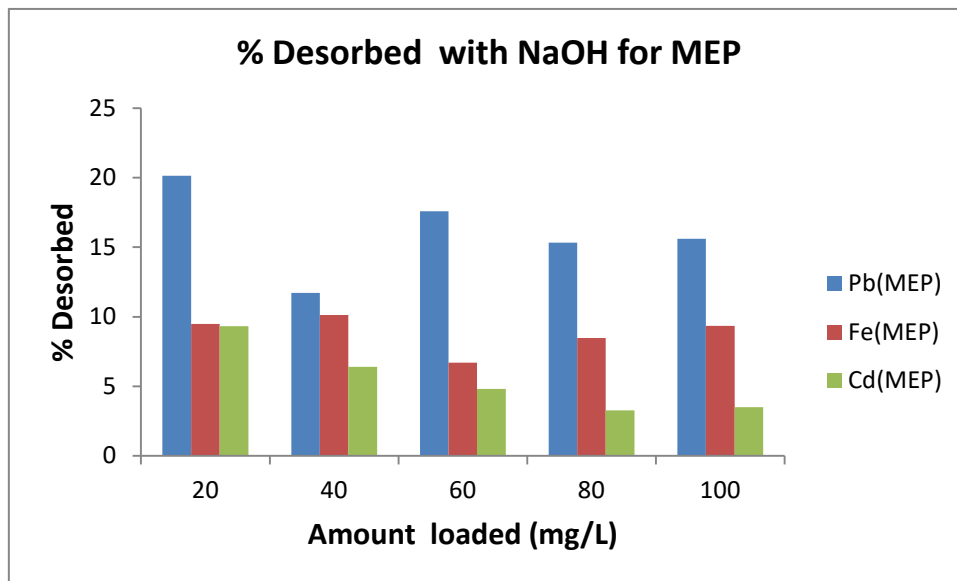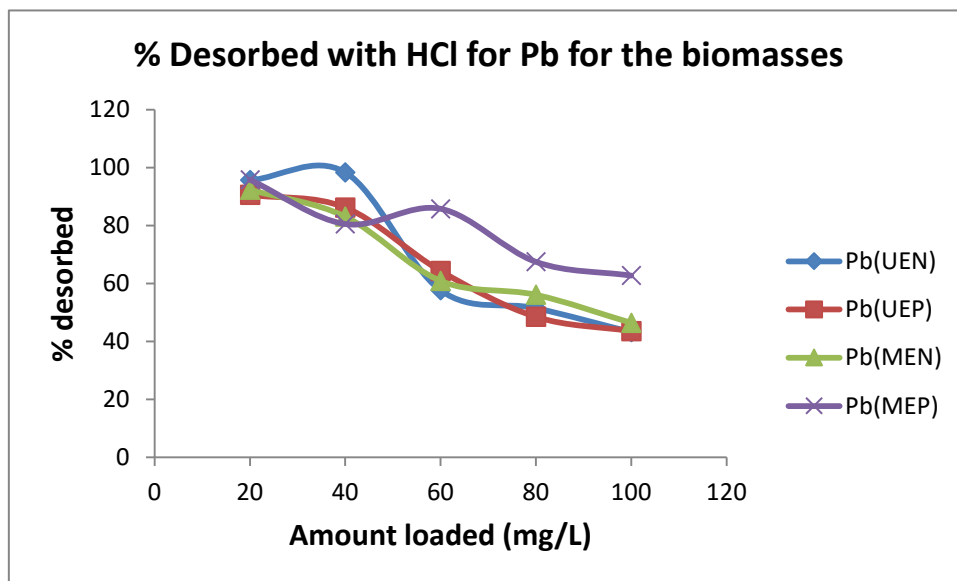

Figure 9: Percentage desorbed with HCl against the amount loaded for the desorption of Pb ion using modified and unmodified raphia palm fruit endocarp and epicarp.
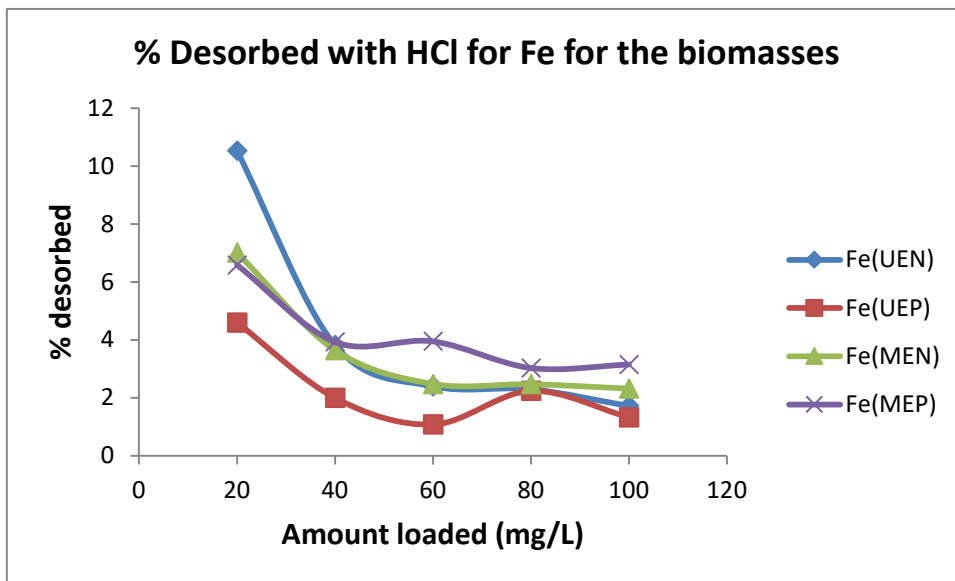
Figure 10: Percentage desorbed with HCl against the amount loaded for the desorption of Fe ion using modified and unmodified raphia palm fruit endocarp and epicarp.
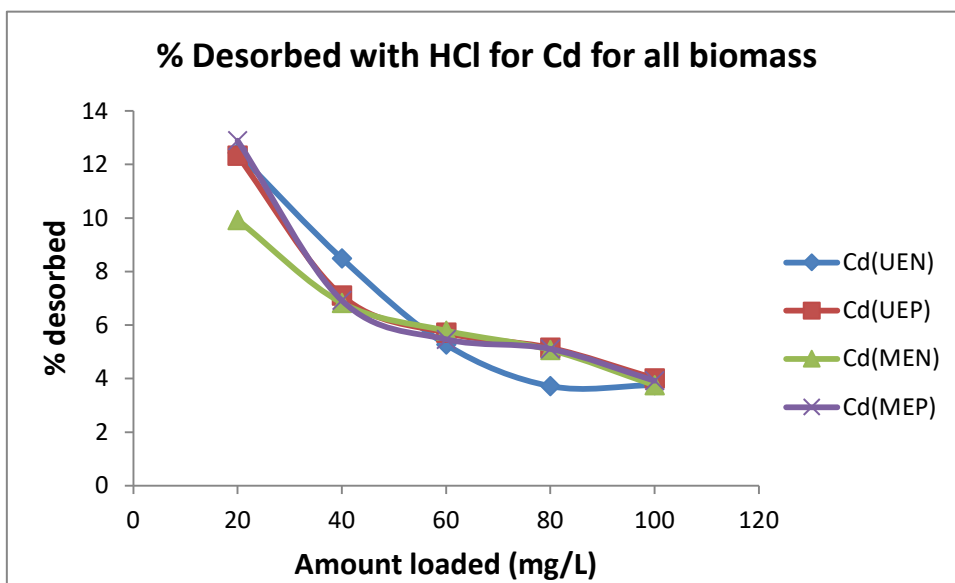
Figure 11: Percentage desorbed with HCl against the amount loaded for the desorption of Cd ion using modified and unmodified raphia palm fruit endocarp and epicarp.

Figure 12: Percentage desorbed with NaOH against the amount loaded for the desorption of Pb ion using modified and unmodified raphia palm fruit endocarp and epicarp.

Figure 13: Percentage desorbed with NaOH against the amount loaded for the desorption of Fe(III) ion using modified and unmodified raphia palm fruit endocarp and epicarp.

Figure 14: Percentage desorbed with NaOH against the amount loaded for the desorption of Cd ion using modified and unmodified raphia palm fruit endocarp and epicarp.
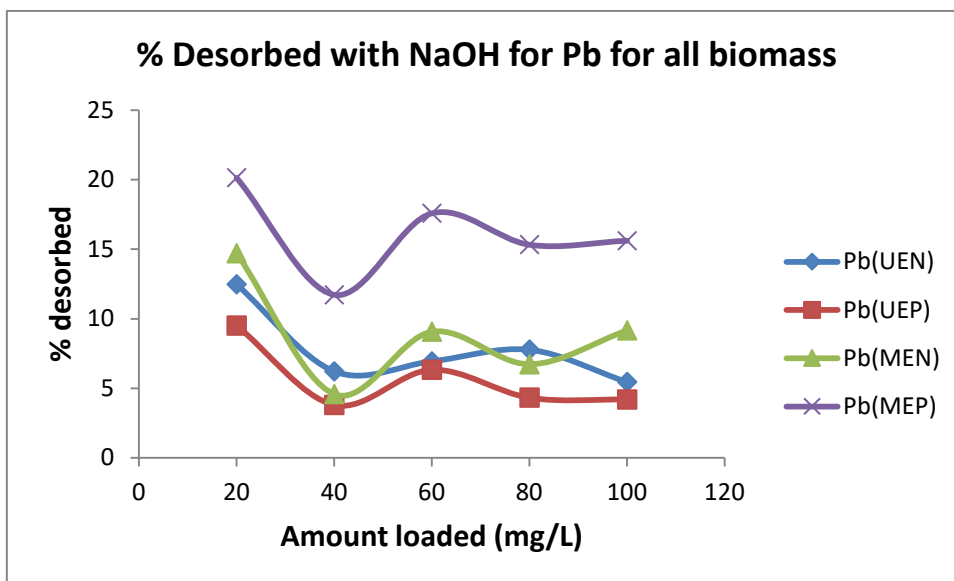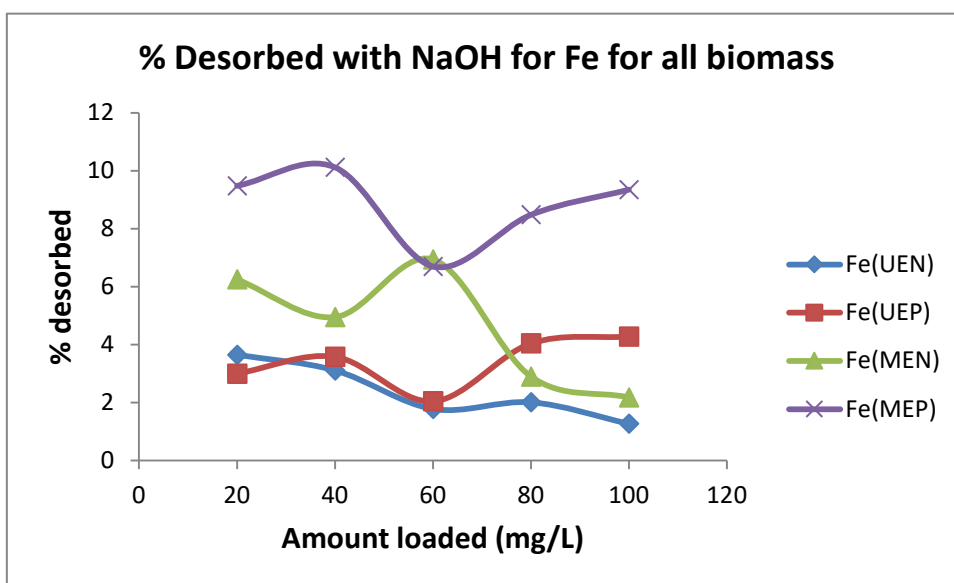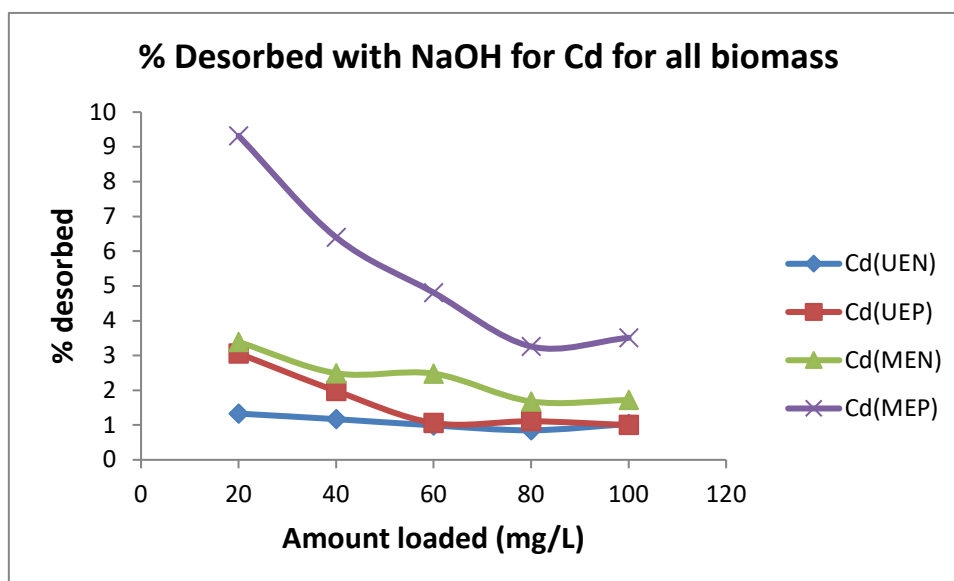
Desorption was carried out to ascertain the possibility of recovery of adsorbed metal ions from the biomasses and hence deduce the most viable part of the fruit for such a process. The data represented in figure 1 to 14 showed that for both acid and alkaline desorption, Pb^{2+} proved to be the most desorbed among the three metal ions considered. Maximum percent desorption was 98.35%, 10.53% and 12.43% for Pb^{2+}, Fe^{3+} and Cd^{2+} respectively on UEN. That for UEP was 90.58%, 4.60% and 12.33% for Pb^{2+}, Fe^{3+} and Cd^{2+} respectively. The maximum percent desorption for MEN biomass were 92%, 7.01% and 9.93% for Pb^{2+}, Fe^{3+} and Cd^{2+} respectively. Maximum percent desorption for MEP were 95.81%, 6.59% and 12.89% for Pb^{2+}, Fe^{3+} and Cd^{2+} respectively. Analysis of the different ions on the same biomass with HCl showed the following trend of occurrence:

UEN (HCl): $Pb^{2+} > Cd^{2+} > Fe^{3+}$
UEP (HCl): $Pb^{2+} > Cd^{2+} > Fe^{3+}$
MEN (HCl): $Pb^{2+} > Cd^{2+} > Fe^{3+}$
MEP (HCl): $Pb^{2+} > Cd^{2+} > Fe^{3+}$

The order of preference of desorption of different ions on the same biomass with NaOH is as follows:

UEN (NaOH): $Pb^{2+} > Fe^{3+} > Cd^{2+}$
UEP (NaOH): $Pb^{2+} > Fe^{3+} > Cd^{2+}$
MEN (NaOH): $Pb^{2+} > Fe^{3+} > Cd^{2+}$
MEP (NaOH): $Pb^{2+} > Fe^{3+} > Cd^{2+}$

It is clear from the given orders that Pb^{2+} was the best desorbed with both acid and alkaline media for all biomasses considered.

Single metal ions desorption concerning different biomass showed the following sequence using the acid:

Pb^{2+}(HCl): MEP > UEN > UEP > MEN (maximum % desorbed)
Fe^{3+}(HCl): UEN > MEN > MEP > UEP (maximum % desorbed)
Cd^{2+}(HCl): UEN > MEP > UEP > MEN (maximum % desorbed)

On a more general consideration of the plot of the acid-desorbed biomasses for single ions, MEP biomass appeared to be the best by which the metal ions could be desorbed. This projection was evident in the case of the alkaline desorption as shown by the order given below:

Pb^{2+} (NaOH): MEP > MEN > UEN > UEP
Fe^{3+} (NaOH): MEP > MEN > UEP > UEN
Cd^{2+} (NaOH): MEP > MEN > UEP > UEN

From the trend, the modified biomasses were more desorbed than the unmodified; and between the two modified forms, MEP gave a better desorption for the metal ions. Though Pb^{2+} was the most desorbed, there was a general pattern of dependence for all the metal ions considered. In general, percent desorption decreased with increase in concentration loaded to the biomasses.

The trend of single ion desorption indicated a differential desorption of the metal ions. Ionic radii have been proposed as one of the enhancing factors for differential adsorption of cationic species on binding sites of biosorbents. It has been observed that the elements with the smaller ionic radius will compete faster for exchange sites than those of larger ionic radius [14]. Previous studies by [15], [16] and [17] also showed that cationic species of smaller ionic radii have a greater affinity for binding sites on biosorbents than larger ones. A corollary of differential adsorption should be a differential desorption: since the affinity of the larger ions is less than the smaller ions towards the biosorbents, it would imply that the element with the larger ionic radius would be desorbed faster and more than the elements with smaller ionic radii. The ionic radii of the metals considered in this work are 1.20 Å, 0.97 Å and 0.64 Å for Pb^{2+}, Cd^{2+} and Fe^{3+} respectively. The Pb ion is the largest of the three ions. Hence its desorption will be more and easier because of its lowest biosorbent affinity, in comparison to the smaller ions. This trend is shown for Pb^{2+} in the acid desorption for all the biomasses used.

Metal ions also act as Lewis-acids capable of accepting electron pairs from donors in solution. Acid strength of metal ions is obtained from their acid-dissociation constants (K_a) for hydrolysis which in general increases with increase in charge and decreasing ionic radius. The acid strength of the metal ions is: $Fe^{3+} > Cd^{2+} > Pb^{2+}$. An element with a higher tendency of accepting electron-pairs is more likely to be retained on the adsorbent than the one with a lower tendency. By the trend of Lewis acidity, Pb^{2+} is most likely to be flushed, then Cd^{2+} and lastly Fe^{3+}.

A probable mechanism of desorption can be derived according to the following reactions:

$HCl \ (aq) + H_2O \ (l) = H_3O^+(aq) + Cl^- \ (aq)$

$MX(s) + H_3O^+ \ (aq) + nCl^-(aq) = M^{n+}(aq) + nCl^-(aq) + HX + H_2O(l)$
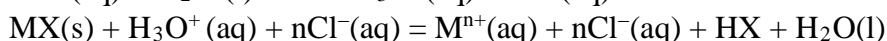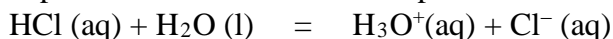
Where, M is the metal atom and X is the adsorbent.

The proposed mechanism could imply that the process of desorption was ion-exchange. Sorption has been observed to occur through processes such as complexation, precipitation [18], and ion-exchange [19], but ion-exchange is more generally prevalent. Mechanism of metal-ion stripping from loaded biomass have been observed to proceed in acidic media [20],[21], [22], [23],[24],[25] and basic media [26] by ion-exchange.

Conclusion

Desorption analysis showed that the adsorbates could be recovered from the raphia palm fruit biomass after adsorption. Acid desorption proved to be a better option than the alkaline desorption. An optimum desorption capacity of 98% showed that the raphia palm fruit biomass could be used as a recycling medium for the adsorbate.

Acknowledgements

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