Preliminary studies on equilibrium and kinetics of heavy metal ion sorption on immobilized *Ficus asperifolia* stembark biomass

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Abstract
In our quest to exploit the biomasses in our local environment for an efficient water treatment at the level of hazardous aqueous ions removal, we furthered here by immobilizing the stem bark biomass of *Ficus asperifolia* in a stable polymer matrix of calcium alginate. The sorption capacity of the immobilized *F. asperifolia* stembark (IFASB) for the heavy metal ions as determined from the percentage change in initial concentrations of their aqueous solutions using atomic absorption spectrophotometer (AAS), were as follows: Cu^{2+} 96.41%, Fe^{3+} 94.15%, Cd^{2+} 99.91%, Zn^{2+} 97.91%, Pb^{2+} 99.30%, Cr^{3+} 97.12%, Mn^{2+} 94.73% respectively. Equilibrium and kinetics investigations were carried out while studying the effect of ionic strength, pH, initial concentration and contact time on the sorption capacity of IFASB. Even though there are some variations within the ranges of investigation, the IFASB can be said to still exhibit an impressive absorption capacity (not less than 80%) for all the ions and under all varied conditions. This study therefore includes the IFASB in the archive of modified biomasses with economic potentials in the removal of heavy metals from wastewater.

Keywords: *F. asperifolia*, heavy metal ions, biosorption, equilibrium

1. Introduction

Aqueous heavy metal ions above some threshold concentration in utility water will pose a wide range of health and environmental challenges to humans and other organisms [1]. One of the sustainable ways to avert this is by removing this dangerous species or reducing them to safe amount in discharges and wastewater before they are allowed to enter the water body. The word "sustainable" will remain in the earlier statement only if extensive research into developing alternatives, efficient and sustainable technologies for the removal of these species. A number of procedures have achieved the removal of these species from aqueous media, but none have been without limitations calling for improvements [2, 3]. Among these limitations, cost has been the most pinching. These therefore place biosorption above other methods being the most cost efficient. There has been a rich archive of reports on biomasses and modified biomasses studied for the removal of toxic metal ions from aqueous media [1, 3, 4, 5, 6], this is to keep obtaining efficient alternatives with reduced cost implications in the biosorption procedure. Absorption and/or adsorption are the two processes with which metal ions are removed from their aqueous media and trapped in the biomass polymeric matrix. For these materials, a stable structure and organic functionalities with affinity for the metal ions are two basic criteria for their efficiency as

a biosorbent, and when these criteria is only partially fulfilled, various modifications may be involved.

Immobilization is a modification procedure in which the sorbent is caged in a stable matrix by physical and/or chemical means. This impact improved structural integrity and functionalities that enhances the sorbent characteristics of the biomasses during sorption and regeneration processes. The alginate media was used in this study. The cross linking of the polymer is due to the binding of divalent cation Ca^{2+} to the carbonyl group(s) on biomass in a higher co-operative manner. This network immobilizes the biomass to produce the stable sorbent (Equation 1). Other media including carrageenan and polyacrylamide gel has also been reported [7], however, immobilization based on these polymeric matrices were said to result in restrictive diffusion because of closed embedding structures with low mechanical strength [6].

$$L + NaAlg + CaCl_{2(aq)} \rightarrow CaLAlg_{(s)} \text{ (Sorbent)} \dots\dots\dots\dots\dots\dots \text{ Equation 1}$$

F. asperifolia (sand paper tree) is an evergreen tree reaching a height range 5-12 m. The tree is widely distributed in Africa specifically in Senegal, Cameroon, Sudan, Central and East Africa and also in Nigeria. In Adamawa State (North Eastern part of Nigeria), the tree is found in Michika, Hong, Gombi and song local government Areas. The root is locally used in the treatment of coughs, gastritis, urinary disorders and haemoorrhoids [8]. It was also gathered that the leaves are traditionally used as a coagulant. As at the time of this study, no industrial relevance of this plant is known to us.

This study seeks the production of a material with great potentials for industrial use in water remediation from a biomass obtained from the stembark of *F. asperifolia.* The equilibrium studies (under some typical conditions) and the kinetic studies of the removal of aqueous heavy metal ions by IFASB will guide in the optimized application of the material. This study will present another cheap alternative biosorbent with potentials in the biosorption of aqueous heavy metal ions from wastewaters.

2. Materials and methods

2.1 Materials
Sodium alginate, sodium chloride, calcium chloride, hydrochloric acid, chromium nitrate, cadmium nitrate, Iron (II) nitrate, manganese nitrate, zinc nitrate, lead (II) nitrate and copper nitrate are analytical grades and products the British drug house (BDH). These materials are used as obtained with no further purification.

2.2 Sampling
F. asperifolia stembarks was cut directly from the plant tree in the morning on 4th November, 2016 in Girei, Adamawa state, Nigeria.

2.3 Sample Preparation
The biomass modified by immobilization was prepared thus; *F. asperifolia* stem barks were air dried in the laboratory for two months, after which it was grounded and sieved through 100 μm mesh to obtain a fine homogeneous particle size, which was kept and sealed in a clean polyethylene to avoid excessive moisture uptake prior to the modification process.

2.4 Immobilization Procedure of *F. asperifolia* Stem barks Solution

The biomass (4 g) was mixed with 100 cm^3 distilled water. An aliquot of the mixture (50 cm^3) was taken and stirred vigorously with 50 cm^3 of 4% stock solution of sodium alginate till a stable homogeneous mixture was obtained. This mixture was quickly transferred into another beaker containing 60 cm^3 of 0.12 M calcium chloride solution to start the crosslinking reactions. The reaction (complete precipitation) was allowed to occur for 1 h after which the precipitate was filtered, washed with distill water and air-dried at room temperature to obtain the IFASB [9].

2.5 Preparation of Metal Ion Stock Solution

These metal ions Pb^{2+}, Fe^{3+}, Cr^{3+}, Cd^{2+}, Zn^{2+}, Mn^{2+} and Cu^{2+} was chosen during the study. Aqueous solutions (1000 ppm) of this metal ions were prepared from their salts by dissolving 1.60, 3.54, 4.10, 2.10, 2.95, 2.90 and 3.46 g of lead (II) nitrate, iron (II) nitrate, chromium (II) nitrate, cadmium nitrate, copper nitrate, zinc nitrate and manganese nitrate respectively in 1 liter distilled water. From these stock solutions, 200 ppm aqueous solution of each metal ion was prepared by serial dilution [10].

2.6 Sorption Capacity of IFASB

An aliquot (50 cm^3) of the 200 ppm solution of each metal ion was introduced into a conical flask, IFASB (0.2 g) was added, the conical flask was quickly corked and set into a flash shaker and shaken for 2 hours. After the time out, the mixture was filtered, and the concentration of the filtrate was determined using AAS (atomic absorption spectrophotometer, Buck Scientific, model: VGP 210) [10]. The percentage sorption capacity was calculated as follows:

$$\% \ sorption = \frac{Ci - Cf}{ci} \times 100$$

Where: Ci = intial concentration (200 ppm)

Cf = final concentration (as obtained from AAS)

Averages of triple determinations were recorded. This was repeated while varying some parameters of the aqueous solutions to study the metal ions' sorption equilibrium and kinetics.

2.7 Determination of the Effect of pH on Sorption Capacity of IFASB

Equilibrium sorption with respect to solution pH was studied within pH range 1 to 6, at room temperature (30º C) .The pH of the solutions was measured using phywe pH meter and adjusted using 1.0 M hydrochloric acid and 1.0 M sodium hydroxide [10].

2.8 Determination of Effect of Ionic Strength on Sorption Capacity

Equilibrium sorption with respect to ionic strength was studied in a solution of 0.2 – 1.0% weight of NaCl/weight of aqueous solution [9].

2.9 Determination of the Effect of Contact Time on Sorption

To determine the kinetics of sorption towards equilibrium for the aqueous metal ions, 8 sorption assembles for each aqueous solution were set shaking on the flash shaker. These were collected for analysis at different time intervals starting from 0.5 hour till the 24th hour, at room temperature 30^0 C [9].

2.10 Determination of the Effect of Initial Concentration on Sorption Capacity

Equilibrium sorption with respect to the initial metal ion concentration was studied in lower concentration (5 ppm – 100 ppm) solutions of each aqueous metal ion. This was achieved by further serial dilutions [5].

3. Results and discussion

3.1 Sorption Capacity of IFASB

Figure 1 presents the sorption capacity of IFASB for the different aqueous heavy metal ions with initial concentration of 200 ppm. Here, 96.41% was recorded for Cu^{2+}, 94.15% for Fe^{3+}, 99.30% for Pb^{2+}, 94.73% for Mn^{2+}, 97.12% for Cr^{3+}, 97.91% for Zn^{2+} and 99.91% for Cd^{2+}. Cu^{2+} was the least while Cd^{2+} was the most sorbed among the aqueous ions; however, with all above 90%, the studied metal ions sorption on IFASB is encouragingly high. This can be most attributed to synergetic effects between the biomass and alginate creating functionalities with strong affinity for these aqueous ions. This can be suspected as the calcium alginate dose used in the immobilization resulted in higher sorption compared to reported calcium alginate matix only [11, 12, 13]. Compared to immobilized *Ficus syncomorus* leaves (IFSL) biomass in our earlier reports [1, 3], IFASB has shown stronger sorption capacity for Cr^{3+}, Cd^{2+}, and Zn^{2+}.
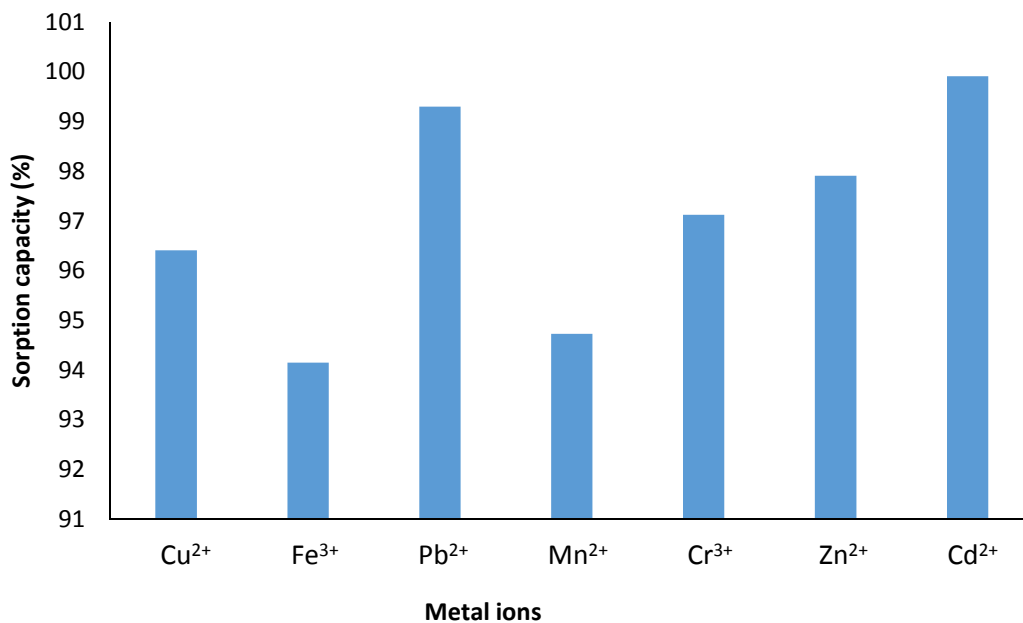

Figure 1: Sorption Capacity of IFASB for metal ions

3.2 Effect of time

Figure 2 presents the effect of contact time on sorption capacity of IFASB for the metal ions under study. It was observed that as the contact time increases, the sorption capacity of metal ions also increases. IFASB reached sorption equilibrium after four hours for Cu^{2+}, Cd^{2+}, Mn^{2+}, Cr^{3+} and six hours for Pb^{2+} and one hour for Fe^{3+} and Zn^{2+}. The variation in the equilibrium sorption time for the aqueous ions can be attributed to their different masses and ionic sizes hence different mobility [1]. Biomass affinity and the ion mobility are the basic factors determining the rate at which the active sites are saturated [14]. For Fe^{3+}, the behavior

observed after the 1st hour may be due to rapid equilibrium attained on the outer/surface active sites, followed by a gradual sorption onto the core active sites of the sorbent.
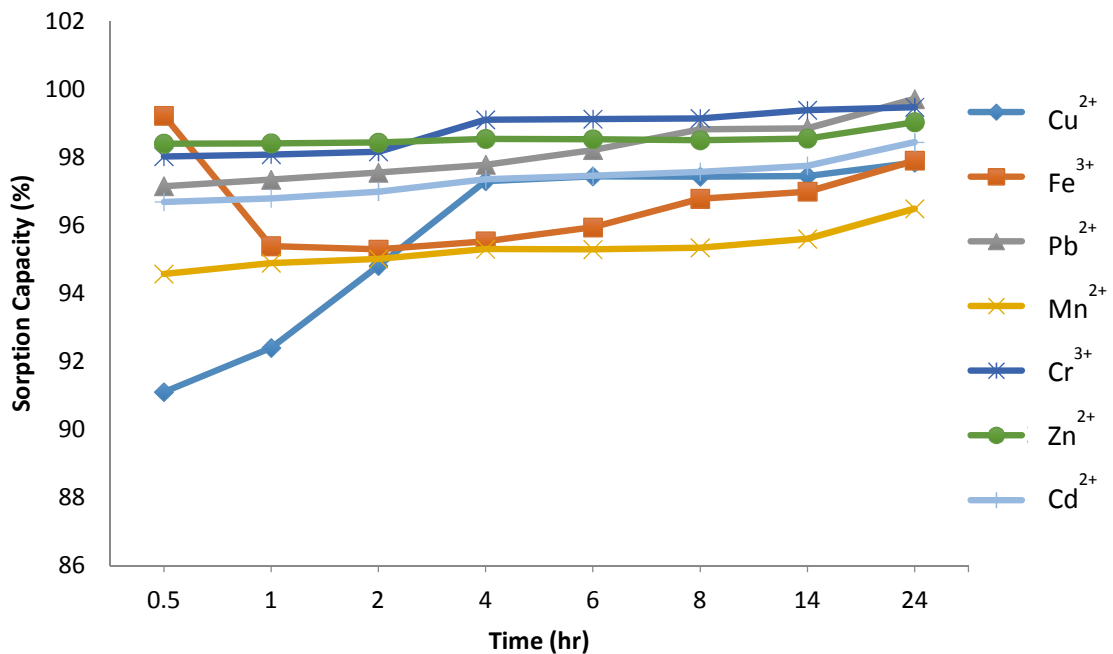

Figure 2: Effect of Contact Time on Sorption by IFASB

3.3 Effect of initial metal ion concentration

Figure 3 illustrates the effect of initial metal concentration on the equilibrium sorption of the aqueous metal ions on IFASB. It can be observed that the removal of metal ions by the bio-sorbent increases with increase in the initial metal ion concentration. This may be due to increase in flux and collision among the metal ions [15]. Increase in the initial concentrations of the aqueous solutions may increase interactions providing driving forces which will influence all mass transfer reactions between the biosorbent (solid phase) and aqueous phase [15, 16]. At 50 ppm, IFASB achieves equilibrium sorption for all the ions; however, the rate for Fe^{3+} was the least. This can be explained in terms of the reactions/interactions between the active sites and metal ions being the slowest for Fe^{3+} under conditions with concentrations lower than 50 ppm.
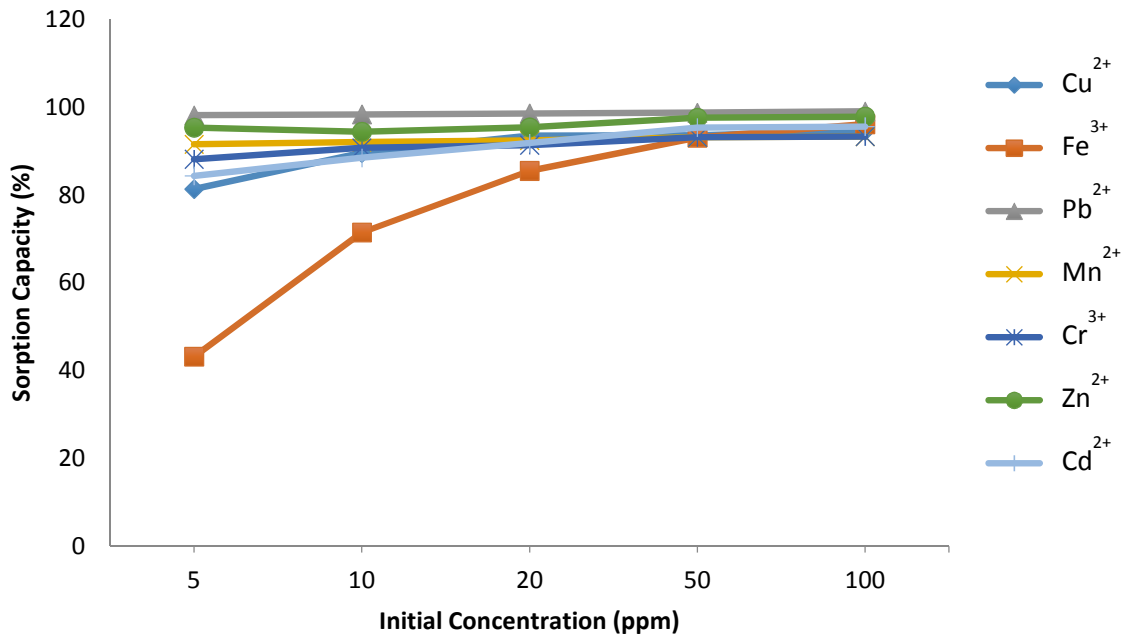
Figure 3: Effect of Initial Concentration on Sorption by IFASB

3.4 Effect of pH

The result obtained from influence of pH on sorption capacities of IFASS is shown in Figure 4. Aqueous solutions with initial concentration of 200 ppm with different pH (1-6) at room temperature (30±2° C) were used in this study. The lower sorption generally observed at the acidic media can be attributed to particle attrition and partial protonation of the active sites with H_3O^+, competing with the metal ions for the available active sites [14]. The effect of pH on the sorption capacity of IFASB for the heavy metal ions depends on their different speciation as the pH value changes [17]. This explains the different fashions of sorption for the different heavy metals as they tend towards equilibrium.
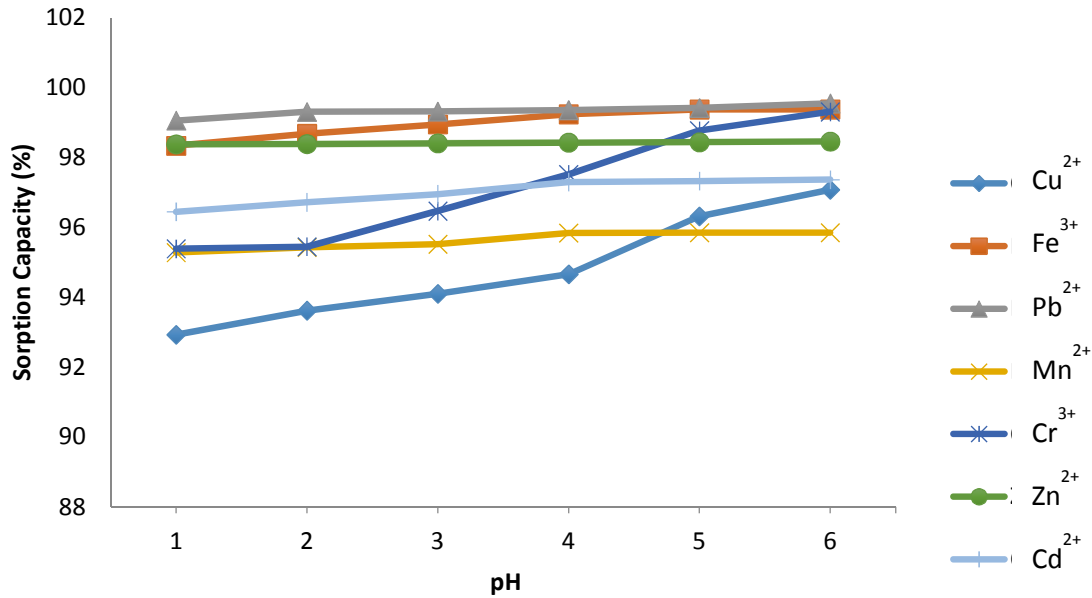
Figure 4: Effect of pH on Sorption on IFASB

3.4 Effect of Ionic Strength on Sorption of IFASB

Figure 5 presents the effect of ionic strength on sorption of the aqueous metal ions on IFASB. Initial concentration of the aqueous heavy metal ions is 200 ppm with 0.2 – 1% NaCl. The results show that sorption capacities of IFASB decreases (slightly for Cu^{2+}, Pb^{2+}, Mn^{2+}, Cr^{3+} and Zn^{2+}) and more significantly for Fe^{3+} and Cr^{3+} with increase in ionic strength. This may signal electrostatic attractions between the ions and the biosorbent. Na^+ competes with the aqueous metal ions in the electrostatic interaction with the active sites, and the sorption of the heavy metal ions reduces as the concentration of the competitive ion and hence ionic strength increases [18]. Increasing concentration of Na+ in the aqueous solution may also increase the repulsive forces on the surface of the biosorbent leading to reduced sorption of the heavy metal ions [6]. NaCl is a typical dissolved salt in wastewater. Even though it's of no significant hazards, its presence and concentration may influence the sorption process [3].
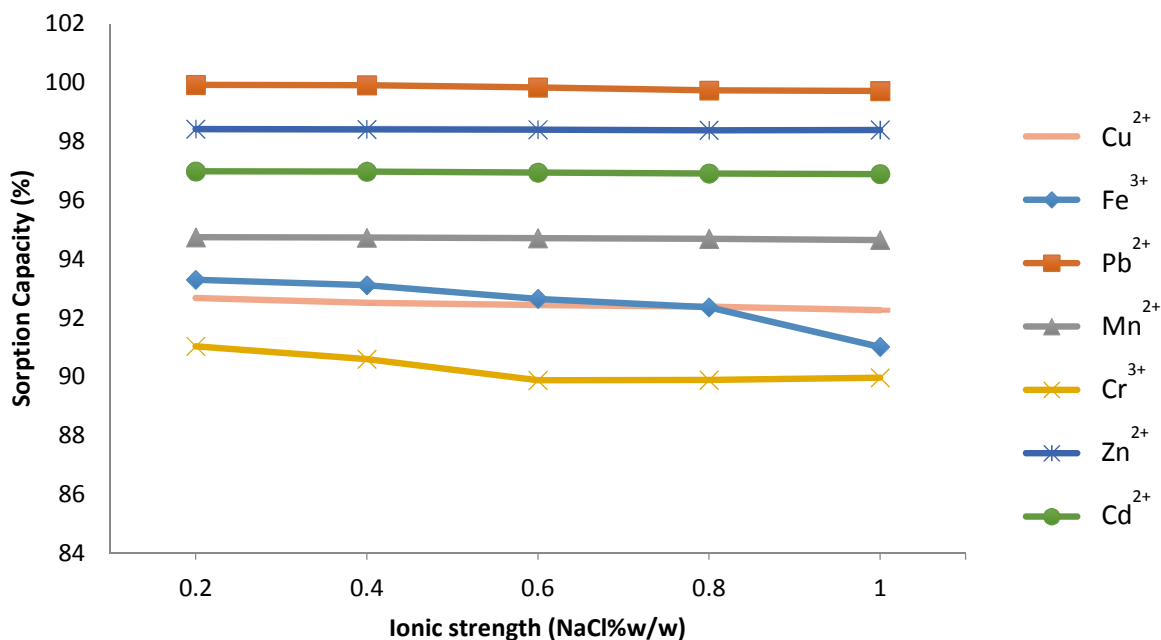
Figure 5: Effect of Ionic Strength on Sorption by IFASB

Conclusion

This study has achieved its aim in establishing the potentials of a biomass prepared from *F.* *asperifolia* stembark, as an alternative material with efficient capability in biosorption. The biomass was modified by immobilization in a calcium alginate matrix. The modified biomass exhibited synergetic effects resulting in a very strong affinity for the aqueous heavy metal ions studied. Equilibrium and kinetic studies on the sorption onto the modified biomass under some typical conditions showed that the material may not require the optimum environmental factors or condition to achieve an efficient sorption of aqueous heavy metal ions from their media. The study therefore has contributed in limiting the current challenges with the remediation of wastewater polluted with heavy metals ions. It has also present *F.* *asperifolia* as a plant with potentials as an industrial raw material.

CONSENT
It is not applicable.

ETHICAL APPROVAL
It is not applicable.

COMPETING INTERESTS
There are no competing interests among authors.

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APPENDIX

Appendix 1: Sorption Capacity

Metal ions	Cu	Fe	Pb	Mn	Cr	Zn	Cd
Sorption capacity of IFASB (%)	96.41 ±0.0011	94.15 ±0.0064	99.30 ±0.0057	94.73 ±0.0042	97.12 ±0.0029	97.91 ±0.0031	99.91 ±0.0048

Appendix 2: Effect of Contact Time on Sorption for IFASB.

Time (hr) Ions (%)	0.5	1	2	4	6	8	14	24
Cu^{2+}	91.10 ±0.033	92.40 ±0.065	94.81 ±0.069	97.30 ±0.011	97.44 ±0.015	97.43 ±0.053	97.45 ±0.063	97.84 ±0.032
Fe^{3+}	99.22 ±0.032	95.39 ±0.043	95.29 ±0.049	95.53 ±0.032	95.94 ±0.084	96.78 ±0.046	96.99 ±0.054	97.90 ±0.045
Pb^{2+}	97.15 ±0.065	97.34 ±0.054	97.55 ±0.065	97.78 ±0.094	98.21 ±0.054	98.82 ±0.083	98.85 ±0.085	99.71 ±0.043
Mn^{2+}	94.57 ±0.095	94.89 ±0.043	95.01 ±0.048	95.30 ±0.049	95.29 ±0.095	95.34 ±0.084	95.60 ±0.084	96.49 ±0.093
Cr^{3+}	98.02 ±0.074	98.08 ±0.084	98.16 ±0.074	99.10 ±0.093	99.12 ±0.087	99.14 ±0.054	99.38 ±0.043	99.47 ±0.084
Zn^{2+}	98.40 ±0.084	98.41 ±0.094	98.43 ±0.082	98.54 ±0.098	98.53 ±0.083	98.50 ±0.093	98.55 ±0.083	99.03 ±0.078
Cd^{2+}	96.69 ±0.093	96.79 ±0.057	96.99 ±0.034	97.35 ±0.068	97.46 ±0.054	97.57 ±0.094	97.75 ±0.037	98.44 ±0.012

Appendix 5: Effect of Initial Concentration on Sorption for IFASB.

Initial concentration (ppm) Ions (%)	5	10	20	50	100
Cu^{2+}	81.40 ±0.092	89.60 ±0.023	93.55 ±0.034	93.64 ±0.034	94.64 ±0.043
Fe^{3+}	43.20 ±0.045	71.50 ±0.064	85.55 ±0.036	93.14 ±0.042	96.19 ±0.093
Pb^{2+}	98.20 ±0.046	98.40 ±0.057	98.60 ±0.035	98.78 ±0.082	99.07 ±.0.033
Mn^{2+}	91.60 ±0.034	92.10 ±0.023	92.45 ±0.034	93.18 ±0.022	93.35 ±0.034
Cr^{3+}	88.20 ±0.034	90.80 ±0.034	91.40 ±0.034	93.18 ±0.023	93.38 ±0.034
Zn^{2+}	95.40 ±0.054	94.46 ±0.034	95.45 ±0.033	97.64 ±0.033	97.90 ±0.011
Cd^{2+}	84.40 ±0.034	88.50 ±.0.034	91.85 ±0.045	95.40 ±0.034	95.63 ±0.034

Appendix 4: Effect of pH on Sorption for IFASB.

pH Ions (%)	1	2	3	4	5	6
Cu^{2+}	92.93 ±0.091	93.62 ±0.022	94.10 ±0.071	94.66 ±0.066	96.32 ±0.019	97.08 ±0.043
Fe^{3+}	98.34 ±0.062	98.68 ±0.054	98.95 ±0.021	99.24 ±0.017	99.38 ±0.042	99.38 ±0.011
Pb^{2+}	99.06 ±0.043	99.31 ±0.088	99.32 ±0.061	99.36 ±0.035	99.42 ±0.081	99.55 ±0.055
Mn^{2+}	95.28 ±0.017	95.43 ±0.052	95.52 ±0.099	95.84 ±0.033	95.85 ±0.071	95.85 ±0.088
Cr^{3+}	95.39 ±0.056	95.45 ±0.051	96.47 ±0.018	97.52 ±0.049	98.77 ±0.012	99.31 ±0.083
Zn^{2+}	98.38 ±0.063	98.39 ±0.087	98.41 ±0.011	98.43 ±0.028	98.44 ±0.086	98.46 ±0.091
Cd^{2+}	96.45 ±0.087	96.72 ±0.016	96.95 ±0.091	97.30 ±0.082	97.33 ±0.012	97.37 ±0.097

Appendix 3: Effect of Ionic Strength on Sorption for IFASB

Ionic strength (NaCl%w/w) / Ions (%)	0.2	0.4	0.6	0.8	1.0
Cu^{2+}	92.68 ±0.093	92.51 ±0.032	92.44 ±0.022	92.38 ±0.023	92.27 ±0.028
Fe^{3+}	93.30 ±0.053	93.11 ±0.057	92.65 ±0.027	92.36 ±0.028	91.02 ±0.021
Pb^{2+}	99.92 ±0.052	99.91 ±0.052	99.83 ±0.072	99.73 ±0.063	99.71 ±0.024
Mn^{2+}	94.74 ±0.035	94.73 ±0.034	94.71 ±0.023	94.69 ±0.023	94.65 ±0.022
Cr^{3+}	91.04 ±0.033	90.60 ±0.032	89.88 ±0.038	89.89 ±0.034	89.97 ±0.022
Zn^{2+}	98.42 ±0.033	98.41 ±0.022	98.40 ±0.033	98.38 ±0.034	98.39 ±0.029
Cd^{2+}	96.98 ±0.035	96.97 ±0.033	96.94 ±0.027	96.91 ±0.022	96.89 ±0.028