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Full Length Research Paper

Transfer zone behaviour of As(III), Co(II) and Mn(II) ions on sulphur-hydryl infused cellulose surface

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Penetrant transport phenomenon was applied to determine the strive of As(III), Co(II) and Mn(II) ions across the adsorbate/cellulose interface. Penetrant-n and K values calculated for the metals on differentially thiolated (mercaptoacetic acid treated) cellulose surfaces were highest for As(III) at UCF-n, K (3.1278, 0.3064), 0.5MF-n, K (2.4248, 0.4716) and 1.0MF-n, K (1.9136, 0.4885). For Co(II), n and K values were UCF (2.8608, 0.3220), 0.5MF (1.6791, 0.5351), 1.0MF (0.9348, 0.6952). For Mn(II), n and K values were UCF (1.2717, 0.6268), 0.5MF (1.1114, 0.6639), 1.0MF (0.5833, 0.7707). As(III) strive depicts 30% adsorption against the non-cationic moieties it generates in a partially electrical double layered adsorption system.

Key words: Adsorption, heavy metals, cassava fiber, penetrant transport, strive.

INTRODUCTION

Toxic metals often discharged by several industrial processes can lead to the contamination of marine and freshwater environment. Save for natural influx industrial wastes constitute the primary source of metal pollution in aquatic environments. Natural influx generates minimal concentrations, which are taken care of by the ecosystem through microbial detoxification. For example *Nitzschia Closterium* adsorbs lipid soluble metal ion complexes onto their body walls (Florence et al., 1992) as it travels from one location to another in the ecosystem. This partially fixates the metal ion. However with increased industrialization wastewaters from industries are laden with toxic substances including heavy metals. This adds to the influx from natural systems increasing problems associated with heavy metal pollution. Hence there is the necessity to treat wastewaters to remove these metal ions before discharge into the environment. Technologies for removing heavy metals from aqueous solution like pH adjustment, ultrafiltration, electrodeposition, ion-exchange and solvent extraction have been used. These methods have proven costly, treat small systems, or are generally inefficient. Hence there arose the need to develop new and effective, but cheap methods and materials that are capable of extracting these metal ions from aqueous solutions. Cellulosic wastes are receiving increased attention as sources for metal ion removal from aqueous solution. This is because the materials are gotten from cheap and available agricultural sources. Compared to classical methods of metal ion removal like ion-exchange, precipitation and electrodeposition this method is cheap and simple. Increased investigation has been carried out on the sorption of toxic metal ions on modified and unmodified adsorbents from these sources. Researches in the use of cellulose based and agricultural by-products include studies in the metal binding capability of groundnut husk, peat, alfalfa, cassava fiber, dead *sargassum,* corncob and teawaste (Okieimen et al., 1991; Ho et al., 1995; Gardea-Torresday et al., 1996; Abia et al., 2003; Cruz et al., 2004; Abia and Igwe, 2005; Mahvi et al., 2005). Studies have shown that thioglycollic acid treated cassava fiber is capable of extracting Cd^{2+}, Cu^{2+}, Zn^{2+} from aqueous solution. This was found to be due to the infusion of sulphur-hydryl groups onto the cellulosic matrix.

In this study cassava fiber was used to take up As^{3+}, Co^{2+} and Mn^{2+} in their aqueous solutions at equilibrium times. The kinetic data obtained was used to study penetrant transport phenomena and to determine the relative strive of the metal ion core across the adsorbate/adsorbent interface.

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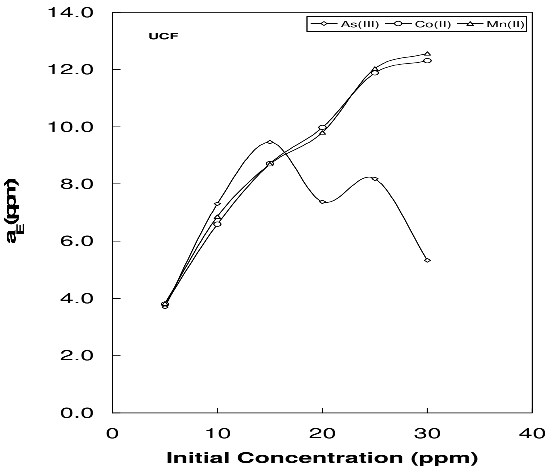

Figure 1. A plot of adsorbed concentration aE versus initial concentration Ci for UCF

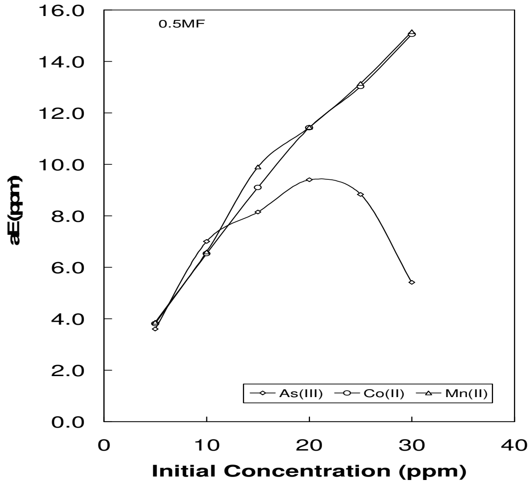

Figure 2. A plot of adsorbed concentration aE versus initial concentration Ci for 0.5MF

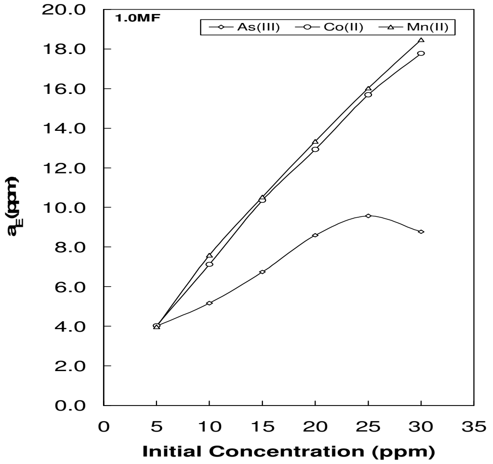

Figure 3. A plot of adsorbed concentration aE versus initial concentration Ci for 1.0MF

MATERIALS AND METHODS

Thiolation of cassava fibre

The fiber lumps obtained from processing mill near Port Harcourt were air-dried, powdered in a grinder and sieved through 425 µm (0.0165 in) and 150 µm (0.0059 in) screens. The material retained on the 150 µm was wet-sieved through a 106 µm screen and air-dried. The air-dried fibre was soaked in 0.3 M HNO_3 solution for 24 h. All through the experiments deionized water was used for the washing and preparation of appropriate solutions. The treatment of cassava fiber with dilute HNO_3 solution helps in breaking the partial hydrogen bonds in the cellulosic material, hence it is expected that the treatment should significantly increase the adsorbent capacity of cellulose. The activated fiber meal was air-dried and divided into three portions, each of 200 g. The first portion labeled 'A' was not treated. The second portion labeled 'B' and the a third 'C' were stirred in excess of 0.5 and 1.0 M thioglycollic acid solutions, respectively, for 24 h at 25°C. The mixtures were filtered off and the fibrous material washed with deionized water and wet-sieved through a 106µm sieve to a pH of 5. They were then dried in air. The chemically unmodified cassava fiber was labeled UCF, while the meal treated with 0.5 and 1.0 M thioglycollic acid were labeled 0.5MF and 1.0MF, respectively.

Preparation of adsorbate solutions and the adsorption process

100 ppm stock solution was prepared from their salts. From the stock working solutions of 5, 10, 15, 20, 25, and 30 ppm were prepared from appropriate aliquots by dilution to the appropriate concentrations. Batch adsorption studies were carried out at 30 min intermittent times at 298 K and pH of 5. 100 ml of 20 ppm solution of metal ions were brought in contact with 1g each of adsorbent at times ranging from 5 to 30minutes, and 90minutes. The equilibrium concentration obtained from the second set of experiments was used to determine the effect of agitation time on adsorption and the transfer zone behaviour of metal ions. The agitations were done with test sieve shaker of the EFL1 mk3 model and the residual concentrations were detected with flame AAS model 200A from Buck Scientific Inc. Data regression analysis of the kinetics was done using excel to obtain linearized penetrant transport constants.

RESULTS AND DISCUSSION

Effect of concentration on metal ion removal

The results from Figure 1 show a complex behaviour for arsenic uptake. Figures 2 and 3 will most likely depict a non-exhaustion of the available adsorption sites on the differentially modified fibre. This is because of the non-flattening of the graphs at the concentration peak of 30 ppm. However there was a proven case of metal ion removal by cassava fibre. Increased modification leads to a corresponding increase in metal ion uptake. This is further corroborated by the distribution coefficients (Table 1). The distribution coefficient is the concentration of a solute in the adsorbent phase divided by the concentration in the continuous phase. It expresses the relative effectiveness of cellulosic materials in binding metal ions.

From the graph plots of equilibrium sorption data it was observed that for any particular modification level there was a general pattern for uptake of metal ions from solution: the larger the metal ion the higher its uptake level. This particular trend can be explained by the fact that

Table 1. Distribution coefficients for metal ion sorption.

Initial Conc.	UCF			0.5MF			1.0MF		
(ppm)	As^{3+}	Co^{2+}	Mn^{2+}	As^{3+}	Co^{2+}	Mn^{2+}	As^{3+}	Co^{2+}	Mn^{2+}
5	3.0000	3.1184	3.2590	2.5950	3.2050	3.3780	3.9360	4.1490	3.8760
10	2.7170	1.9380	2.1880	2.3310	1.8830	1.9380	0.6950	2.4750	3.1450
15	1.7100	1.3850	1.3790	1.1890	1.5410	1.9380	0.6200	2.2270	2.3470
20	0.5840	0.9950	1.0090	0.9240	1.3310	1.3350	1.4250	1.8280	2.0000
25	0.4870	0.9060	0.9280	0.6210	1.0870	1.1090	2.1830	1.6840	1.7830
30	0.2170	0.6960	0.7200	0.2200	1.0060	1.0200	0.4130	1.4530	1.6000

metal ions form aquo complexes when dissolved in water Abia et al. (2002). The aquo complex is of the form $[M(H_2O)_x]^{n+}$, where M denotes the metal ion, n+ the net charge on the complex, and x the co-ordination number. The relative uptake levels of different ions are therefore seen to be inversely dependent on the hydration energies. The ionic radius of As^{3+} is 0.058 nm. Co^{2+} with ionic radius of 0.065 nm has hydration energy of –1996 KJ mol^{-1}. Mn^{2+} (ionic radius =0.083 nm) has hydration energy of -1841 $KJmol^{-1}$.

Because the displacement of water molecules from the aquo ion is the core of adsorption dynamics the stability of the aquo ion plays a vital role in the adsorption process. The aquo ion stability can be estimated from the hydration energy of the metal ion and found to be dependent on the size of the ion. Therefore, an ion with a relatively large size (and low hydration energy) will hold less strongly to the water molecules than an ion with a smaller size (and of course relatively higher hydration energy). This implies that an ion with a large size will interact with substrates than those with small sizes.

Secondly, the uptake level of arsenic is the lowest among the three metal ions. This is also attributable to the unique chemistry of arsenic in aqueous solution. A further development is that arsenic (III) ion adsorption is not adequately explained by either the Freundlich or Langmuir isotherms. In aqueous solution arsenic exists either as arsenic (III) or arsenic (V). Arsenic (V)-arsenate exists in four forms in solution depending on pH: H_3AsO_4, $H_2AsO_4^-$, $HAsO_4^{2-}$ and AsO_4^{3-}. Also depending on pH arsenite-arsenic (III) exists in five forms: $H_4AsO_3^+$, H_3AsO_3, $H_2AsO_3^-$, $HAsO_4^{2-}$ and AsO_3^{3-}. Positively charged ionic forms of arsenic (V) dominate at pH>3, while arsenite is neutral at pH<9 and ionic at pH>9, (Wang et al., 2000). Ion exchange does not remove As (III) because As (III) occurs predominantly as an uncharged ion (H_3AsO_3) in water with a pH value of <9.0 (Ficklin, 1983; Clifford, 1999). The predominant form of As (V), $H_2AsO_4^-$ and $HAsO_4^{2-}$ are negatively charged, and could be removed from solution by an anionic exchanger. If As (III) is present, oxidizing the species to As (V) is necessary before removal using an anionic exchanger (Fox, 1989; Clifford and Lin, 1986).

It is observed (Table 1) that for initial metal ion concentration below 20 ppm the distribution co-efficient was greater than unity for almost all the metal ions and for the differentially thiolated cassava fibre. This implies an uptake of more than 50%. The distribution coefficient which generally decreased as initial metal ion concentration increased went below 50% uptake at above 15 ppm initial concentration. However this is not the case with Co^{2+} and Mn^{2+} interacting with 1 g of 0.5MF and 1.0MF cellulose fibre. This could be attributed to the fact that Co^{2+} and Mn^{2+} ions uptake is improved with infusion of more binding groups into the cellulosic matrix. Hence it can be stated that there exists a greater interaction of Co^{2+} and Mn^{2+} with thiolated cellulose fibre than As^{3+}.

These results show that the bulk of the sorption process was improved by modifying the surface characteristics of the fibre. The results also show that Mn^{2+} and Co^{2+} ions were taken up from aqueous solution more than As^{3+}.

Time dependent metal ion removal: penetrant transport

The adsorbent surface and the overlying interface are most often considered a mass transfer zone. Adsorption unto the adsorbent surface translates into a decrease in the concentration of the adsorbate in solution. Considering a situation where applied pressure is zero and temperature is kept constant, for adsorption to take place diffusion becomes the operating transport phenomena, (Levine, 1995; Aithal and Aminabhavi, 1990). For a single component adsorbate system, diffusion through the adsorption interface is governed by an internal driving force of the sorbate moiety.

Diffusivity, permeability and sorptivity are often coupled processes in the adsorption system. In most cases time dependency of the sorption process is based on the outline that the curves derived exhibit a linear relationship initially, followed by a plateau region which goes flat at extended times.

Considering the penetrant transport through the mass transfer zone, the type of diffusion mechanism could be established by fitting the data derived from kinetic experi-

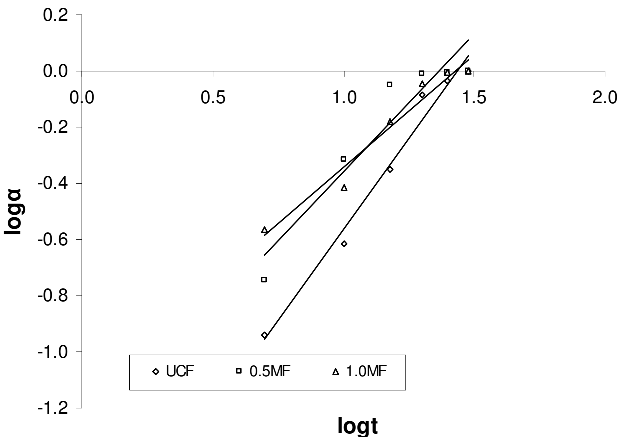

Figure 4. A plot logα versus logt for As^{3+}.

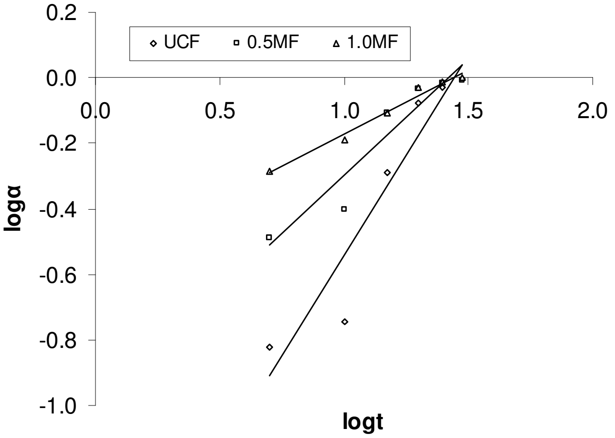

Figure 5. A plot logα versus logt for Co^{2+}.

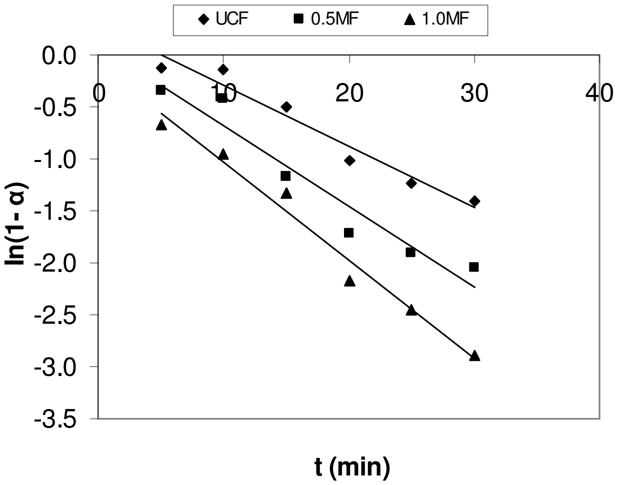

Figure 6. A plot logα versus logt for Mn^{2+}.

mental studies to an empirical equation of the type;

$M_t/M_\infty = Kt^n$ [1]

Where M_t is adsorbed concentration at time, t, M_∞ the adsorbed concentration of sorbate at assumed infinity. K is a constant that depends on the structural character-ristics of the fibre and its interaction with the sorbent. The value of n determines the type of transport mechanism.

Hence, logα = logK + nlogt [2]

Plots of logα against logt for the different metal ions are presented in Figures 4 to 6. For the kind of system being dealt with, the adsorbent stationary phase and the liquid mobile phase present a possible picture of a partial electrical double layer. The adsorbent active sites are considered negatively charged and the metal ions in solution, notwithstanding the covalent orientation of some of their moieties, have a positively charged core. Penetrant transport will, for this kind of system depict the 'strive' of the metal core to penetrate the mass transfer zone and drive the metal moiety to the active sites of the adsorbent surface.

Penetrant n-values represent the likelihood and degree of strive. n >1 indicates the presence of high strive. n ≈ 1 depicts moderate strive while for n < 1 the adsorption process may not be due to metal ion core strive. Penetrant K-value of the adsorption system is usually less than 1 for an interaction between adsorbent and adsorbate, which is dominated by ion-exchange. For our adsorption system there are O-H and S-H active sites with exchangeable protons. If the K-value is greater than 1 there is indication that dipole induced dipole interactions are dominant in the adsorption process.

From Table 2 the high strive exhibited by arsenic (III) ions with UCF (3.1278), 0.5MF (2.4248) and 1.0MF (1.9136) indicates that the adsorption process taking place was by penetrant transport. This phenomenon was also observed for Co^{2+}/UCF (n=2.8608, R^2=0.8722) Co^{2+}/0.5MF(n=1.6791, R^2=0.8984), Mn^{2+}/UCF (n=1.2717, R^2=0.8020) and Mn^{2+}/0.5MF (n=1.114, R^2=0.8880). However with Co^{2+}/1.0MF system penetrant n-value was about 1, which makes the strive moderate. The penetrant n-value for Mn^{2+}/1.0MF is less than 1. This indicates that the adsorption process is not basically due to much core strive by the manganese (II) ion but due to its large ionic size coupled with other factors like low solvation energy and linear driving force.

Conclusion

Sulphur-hydryl infused cellulose surfaces are used in this work to take up metals from aqueous solutions. Time dependent batch adsorption systems have been used to study the transfer zone behaviour of the metal ion transfer across the adsorption interface. The penetrant trans-

Table 2. Penetrant transport constants

		As^{3+}			Co^{2+}			Mn^{2+}	
	logK	**n**	**R^2**	**logK**	**n**	**R^2**	**logK**	**n**	**R^2**
UCF	0.3064	3.1278	0.9673	0.3220	2.8608	0.8722	0.6268	1.2717	0.8020
0.5MF	0.4716	2.4248	0.9482	0.5351	1.6791	0.8984	0.6639	1.1114	0.8880
1.0MF	0.4885	1.9136	0.9439	0.6952	0.9348	0.9685	0.7707	0.5833	0.8982

port n-values derived from linearized plots were high for As^{3+} compared to those of Co^{2+} and Mn^{2+}. The high strive shown by arsenic indicates that the bulk of its adsorption is by penetrant transport. The penetrant transport model appears to explain arsenic (III) adsorption on a partially electrical double layered interface.

REFERENCES

Abia AA, Horsfall M Jr, M, Didi O (2002). Studies on the use of agricultural bi-product for the removal of trace metals from aqueous solution. J. Appl. Sci. Environ. Mgt. 6(2): 89-95.

Abia AA, Horsfall M Jr, Didi O (2003). The use of chemically modified and unmodified cassava waste for removal of Cd, Cu and Zn ions from aqueous solution. Biores. Technol. 90(3): 345-348.

Abia AA, Igwe JC (2005). Sorption kinetics and intraparticulate diffusivities of Cd, Pb and Zn ions on maize cob. Afr. J. Biotechnol. 4(6): 509-512.

Aithal US, Aminabhavi TM (1990). Diffusivity, permeability, and sorptivity of aliphatic alcohols through polyurethane membrane at 25, 44, and 60°C. J. Chem. Eng. Data. 35: 298-303.

Clifford D, Lin CC (1986). Arsenic Removal from Groundwater in Hanford, California - A Preliminary Report. University of Houston, Department of Civil/Environment Engineering.

Clifford D (1999). Ion Exchange and Inorganic Adsorption. In American Water Works Association (Eds), Water Quality and Treatment: A Handbook of Community Water Supplies. 5th ed. New York: McGraw Hill.

Cruz CCV, da Costa AC, Henriques CA, Luna AS (2004). Kinetic modeling and equilibrium studies during cadmium bioadsorption by dead *Sargassum* sp. biomass. Bioresource Technol. 91(3): 249-257.

Ficklin WH (1983). Seperation of arsenic (III) and arsenic (V) in groundwaters by ion exchange. Talanta. 30(5): 371-373.

Florence TM, Powell HKJ, Stauber JL, Town RM (1992). Toxicity of lipid-soluble copper(II) complexes to the marine diatom *Nitzschia Closterium*: Amelioration by humic substances. Wat. Res. 26(9): 1187-1193.

Fox K (1989). Field experience with point-of-use treatment systems for arsenic removal. J. AWWA. 94-01.

Gardea-Torresdey JL, Tiemann KJ, Gonzalez JH, Henning JA, Townsend MS (1996). Ability of silica-immobilized *Medicago Sativa* (Alfalfa) to remove copper ions from solution. J. Hazard Mater. 57: 29-39.

Ho YS, John Wase, DA, Forster CF (1995). Batch nickel removal from aqueous solution by sphagnum moss peat. Water Res. 29(5): 1327–1332.

Levine IR (1995). Physical Chemistry. 4th Ed. McGraw-Hill Book.

Mahvi AH, Naghipour D, Vaezi F, Nazmara S (2005). Teawaste as an adsorbent for heavy metal removal from industrial wastewaters. American Journ. of Applied Sciences. 2(1): 372-375.

Okieimen FE, Okundia EU, Ogbeifun DE (1991). Sorption of cadmium and lead ions on modified groundnut husks. J. Chem. Tech. Biotech. 51: 97–103.