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REMOVAL OF CADMIUM FROM AQUEOUS SOLUTION USING MANGANESE HEXACYANOFERRATES (II)/(III)

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ABSTRACT. A series of solid insoluble mixed potassium manganese hexacynoferrates (II) and (III) of the general formula $K_yMn_xFe^{II/III}(CN)_6.zH_2O$ were prepared by classical precipitation and local growth methods. All synthesized products were thermally stable up to 300 °C and were highly insoluble in most mineral acids except hot perchloric acid. The sorption of cadmium ion from 0.1 M HNO_3 solutions on manganese hexacyanoferrates (II) and (III) was investigated. Both sorption kinetics and isotherms were studied. The sorption kinetics for cadmium uptake was observed to follow two steps with fast kinetics in the first step within 5 min. The manganese hexacyanoferrate(III) was found to exhibit higher sorption capacities than manganese hexacynoferrates(II). The highest sorption capacity was achieved with manganese hexacyanoferrate(III) prepared by local growth method. The uptake of cadmium from aqueous solution appeared to follow adsorption mechanism and not ion exchange as characteristic of many other divalent hexacyanoferrates. The sorption data were fitted with Langmuir adsorption isotherm.

KEY WORDS: Cadmium removal, Potassium manganese hexacynoferrates(II)/(III)

INTRODUCTION

The discharge of industrial effluents containing appreciably high concentrations of heavy metals such as zinc, cadmium, lead, mercury and silver into the environment, particularly natural water have constituted environmental nuisances.

The need for the recovery of heavy metals from either their ores or from industrial effluents has been of great interest to the environmental analytical chemists. Metals such as cadmium, arsenic, mercury and lead are highly toxic and the government policy on environmental protection requires that the concentration of these metals in the effluent must be reduced to the barest minimum before industrial effluents are discharged [1]. The continued downward review of the maximum permissible levels of these highly toxic metals arising from greater understanding of their toxicological effects, make the task of search for effective method of abatement a continuous effort.

Some hydrometallurgical processes have been proposed [2] in order to "by pass" problems encountered in the use of the classical processes of separation such as solvent extraction. These processes include thermal decomposition, sorption on a solid substrate material and ion exchange fixation. Divalent metal ions of hexacyanoferrate (II) and (III) have been found to exhibit a high degree of efficiency for the sorption of several metallic ions in dilute aqueous solution [3]. Among the products studied, nickel and copper hexacyanoferrate (II) and (III) have been identified as the best products [4]. Though little work has been done on the manganese hexacynoferrates generally, they have been reported to be highly porous and to possess high sorption interaction capabilities [5].

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The first part of this work is concerned with the synthesis and characterization of the various manganese hexacyanoferrates (II) and (III), while the second part deals with the application of synthesized products for the removal of cadmium ion from aqueous solution. This involves investigation of the sorption kinetics and capacity of cadmium uptake by prepared products using batch experiments.

EXPERIMENTAL

Materials

All the chemical reagents used including mineral acids, alkaline hexacyanoferrates, manganese chloride, potassium nitrate and potassium chloride were of reagent grade and were supplied by BDH Chemicals Ltd. (Poole, England). An initial stock solution of cadmium (1000 mgL^{-1}) was prepared by dissolving 0.508 g of $CdCl_2.2.5H_2O$ in 250 mL deionized water. All solutions were prepared using deionized water.

Preparation of manganese hexacyanoferrates. Manganese hexacyanoferrates (II) and (III) were prepared by classical precipitation and local growth methods.

Classical precipitation. This preparation was done according to a method derived from [6]. Solutions of $MnCl_2$ (0.06 M, 100 mL) and $K_4Fe(CN)_6/K_3Fe(CN)_6$ (0.02 M, 100 mL) (atomic ratio, Mn/Fe = 3:1) were gradually and simultaneously discharged at the rate of 0.8 mL min^{-1} into a glass container containing 250 mL of 0.1 M HNO_3 solution [6]. The reaction mixture was slowly agitated with a mechanical stirrer continuously at 27 ± 2 ^{o}C. The slurries obtained were filtered, washed with 0.01 M KCl solution to remove any occluded chloride ion. It was then washed several times with deionized water, followed by 95 % methanol and finally, dried in an oven between 80-90 ^{o}C for 3 hours. The precipitate was sieved and fraction less than 100 μm was retained for subsequent experiments.

Localized growth method. This was done according to the procedure derived from Abousahl *et al.* [8]. 2.5 g of $K_4Fe(CN)_6/K_3Fe(CN)_6$ was introduced into a solution of 0.40 M $MnCl_2$ in 0.1 M HNO_3 contained in a 1000 mL beaker covered with a lid. The reaction mixture was stirred mechanically for 18 h [6]. The stirring was done gently to avoid breaking the thin film that separates the solid-solution interface [7]. The granular product formed was washed thoroughly firstly by 0.01 M KCl, followed by abundant deionized water and 95 % methanol in that order. About 90 % of the particles have diameter greater than 100 μm.

Physical and chemical analysis. Melting points were determined using a Griffin electrothermal melting point apparatus. The metal analysis of the prepared products for was carried out using a flame photometer for Na and K and an atomic absorption apectrophotometer (AAS) for Mn and Fe after dissolution of 20 mg sample in 10 mL of 11.6 M $HClO_4$. If we assume that one Fe atom is bound to six cyanide groups, the sum of the concentrations of K, Mn, Fe and CN does not equal 100 %. The difference to 100 % was attributed to the presence of water. This was further confirmed by subjecting the products to thermal treatment and to constant weight at 105 °C. The absence of suspect anions such as nitrate and chloride from the reagents used, which could be occluded within the prepared products, were confirmed by colorimetric analysis using xylenol reagent at 432 nm for nitrate and by Mohr’s method based on silver nitrate titration using potassium chromate as indicator for chloride [6].

Infrared (IR) spectroscopy. Infrared spectra of samples were recorded in the range 500-4000 cm^{-1} with nujol mulls between KBr plates using Buck Scientific model 500 Infrared Spectrophotometer.

Sorption experiments. Eight different concentrations of cadmium chloride in 0.1M HNO_3 (0.1, 0.2, 0.5, 1.0, 2.0, 5.0 and 10 mg L^{-1}) were prepared. 20 mg of the solid products was contacted with 25 mL of each solution and allowed to equilibrate for a period of 48 hours, a time considered sufficient for equilibrium to be attained [8].

Kinetics of batch equilibration of cadmium ion with the prepared solid products: This was investigated by contacting 20 mg of the solid product with a maximum equilibrium concentration of 10 mg L^{-1} for various times durations ranging between 2 min – 48 h. The solutions were filtered and the filtrates analyzed for K, Fe and Cd metal ions by AAS [8].

RESULTS AND DISCUSSION

Chemical compositions of prepared products

The chemical compositions of the prepared products are summarized in Table 1. All the products are hydrated, non-stoichiometric and mixed potassium manganese hexacyanoferrates.

High value of K/Fe mole ratio has been calculated for all the products and this was attributed possibly to the occlusion of $K_4Fe(CN)_6$ or $K_3Fe(CN)_6$ as impurities on the manganese hexacyanoferrates (II) or (III), respectively. This kind of solid mixture has often been reported by some authors [9-12]. The charge balance for potassium for these products was therefore deduced by difference [12]. The compositions of all prepared products are notably deficient in manganese, and the charge is not compensated by the presence of other cation.

Table 1. Composition, molecular mass, decomposition temperature and colour change upon decomposition of prepared products.

Product	Composition	Molecular mass (g/mol)	Decomposition temp (°C)	Colour change upon decomposition
1. $^{*}\delta\sigma$	$K_{2.21}Mn_{0.79}Fe(CN)_6.4.9H_2O$ with $2.5K_4Fe(CN)_6$	438.07	337.9	Pale blue → Ash
2. $^{*}\delta\psi$	$K_{0.29}Mn_{1.21}Fe(CN)_6.3.3H_2O$ with $2K_3Fe(CN)_6$	360.29	328.5	Brown → Green
3. $^{*}\gamma\sigma$	$K_{2.29}Mn_{0.71}Fe(CN)_6.3.5H_2O$ with $0.5K_4Fe(CN)_6$	414.63	333.3	Grayish-white → Ash brown
4. $^{*}\gamma\psi$	$K_{1.2}Mn_{0.8}Fe(CN)_6.2.2H_2O$ with $2.5K_3Fe(CN)_6$	350.10	319.2	Brown → Green

*The molecular weight of $K_4Fe(CN)_6$ or $K_3Fe(CN)_6$ was not used in calculating the molecular mass of the products. δ or γ represents products synthesized via localized growth or classical precipitation respectively. σ manganese hexacyanoferrate(II). ψ manganese hexacyanoferrate(III).

Melting point of the products

None of the products melted but they exhibited a characteristic behaviour of undergoing colour change at a particular temperature but vary from one product to the other (Table 1). This change in colour may be attributed to the loss of water of crystallization in the compound, or could be ascribed to a possible decomposition of the products [14]. They all, however, exhibited a fairly high thermal stability.

Solubility test

All the products were insoluble in either cold or hot deionized water, dilute/concentrated hydrochloric, nitric, and sulfuric acids and in cold perchloric acid. They were, however, soluble in hot perchloric acid. This observation is in agreement with some of the previous works on divalent metals hexacyanoferrates [11, 13].

Infrared spectra of the products

All the products exhibited similar infrared spectra. There is a broad band of varying intensity, between 3377 and 3416 cm^{-1}, for all the products due to O-H stretching vibrations of water molecules [15]. The absorption bands observed in the region 2064-2152 cm^{-1} are all due to the stretching vibration of the CN bond. Absorption bands at 2064/2069 cm^{-1} were recorded for the manganese ferrocyanide, and at slightly higher wave number of 2152 cm^{-1} for the manganese ferricyanide. All the products present vibration bands between 1370 and 1470 attributed to the presence of nitrate impurities.

Cadmium sorption kinetics

The kinetics of cadmium interaction with products 3 and 4, prepared via the classical precipitation method and used as a case study, was investigated using an equilibrium concentration of 10 mg L^{-1}. The amount of cadmium fixed per mg of the adsorbent was plotted as a function of the square root of time (Figure 1). The square root was chosen in order to expand the smallest time intervals. The kinetics was observed to take place in two steps: a rapid step within 5 min, where almost all the cadmium is adsorbed, and a second step indicating a slowing down in the cadmium uptake within 10-40 min until the curve plateaus. This is an indication that most of the pores in the adsorbent have been occupied, becoming increasingly difficult for further cadmium uptake. A good fitting of data with square root of time variation has often been connected to a diffusion process [16].

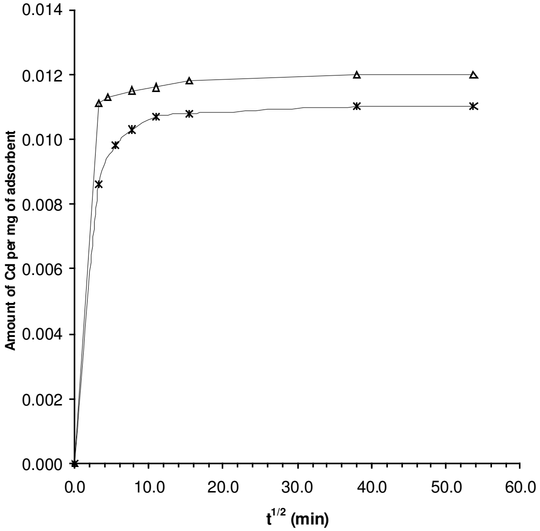
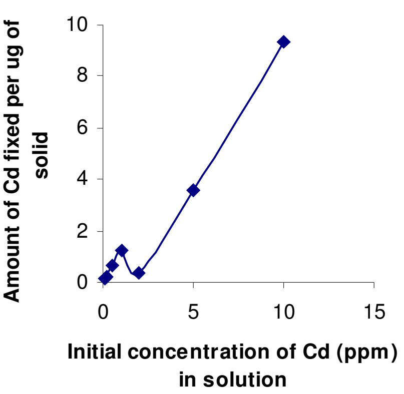
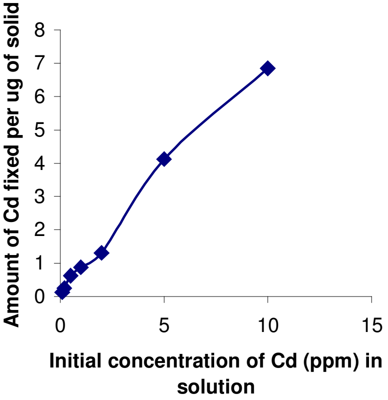
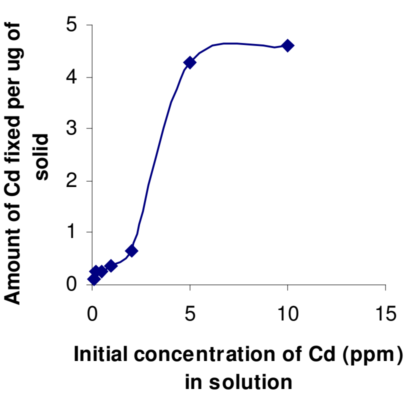


Figure 1. Sorption kinetics of cadmium on products 3 and 4 as a function of square root of time.







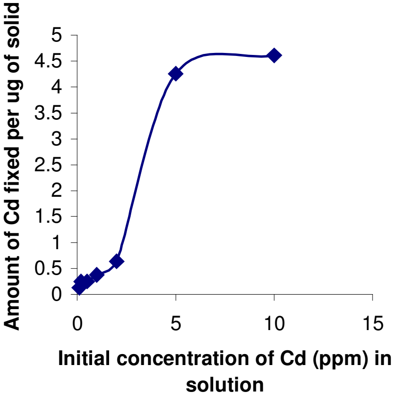


Figure 2. Adsorption isotherm for cadmium uptake by product 1.

Figure 3. Adsorption isotherm for cadmium uptake by product 2.

Figure 4. Adsorption isotherm for cadmium uptake by product 3.

Figure 5. Adsorption isotherm for cadmium uptake by product 4.

Capacity of fixation

The difference between the amount of cadmium before and after contacting with each of the four solid products has been calculated and used for the establishment of sorption isotherms at varying initial concentrations of cadmium ion in solution. The graphical plots of the amount of cadmium sorbed per mg of the solid against the initial cadmium concentrations in solution are illustrated in Figures 2-5. The sorption isotherms are similar and appear to be in two stages. At low initial concentrations up to 0.6 mg/L, there is 100 % cadmium removal and this gives a higher slope of about one. While the second stage corresponds to a lower sorption yield and this is reflected by a change of slope to a smaller one. The sorption data obtained for cadmium uptake by the prepared products fitted Langmiur adsorption isotherm plots with maximum adsorption capacities of 2.19 x 10^{-3} mg Cd per mg of solid for $K_{2.42}Mn_{0.79}Fe(CN)_6.4.9H_2O$ synthesized via the localized growth method, respectively for the Langmuir. The isotherms for the four products are shown in Figures 6-9. The Langmuir adsorption constants for the four products are shown in Table 2. This was expected since the particle diameter of products prepared by localized growth method is larger than those prepared by classical precipitation. The former is therefore expected to be more porous than the latter.

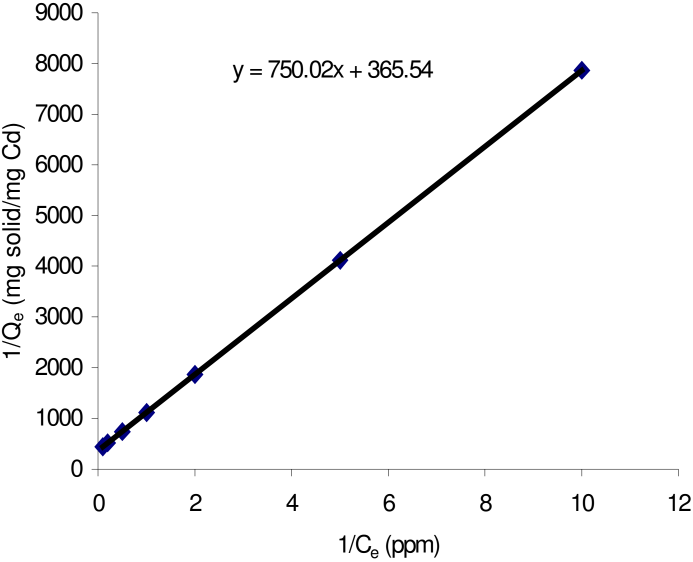


Figure 6. Langmuir isotherm plot for adsorption of cadmium on $K_{2.42}Mn_{0.79}Fe(CN)_6 4.9H_2O$.

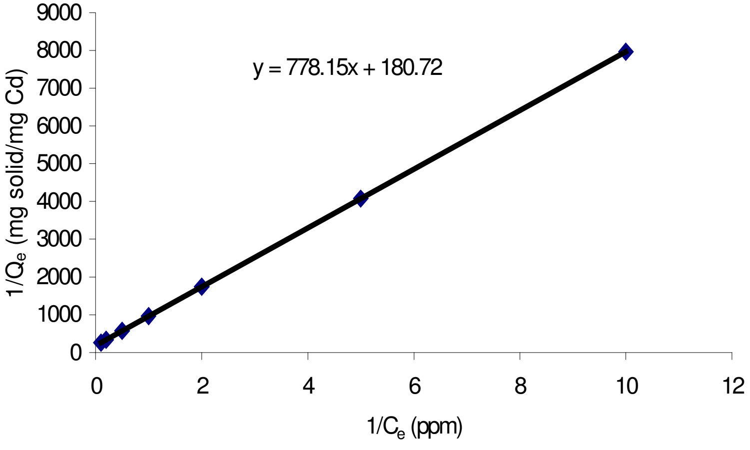


Figure 7. Langmuir isotherm plot for adsorption of cadmium on $K_{0.58}Mn_{1.21}Fe(CN)_6 3.3H_2O$.

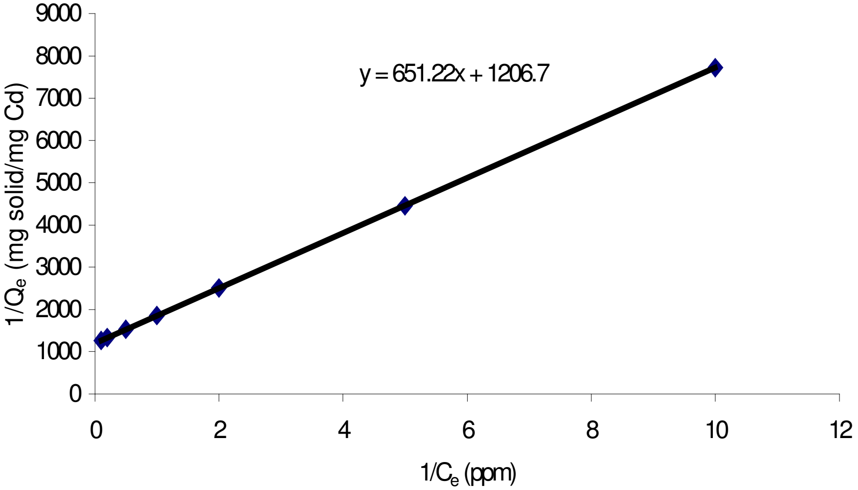


Figure 8. Langmuir isotherm plot for adsorption of cadmium on $K_{2.58}Mn_{0.71}Fe(CN)_6 3.5H_2O$.

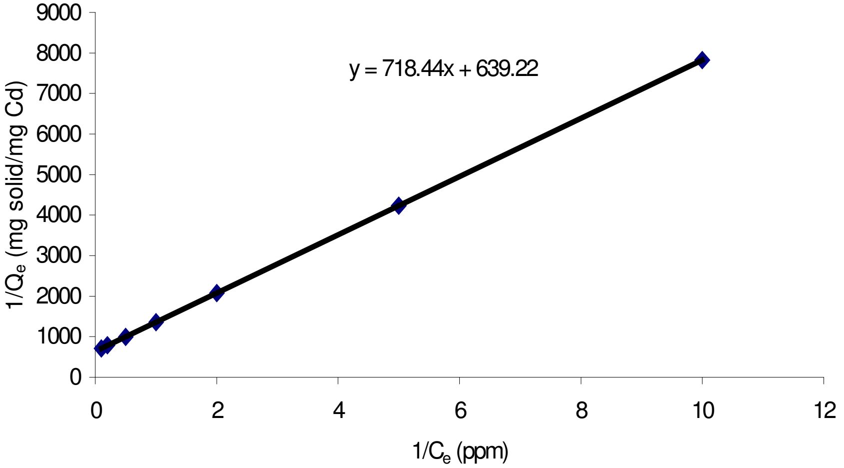


Figure 9. Langmuir isotherm plot for adsorption of cadmium on $K_{1.4}Mn_{0.8}Fe(CN)_6 2.2H_2O$.

Table 2. Summary of Langmuir adsorption constants.

Products	$1/Q^0b$	Q^0	b
1	750.02	2.73×10^{-3}	0.48
2	778.15	5.56×10^{-3}	0.23
3	651.02	8.29×10^{-4}	1.85
4	718.44	1.56×10^{-3}	0.89

$^*Q^0$ is the maximum amount of cadmium adsorbed per mg of the solid; b is a measure of the binding energy of cadmium on the solid surface.

CONCLUSIONS

All the four products used are capable of sorbing Cadmium and can be proposed as good materials for the recovery of Cadmium from industrial effluents. The product giving the best result was $K_{2.42}Mn_{0.79}Fe(CN)_6.4.9H_2O$ prepared by the localized growth method. However, further work is in progress on this category of products on the modifications of some of the conditions of preparation such as aging period, drying and washing conditions of precipitates in order to obtain near-stoichiometric products. Investigation is also in progress on the deposition of manganese hexacyanoferrates on inactive supports for an eventual column application.

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