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Cobalt, chromium and mercury uptake by sol-gel immobilized humic acid

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ABSTRACT

In this work humic acid was immobilized in sol-gel matrix. The immobilized polymer was used to remove cobalt, chromium and mercury from water. Maximum uptake was almost achieved after 3 hours with a values of 51 mg/g imm. HA for cobalt, 55 mg/g imm. HA for chromium and 39.9 mg/g imm. HA mg for mercury,. The uptake of the mentioned metals was almost completed after 3 hours. It was found the uptake was pH dependant that is; Maximum uptake for cobalt and mercury was at pH 6, while pH 5 was the optimum for chromium. Buffer type and buffer concentration exhibit a significant effect on the uptake of the metals under study. The effect of temperature was investigated and optimum temperature was 30°C for cobalt and chromium and 40°C for mercury.

KEYWORDS

Humic acid;
Sol-gel;
Uptake;
Cobalt;
Chromium;
Mercury.

INTRODUCTION

Heavy metal as water pollutant

Heavy metals exist in surface waters in colloidal, particulate, and dissolved phases, although dissolved concentrations are generally low**.** The colloidal and particulate metal may be found as hydroxides, oxides, silicates, or sulfides; or adsorbed to clay, silica, or organic matter. The soluble forms are generally ions or unionized organometallic chelates or complexes. The solubility of trace metals in surface waters is predominately controlled by the water pH, the type and concentration of ligands on which the metal could adsorb, and the oxidation state of the mineral components and the redox environment of the system Heavy metals are dangerous because they tend to bioaccumulate. Bioaccumu lation means an increase in the concentration of a chemical in a biological organism over time, compared to the chemical's concentration in the environment. Compounds accumulate in living things any time they are taken up and stored faster than they are broken down (metabolized) or excreted. Heavy metals can enter a water supply by industrial and consumer waste, or even from acidic rain breaking down soils and releasing heavy metals into streams, lakes, rivers, and groundwater[2]. Heavy metals are present in abundance naturally and enter the water cycle through a variety of geochemical processes. Many metals are added to water by industrial process. Disposal of untreated wastes, surface runoff and highway run-off also cause metal pollution of surface water. Heavy metals are also present in solid wastes, municipal sewage sludge's and landfill leachate. High concentration of heavy metal in water supplies are undesirable because of the adverse effects on Health, environmental toxicity, corrosion of pipeworks and the esthetic quality environmental[17].

Humic substance

Humic substances (HS) are amorphic, dark and have a large content of oxygenated organic groups, such as carboxylic, phenolic, enolic, alcoholic and quinone groups, among others. Humic material, a decay product of living organisms, constitutes a major form of organic matter in soils, peat lands, and aquatic environments**.** It is composed of complex heterogeneous mixtures of polyfunctionalised macromolecular systems, which are variable with respect to source and stage of maturation[5]. This material is characterised by an average molecular mass from a few thousands to several hundred thousand daltons, with relatively high oxygen, low nitrogen, and low sulphur content Humic substances are considered as the end product of the decomposition of plant material in soil[34]. Humic substances are group of organic compounds formed by the association of high-molecular-mass substances from microbiological, vegetative and animal origin. They are organic macromolecules with multiple properties and high structural complexity. They exist abundantly in soil, natural water and various terrestrial and aquatic environments[8]. Humic substances can be differentiated into 3 fractions namely (i) humic acid, fraction of insoluble humic substances in acidic water (pH< 2), but soluble in water having higher pH, (ii) fulvic acid, fraction of humic substances soluble in all pH range, and (iii) humin, fraction of humic substances that are insoluble in water in all pH conditions. Humic acid is a very good adsorbent in term of capacity and rate of adsorption for various metal cations. In comparison to the commonly used adsorbent such as metal oxides and active carbon[32]. Humic acid generally possesses higher capacity and energy of adsorption, and also has faster rate of adsorption[33].

Humic acid it consists of 40-60% carbon, 30-50% oxygen, 1-3% nitrogen and 0.1-2% sulfur combined in aliphatic and aromatic ring structures associated with carbonyls, alcoholic and phenolic hydroxyl, carboxylates, amines, amides, and other functional groups[19]. All of these features make humic acid hydrophilic and hydrophobic. Fulvic and humic acids are recognized to play an important role in the aquatic environmental system **.**The strongest acid group was classified as carboxylates ortho to a phenolic group. Clustering of these carboxyl groups results in strong acid characteristics by electrostatic field effects and also results in strong metal binding by polydentate mechanisms. All the other carboxylates fall in the second weaker group in addition to the hydroxylphenolic group. These carboxylic groups (strong and weak) and hydroxyl groups (aromatic and aliphatic) are capable of complexing metal ions[33]. Humic substances must be studied because they have acid-base properties with a wide range of pKa values and are mixtures of cross-linked polymers of different molecular weight and charge densities. They have high affinities for surfaces, both organic and inorganic .humic substance contain long lived (almost stable populations) of free radicals which are capable of reducing inorganic species such as Hg, Cr and Co to name a few. They are also capable of interacting with anthropogenic, including the know carcinogen benzo (a) pyrene, again altering the chemical reactivity of these important chemicals[6].

Metal Ion Interactions with humic acid was reported that there are four possibilities of binding of humic acid with metal ions[24]. 1. By chelation between carboxyl and phenolic hydroxyl groups. 2. By chelation between two carboxyl groups. 3. By complexation with one carboxyl group. 4. by phenols and phenolic ethers. Humic acid structures will be sites where several carboxylic acids, phenolate, thiolate, amino, or other metal-binding groups come together. These sites are where a metal ion will be most strongly bound. Structurally, it is hard to show a “typical” humic acid binding to copper for example, but structure below show one possibility.

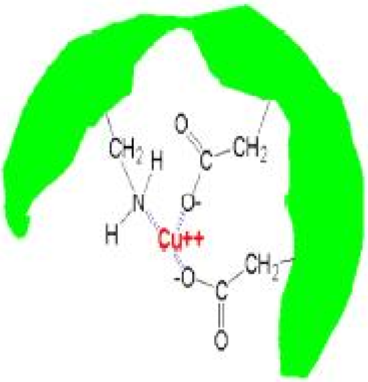

Figure 1: A schematic of a copper ion (Cu^{++}; shown in red) being chelated by a naturally occurring humic acid (shown in green).

As shown in figure 1, the central positively-charged copper ion (Cu^{++}) is chelated by the larger humic acid shown in green. It is bound ironically by two negatively charged carboxylic acid groups and complexed by one neutral amino group. Together these three groups may hold the copper ion more strongly by many orders of magnitude more strongly than could any individual binding group[12]. Heavy metals may be bound to humic substance through much stronger covalent bonds with the later often resulting in the formation of stable chelating rings. Humic acid is particularly effective in chelating heavy metals due to it high content of oxygen containing functional. The strength of associations between organic matter and heavy metals will depend on the type of binding site available, their abundance and distribution, the equilibrium constant. However, stability constant data generally indicates that under the same experimental conditions. Cadmium nickel and zinc are less strongly complexed to humic acid than are copper or lead with ranking such as Pb>Cu>Ni>Co>Zn>Cd> Fe>Mn>Mg [27]. The hypothetical structure for humic acid is shown in figure 2 below. It contains free and bound phenolic OH groups, quinone structures, nitrogen and oxygen as bridge units and carboxylic acid groups variously placed on aromatic ring.

As for the structure, it is still not known, although there has been a breakthrough by research group indicating that HAs should not be considered as high molecular weight compounds Regardless of the still unknown structure of humic substances and the great efforts to elucidate, it is known that their major functional groups include carboxylic, phenolic, carbonyl, hydroxyl, amine, amide and aliphatic moieties, among others. Due to this polyfunctionality, humic substances are one of the most powerful chelating agents among natural organic substances. The zwitterionic character of humic substances allows the interaction of anions with positively charged groups of humic and cations with negative charged groups of these substances**.** The oxygen containing functional groups in HA represents a quarter of the total molecular weight of HAs**).** The carboxyl (COOH) group increases in abundance with humification, reacts readily with metals[30] and gradually dissociates between pH 2.5 and 7 to form the carboxylate (COO^-) group[21]. The phenolic hydroxyl (OH) group is more abundant in the early stages of decomposition is derived from lignin in woody plants[23], reacts less with metals, and dissociates between pH 8 and 13.5. The COOH and phenolic OH groups account for the total acidity of HA[26] while the alcoholic OH group is only weakly acidic and reacts minimally with metals**.** The carbonyl (C=O) group increases in abundance with humification[18,25], is the main functional group in sediments and transforms into the COOH group under oxidizing conditions or when exposed to clay**.** The pH dependent surfaces of HA cause flocculation at low pH and dispersion at high pH[11]. SEM images of HA reveal smooth, compact shapes at pH 3 and rough, elongated and dispersed shapes at pH 7[29] and HA also begins to dissolve at higher pHs**.** HA may remove metals from solution at low pH but at high pH metal bonding with dissolved HA results in the formation of soluble metal humate species[13]. It is also believed that small materials can become trapped inside voids within the

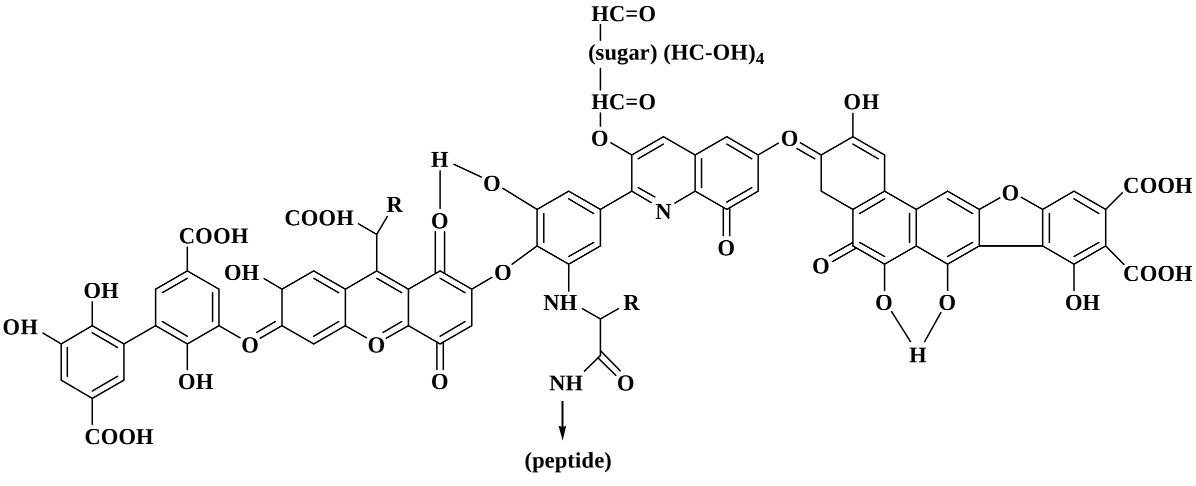

Figure 2 : Model structure of humic acid according to stevenson

HA molecules[28].

HAs are highly negatively charged and organic matter contributes towards the lowering of the zero point of charge (zpc) of soils[36]. Humic acids (HAs) immobilized on solid particles can also be used as high capacity, selective sorbents for the recovery of trace amounts of metal ions and/or xenobiotic organics from solution. Silica and its derivatives have been used extensively in chromatography because of their excellent mechanical strength, well-controlled structural parameters (e.g. surface area, pore size and particle shape and size) and chemical stability. If HAs can be immobilized successfully on silica. HAs were immobilized chemically on silica or adsorbed directly on polysiloxane silica. Used the phenolic groups of the HA for the chemical immobilization[16]. HA-silica could be useful for the investigation of the binding properties of radio nuclides and organic pollutants to soil and sediment. In the design of the immobilization methods, the use of carboxylic groups, that are abundant in humic substances.

Entrapment in crosslinked organic polymers is a well known method for the immobilization of enzymes and whole cells. Entrapped biomolecules are physically confined within the polymer matrix and can be reused several times. Organic polymers such as polyacrylamide gels are currently used in biotechnology but silica glasses could offer some advantages such as improved mechanical strength and chemical stability. Moreover they don't swell in aqueous or organic solvents preventing leaching of entrapped biomolecules. However glasses are made at high temperature and, up to now, enzyme immobilization can only be Performed *via* adsorption or covalent binding onto the surface of porous glasses[9]. The so-called sol-gel process opens new possibilities in the field of biotechnology. Sol-gel glasses are formed at room temperature *via* the polymerization of molecular precursors such as metal alkoxides. Proteins can be added to the solution of precursors. Hydrolysis and condensation then lead to the formation of an oxide network in which biomolecules remain trapped. Small analytes can diffuse through the pores allowing bioreactions to be performed inside the sol-gel glass. Trapped enzymes still retain their biocatalytic activity and may even be stabilized within the sol-gel cage. A wide range of biological species such as antibodies and whole cells have been trapped within sol-gel matrices. They usually retain their activity but weak interactions with the silica cage actually occur that can change their behavior[15,7]. On the other hand immobilization of reagents or cells in sol-gel matrices that have the ability to bind with metals and as a result reduce concentration of heavy metals.

SOL-gel confinement in silica matrices

Sol-gel silica can be synthesized at room temperature via the hydrolysis and condensation of

Tetramethyl OrthoSilicate (TMOS), $Si(OCH_3)_4$. Hydrolysis gives reactive silanol groups whereas condensation leads to the formation of bridging oxygen as follows:

$$\text{-Si-OCH}_3 + \text{H}_2\text{O} \rightarrow \text{-Si-OH} + \text{CH}_3\text{OH (hydrolysis)}$$

$$\text{-Si-OH} + \text{HO-Si-} \rightarrow \text{-Si-O-Si-} + \text{H}_2\text{O (condensation)}$$

The overall reaction is then

$$\text{Si(OCH}_3)_4 + 2\text{H}_2\text{O} \rightarrow \text{SiO}_2 + 4\ \text{CH}_3\text{OH}$$

EXPERIMENTAL

Instrumentation

A Perkin Elmer Analyst 100 Atomic Absorption Spectrometer, with deuterium lamp as background correction method was used for metals determination. A Hana pH meter was used to adjust the pH of different solutions.

Chemicals and reagents

Tetraethoxysilane (TEOS), Humic acid (HA), Cobalt nitrate, chromium nitrate, and mercury nitrate were obtained from Merck, Germany. Other chemicals were purchased from Fluka. All reagents and chemicals used in this study were of the analytical grade. Distilled, deionised water were used throughout this study

Preparation of stock solutions

A series of buffer solution of phosphate buffer that cover the pH range from 2.0 to 8 were prepared. Other buffers, at pH 6.0 were prepared from tartaric acid, acetic acid, citric acid and sodium dihydrogen phosphate. Chromium and cobalt ion were prepared in deionized water so that 100 ppm of each metal were obtained. All metal ion solutions were stored in polyethylene bottles. compounds.

Preparation of sol stock solution

Using 20 ml pipette, 13.5 ml of TEOS were transferred into 50.0 ml glass vial followed by addition of

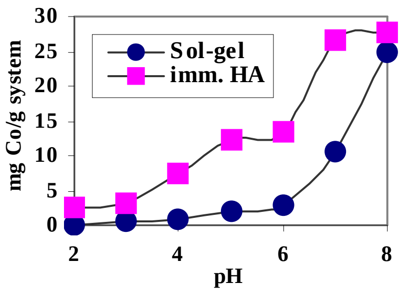

Figure 3: Effect of pH on the uptake of cobalt by immobilized humic acid and free sol gel after one hour and at room temperature

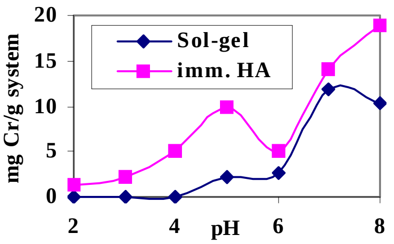

Figure 4: Effect of pH on the uptake of chromium by immobilized humic acid and free sol-gel after one hour and at room temperature

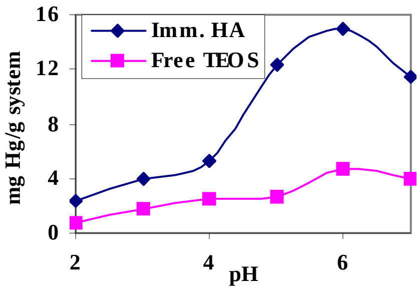

Figure 5: Effect of pH on the uptake of mercury by immobilized humic acid and free sol-gel after one hour and at room temperature

4.2 ml of 10^{-4} M HCl. The vial was firmly corked and stirred by means of magnetic stirrer for three hours. A homogeneous sol, due to partial hydrolysis of TEOS was obtained. This was stored in a desiccator for further use[20].

Humic acid entrapment system

A 10 ml portion of phosphate buffer, pH 5.0, containing 20% (w/v) humic acid was mixed with 10 ml TEOS sol in 50 ml glass vial. The mixture was shaken gently in which a gel of homogeneously entrapped humic acid was formed in about 3-5 minutes. The gel was allowed to dry for three weeks. A monolith containing entrapped humic acid resulted which was powdered to a particle size of (4-60μm), washed several times with small portions, 50 ml each, of 1M sodium chloride. Followed by washing three times with plenty of distilled water. Finally the entrapped HA was left in the desired buffer for equilibration before use for one hour, and left to dry for a weak at room temperature[14].

Analytical method

Chromium, cobalt and mercury, were determined using a Perkin elmer analyst 100 atomic absorption spectrometer using an air/acetylene flame. chromium, cobalt and mercury were determined at the 240.7, 357.9 and 253.7 nm resonance lines respectively.

Metal uptake

A 0.10 g of either sol-gel immobilized humic acid or blank sol-gel was added to 25 mL standard solutions of chromium, cobalt and mercury that contain 100 mg/L of the metal under investigation.

The uptake was calculated as followed:

Suppose that the 50 mL of chromium with initial concentration of 100 mg/L in contact with 0.10 g immobilized humic acid which was reduced to 20 mg/L the uptake in(mg Cr/ gram immobilized humic acid)=

$$\frac{0.05\,\mathrm{L}(100\,\mathrm{mg/L}\quad 20\,\mathrm{mg/L})}{0.10\,\mathrm{g\ immobilized\ humic\ acid}} = 40\,\mathrm{mg\ Cr/g\ imm.\ HA}$$

RESULT AND DISCUSSION

Effect of pH on the uptake of cobalt, chromium and mercury

The effect of pH on the uptake of Co, and Cr by free sol gel and sol-gel immobilized humic acid (imm. HA) was investigated in the 2-8 pH range using phosphate buffer after one hours and at room temperature. As demonstrated in figures 3-5 the uptake of cobalt ,chromium and mercury by free sol-gel and immobilized humic acid is strongly effected by pH that is the uptake of the three metals increases with increasing pH. This trend with immobilized humic acid could be due to the presence of humic acid in the deprotanated form. At pH>7 it is assumed that hydroxide ion concentration is high enough to cause partial precipitation of the metal ions under study, for this reason pH 6 was found as optimum pH for the uptake of cobalt and mercury and pH 5 was chosen as optimum value for chromium uptake. This coincide with work done before in which maximum metal uptake by immobilized humic acid was

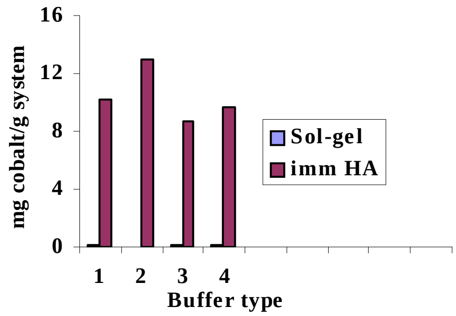

Figure 6: Effect of buffer type on the uptake of cobalt,at pH =6.0, after one hours and at room temperature. 1-acetate buffer, 2-citrate buffer, 3-phosphate buffer, 4- tartrate buffer

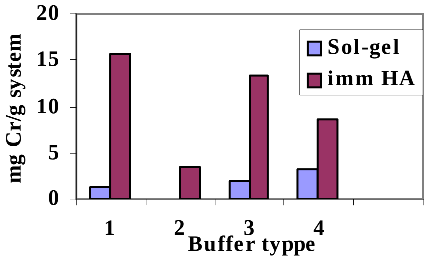

Figure 7: Effect of buffer type on the uptake of chromium, at pH =5.0, after one hour and at room temperature. 1-acetate buffer, 2-citrate buffer, 3- phosphate buffer, 4-tartrate buffer

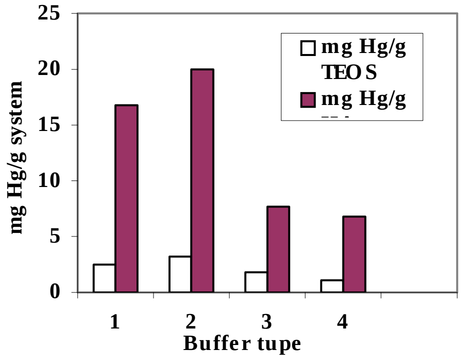

Figure 8: Effect of buffer type on the uptake of mercury, at pH =6.0, after one hours and at room temperature. 1-acetate buffer, 2-phosphate buffer, 3- tartrate buffer, 4- citrate buffer.

found at pH 5-6. It was concluded by that maximum uptake of mercury by humic acid was showed at pH 4.5[1].

Effect of buffer type

The effect of buffer type on the uptake of Co, Cr and and Hg by blank polysiloxine and sol-gel imm. HA was examined at room temperature and after one hour period of time using four different type of buffer namely acetate, citrate, phosphate and tartrate buffers.As shown in figures 6-8 maximum uptake of cobalt was observed using citrate buffer, while acetate buffer among the four types of tested buffers exhibits the highest chromium uptake. The uptake of Hg by immobilized HA was maximum when phosphate buffer was used. On the other hand the type of buffer has no considerable effect on the uptake of mercury by blank polysiloxane. While maxiumum uptake of cobalt and chromium was obtained by the blank polysiloxane using acetate and tartrate respectively.

Effect of buffer concentration

The effect of buffer concentration on the uptake of cobalt, chromium and mercury was examined using 0.010-1.0 M of the optimum type of buffer regarding to each metal(citrate for Co, acetate for Cr and phosphate for Hg). Figures 9-11. The pH was adjusted 6.0 for both cobalt and mercury and 5.0 for chromium. The study was performed at room temperature. It was found that the uptake of cobalt, chromium and mercury by free sol-gel and sol-gel immobilized humic decreases with increasing buffer concentration This can be explained as following; increasing buffer concentration increases the concentration of other cations mainly sodium which competes with Co, Cr and Hg in chelation with either chelating functional groups in the imm. HA

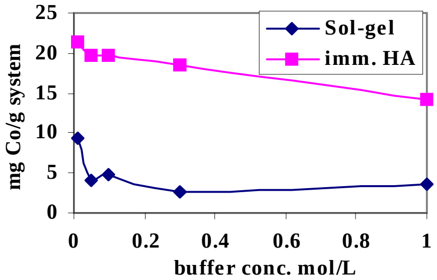

Figure 9: Effect of buffer conc. (citrate buffer) on the uptake of cobalt at pH= 6.0 after one hours and at room temperature

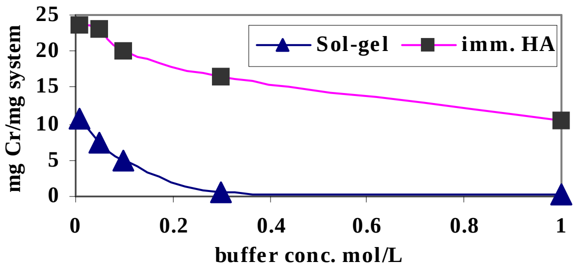

Figure 10: Effect of buffer conc. (citrate buffer) on the uptake of chromium at pH= 5.0 after one hours and at room temperature

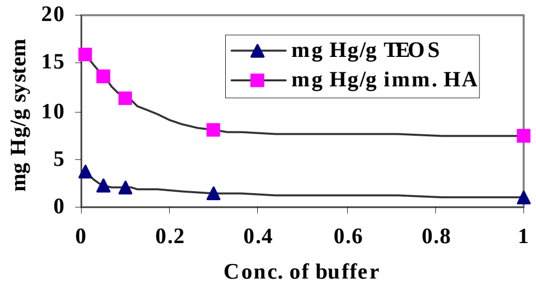

Figure 11: Effect of buffer conc. (phosphate buffer) on the uptake of mercury at pH= 5.0 after one hours and at room temperature

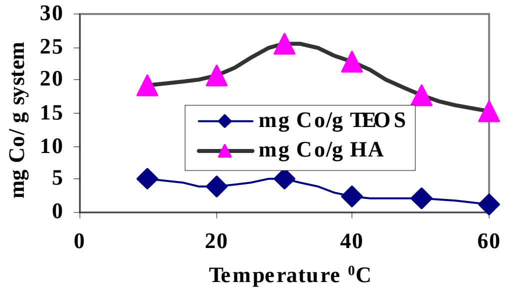

Figure 12: Effect of temperature on the uptake of cobalt at pH= 6.0 using 0.010 M citrate buffer after one hour and at room temperature

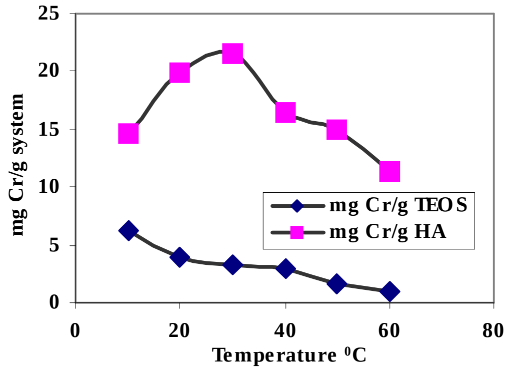

Figure 13: Effect of temperature on the uptake of chromium at pH= 5.0 using 0.010 M citrate buffer after 1 hours

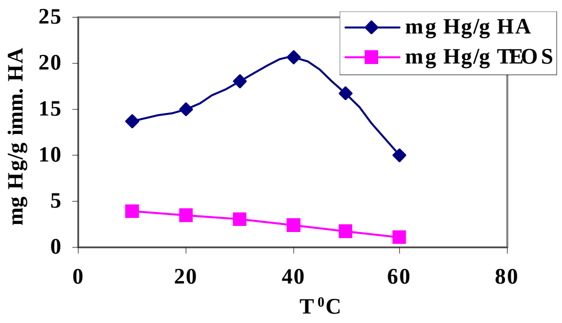

Figure 14: Effect of temperature on the uptake of mercury at pH= 5.0 using 0.010 M phopspate after 24 hours

or terminal hydroxyl in polysiloxane or at least introduces enough electrostatic buffering effect which lower the tendency for Co, Cr and Hg ions to transfer to the chelating groups of polymer[35].

The effect of buffer concentration on the uptake of lead, copper, cadmium, nickel, iron and zinc by immobilized HA was examined in previous work. It was found decreasing buffer increases the uptake of these metals[14].

Effect of temperature on the uptake of cobalt, chromium and mercury

The effect of temperature on the uptake of cobalt, chromium and mercury by free and imm. HA was examined in the 10 -60 range at optimum conditions for each metal at pH= 5.0 using 0.010 M acetate buffer for cobalt, at pH= 6.0 using 0.010 M acetate buffer for chromium and at pH 6.0 using 0.010 M phosphate buffer for mercury. Results in figures 12-14 demonstrate that the uptake of both chromium, cobalt and mercury by imm. HA is affected by temperature in which the uptake of both chromium, cobalt and mercury increases with increasing temperature maximum uptake of cobalt and chromium was 27 mg Co/g imm. HA and 22 mg /g imm HA was obtained at 30°C, while highest uptake for mercury was obtained at 40 °C with a value 20.6 mg/g imm. HA, then the uptake of the three metals decreases with increasing temperature till it drops to 16 mg /g imm HA for cobalt, 13 mg /g imm HA for chromium and 9.9 mg /g imm HA at 60 °C,

The effect of temperature on cobalt,chromium and mercury by blank sol-gel had a different trend where uptake decreased when temperature was increased suggesting physical adsorption at the polysiloxane surface [14].

Kinetic study of the uptake of cobalt, chromium and aluminum by free sol-gel and sol-gel immobilized himc acid

At optimum condition for the uptake of each metal by blank sol-gel and sol-gel immobilized humic acid that is; (at pH = 6, 0.010 M citrate buffer for cobalt), at pH = 5 0.01M acetate buffer for chromium and at pH 6.0 using 0.010 M phosphate buffer for mercury) the uptake of the three metals was monitored against time as shown in figures 15-17 the uptake of cobalt, chromium and mercury by immobilized HA starts immediately after contact with matrix and increases with time

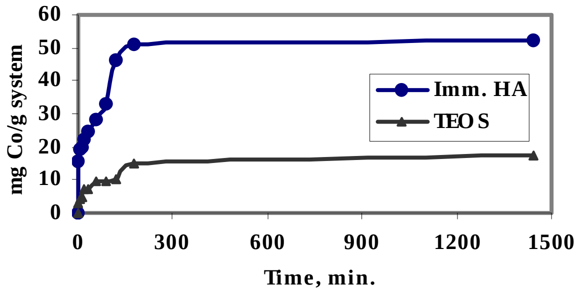

Figure 15: Cobalt uptake by sol-gel and immobilized humic acid against time at pH = 6.0 using 0.010 M citrate buffer

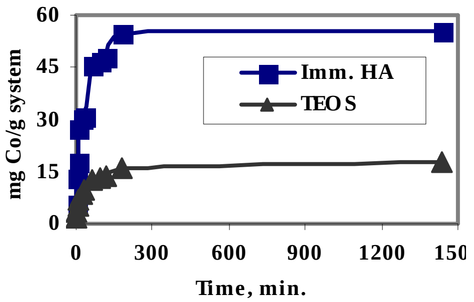

Figure 16: Chromium uptake by sol-gel and immobilized humic acid against time at pH= 5.0 using 0.10 M acetate buffer

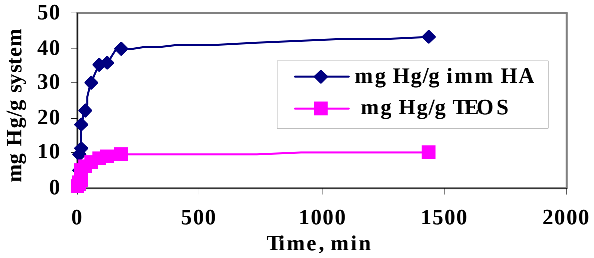

Figure 17: Mercury uptake by sol-gel and immobilized humic acid against time at pH= 5.0 using 0.10 M phosphate buffer

TABLE 1: Reuse of sol-gel Immobilized Humic acid after treated with some reagents. (at optimum condition for each metals) and after 3 hours

Condition	mg Co/g imm.HA	mg Cr/g imm.HA	mg Hg/g imm.HA
*NT	44	47	36.6
H_2O	44	46	36.8
EDTA	50	54	38.4
NaOH	42	42	35.9
HCl	32	34	32.3

*NT, no treatment

till it almost reached a plateau after three hours with a values of 51 mg/g imm. HA for cobalt, 55.0 mg Cr/g imm. HA for chromium and 39.9 mg Hg/g imm. HA for mercury. As shown from figures 15-17 the uptake Co, Cr and Hg by blank polysiloxane (TEOS) was much lower than that of the immobilized humic acid in which, it exhibits 15 mg/g for cobalt, 16 mg/g for chromium and 9.9 mg/g for mercury which indicates that most of the metal uptake is due to chelation with humic acid rather than adsorbed at the polysiloxane.

Recovery of immobilized humic acid

The ability of sol-gel immobilized humic acid for further use to reduce the concentration of Co, Cr, and Hg TABLE 1 was examines first without any treatment, and after treatment with water, EDTA NaOH and HCl. Resultes indicate that the immobilized humic acid can be reused without any treatment with high efficiency to remove Co, Cr, and Hg with an uptake of 44 mg Co/g imm.HA, 47 mg Cr/g imm.HA and 36.6 mg Hg/g imm.HA compared with of 51 mg/g imm. HA for cobalt, 55.0 mg Cr/g imm. HA for chromium and 39.9 mg Hg/g imm. HA for mercury in the first use. No further gain for the uptake of the three metals when imm. HA was washed with water. On the other hand when imm. HA was treated with EDTA the uptake of the three metals was improved which is due to chelation of EDTA with any metals that were interact with chelating functional groups of humic acid. Treatment with HCl reduce the efficiency of imm.HA to reduce the concentration of the three mentioned metals that is; the uptake was reduced to 32.0 mg Co/g imm.HA, 34.0 mg Cr/g and 32.3 mg Hg/g imm.HA. No gain on the uptake of the three metals was obtained when imm.HA was treated with NaOH.

CONCLUSION

Heavy metal pollution has become one of the most serious environmental problems today. Biosorption, using biomaterials such as bacteria, fungi, yeast ,algae and humic substances, is regarded as a cost-effective biotechnology for the treatment of high volume and low concentration complex wastewaters containing heavy metal(s) in the order of 1 to 100 mg/L. Among the promising biosorbents for heavy metal removal which have been researched during the past decades, *humic acid* has received increasing attention due to the unique nature . biosorption largely depends on parameters such as pH, temperature, buffer type and buffer concentration.

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