

# Surface Adsorption of some Heavy Metal Ions in Waste and Underground Waters in Agbara Industrial Estate using Sodium Metasilicate

Madu A. N., Folawewo, A. D., Adebajo M. G.

Industrial Chemistry Department Crawford University Faith City Igbesa, Ogun State Nigeria

## ABSTRACT

The surface adsorption of some heavy metals ions in waste and underground waters in Agbara industrial estate using sodium silicate has been investigated and results show that the percentage of metal ions adsorbed by the sodium metasilicate from prepared salts were least in iron Fe 0.0382 % (38.20 ppm), followed by copper Cu 0.0583 % (58.20 ppm). This was closely followed by zinc Zn 0.0590 % (57.70 ppm), nickel Ni 0.0663 % (59.91 ppm) and finally cadmium Cd 0.0698 % (68.765 ppm). Results of the adsorbed concentration and adsorption coefficient of the metasilicate on the waste and underground water samples showed that zinc ranged from 0.354 ppm amounting to adsorption coefficient of 0.334 to 0.550 ppm amounting to an adsorption coefficient of 0.316, copper ranged from 0.420 ppm equivalent to a coefficient of 0.241 ppm to 0.505 ppm equivalent to a coefficient of 0.246. The values for cadmium ranged from 0.326 ppm to 0.446 ppm equivalent to adsorption coefficient of 0.337 and 0.357 respectively. Nickel had values ranging from 0.248 ppm to 0.380 ppm equivalent to adsorption coefficient of 0.242 and 0.393 respectively while iron had the highest values ranging from 0.664 ppm to 0.878 ppm equivalent to an adsorption coefficient of 0.270 and 0.283 respectively.

**Keywords:** Adsorption, Waste, Metasilicate, Metals, Ions, Coefficient.

## I. INTRODUCTION

The present population of the world requires increase in the application of science and technology to explore and exploit natural resources and other necessities. This situation leads to increase in industrialization, which also results in the release of various types and amounts of waste causing pollution in the environment. According to Voutsinou, (1987); Prodi (1986), heavy metals are important source of pollution not just because they are toxic above a relatively low concentration but also because they are persistent, remaining in the environment long after the sources of pollution has been removed (Madu, Njoku, Agbasi, Folawewo, and Ogunlana, 2015). Furthermore, many metals form organometallic

compounds, which are more toxic than their elemental or ionic forms in the environment (Toggle, 1998). Many studies on heavy metals pollution have been carried out in the industrialized countries of Europe, America and Asia and also in developing countries including Nigeria. Akinola, John, Titiloye, (1981) analyzed industrial effluents from Lagos, Ogun, Kwara and Sokoto states and results showed that they contain heavy metals ranging in concentrations. The term 'heavy metal' is least satisfactory for those metals involved in biochemical and toxicology processes (Phipps, 1981). Heavy metals are chemical elements with a specific gravity that is at least 5 times the specific gravity of water. Heavy metals are often problematic environmental pollutants, with well-known toxic effects on living systems (Evanko and

Dzombak, 1997). The effects of ferric/ferrous chlorides and ferric oxide on emissions in Tongchuan, coal combustion process were experimentally investigated using a thermo gravimetric analyzer (Liu, Hhe, Hui, Xu, 2000). The results showed that all iron compounds used in the experiments which are  $\text{FeCl}_3$ ,  $\text{FeCl}_2$  and  $\text{Fe}_2\text{O}_3$  can change the emissions of  $\text{SO}_2$  and  $\text{NO}$ , but with different mechanisms and different magnitudes. Iron is a natural component of soils, but its concentration can be influenced by some industries. It has been reported that urban soils showed different heavy metal characteristics (Yang, Paterson, Campbell, 2001). Actual accumulations of Pb, Zn, Cu, and Ni were observed, of which Pb occurred mainly in conjunction with iron oxides, and Ni and Zn existed in residual forms. Cu showed the same importance of different chemical forms but for soluble forms. Iron also is present in Water and according to Abal, Dennison, Greenfield, (2001); Trindade and Cavalheiro, (1990). A study has reported that, due to agricultural activities and increased water extraction, ground water levels have generally decreased in large areas of the peaty lowlands in the Netherlands (Smolders, Roelofs, 1995). Zinc is ubiquitous in the environment and occurs in the earth crust at an average concentration of about 70 mg/kg (Thomas, 1991). The sources of zinc in the environment are from metal smelters and mining activities. It exhibits one oxidation state +2. Typical Zn concentrations in river water are about 10 to 50  $\mu\text{g l}^{-1}$  (Hempe and Cousins, 1992). Chromium is commonly present in soils as Cr (III) and Cr (VI), which are characterized by distinct chemical properties and toxicities. Cr (VI) is a strong oxidizing agent and is highly toxic, whereas Cr (III) is a micronutrient and a non-hazardous species 10 to 100 times less toxic than Cr (VI). Cr (VI) has been reported to cause shifts in the composition of soil microbial populations, and known to cause detrimental effects on microbial cell metabolism at high concentrations (Shun-Hong, Bing, Zhi-Hui, Li-Yuan and Li-Cheng, 2009). Nickel finds its way into the ambient air as a result of the combustion of coal,

diesel oil and fuel oil, the incineration of waste and sewage, and miscellaneous sources. Environmental sources of lower levels of nickel include tobacco, dental or orthopedic implants, stainless steel kitchen utensils and inexpensive jewelry. Nickel is a ubiquitous metal frequently responsible for allergic skin reactions and has been reported to be one of the most common causes of allergic contact dermatitis, as reflected by positive dermal patch tests (Cavani, 2005). Heavy metals exhibit toxic effects towards soil biota by affecting key microbial processes and decrease the number and activity of soil microorganisms. Also, long-term heavy metal effects can increase bacterial community tolerance as well as the tolerance of fungi such as carbuncular mycorrhiza (AM) fungi, which can play an important role in the restoration of contaminated ecosystems. (Chen, Chen, Zeng, Zhang, Chen, Wang and Zhang 2010) suggested that heavy metals caused a decrease in bacterial species richness and a relative increase in soil actinomycetes or even decreases in both the biomass and diversity of the bacterial communities in contaminated soils. Also Karaca, Cetin, Turgay, Kizilkaya, (2010) reported that the enzyme activities are influenced in different ways by different metals due to the different chemical affinities of the enzymes in the soil system. Cd is the more toxic to enzymes than Pb because of its greater mobility and lower affinity for soil colloids. Ashraf and Ali (2007) also reported that the heavy metals exert toxic effects on soil micro-organism hence results in the change of the diversity, population size and overall activity of the soil microbial communities and observed that the heavy metal (Cr, Zn and Cd) pollution influenced the metabolism of soil microbes in all cases. Uptake of heavy metals by plants and subsequent accumulation along the food chain is a potential threat to animal and human health (Sprynoxyy, Kosobucki and Buszewsk, 2007). The absorption by plant roots is one of the main routes of entrance of heavy metals in the food chain (Jordao, Nascentes, Cecon, Fontes and Pereira, 2006). Absorption and accumulation of heavy metals in plant tissue depend upon many factors which include

temperature, moisture, organic matter, pH and nutrient availability. The uptake and accumulation of Cd, Zn, Cr and Mn in *Beta vulgaris* (Spinach) were higher during the summer season, whereas Cu, Ni, and Pb accumulated more during the winter season. Heavy metal accumulation in plants depends upon plant species and the efficiency of different plants in absorbing metals is evaluated by either plant uptake or soil to plant transfer factors of the metals (Khan, Zheng, Cao, Huang, and Zhu, 2008). Heavy metals are potentially toxic and phytotoxicity for plants resulting in chlorosis, weak plant growth, yield depression, and may even be accompanied by reduced nutrient uptake, disorders in plant metabolism and reduced ability to fixate molecular nitrogen in leguminous plants (Guala, Vega and Covelo, 2010). Thus, these contaminants are highly significant in terms of ecotoxicology. Moreover, metals are not subject to bacterial degradation but remains permanently in the marine environment (Woo, Yum, Park, Lee and Ryu, 2009). Contamination of a river with heavy metals may cause devastating effects on the ecological balance of the aquatic environment, and the diversity of aquatic organisms becomes limited with the extent of contamination (Ayandiran, Fawole, Adewoye and Ogundiran, 2009). Because a major fraction of the trace metals introduced into the aquatic environment eventually become associated with the bottom sediments, environmental degradation by metals can occur in areas where water quality criteria are not exceeded, yet organisms in or near the sediments are adversely affected (Guirrieri, 1998). Diatom community structure can be affected by high levels of micro pollutants, and in particular by metals, which are often found in rivers (Jongea, Vijverb, Blusta and Bervoesta, 2009). Carnivores at the top of the food Chain including humans, obtain most of their heavy metal burden from the aquatic ecosystem by way of their food, especially where fish are present so there exist the potential for considerable bio magnifications (Ayandiran *et al.*, 2009). Contaminants in aquatic systems, including heavy metals, stimulate the production of reactive oxygen species (ROS) that can

damage fishes and other aquatic organisms (Woo *et al.*, 2009). Heavy metals become toxic when they are not metabolized by the body and accumulate in the soft tissues (Sobhak, Promina, Harini, and Veeraiah, 2007). Chronic level ingestion of toxic metals has undesirable impacts on humans and the associated harmful impacts become perceptible only after several years of exposure (Khan *et al* 2008). The ground water contamination, however, is detected only sometime after the subsurface contamination begins (Bhu-Jal news, 1997). Ground water pollution causes irreparable damage to soil, plants, human and animals and spread epidemics and chronic diseases (Srinivas, Ravi, Venkateshwar, Satyanayana, and Reddy, 2000). Some metals find their way into water bodies because of industrial activities. The effect of tropical clay minerals (alumino silicates) on the organic reduction of hexavalent chromium as a potent form of chemo-remediation has been achieved (Madu and Ijiwade, 2017). In the research, tropical bentonite showed higher ability to catalyze the reduction of hexavalent chromium to a more stable oxidation state in the presence of an organic acid than kaolin. Removal of heavy metals from waste water using agricultural and industrial wastes such as rice husk and fly ash as adsorbents was carried out by Hegazi, (2013). The adsorption of the metal ions by low cost adsorbent (rice husk and fly ash) was evaluated under different conditions such as pH, heavy metal concentration, mixing speed, adsorbent dose through both kinetic and isotherm studies. Heavy metals removal using activated Carbon, Silica and Silica Activated Carbon Composite was another experiment carried out by Mona, Ahmad, Hanafy, Zakia (2014). Removal of heavy metals from industrial wastewaters by adsorption onto activated carbon prepared from an agricultural solid waste by Kadirvelu, Thamaraiselvi, Namasivayam, (2000). Waste coir pith was collected from coir processing industries and dried in sunlight. Adsorption of heavy metals from water using banana and orange peels was carried out by Annadurai, Juang and Lee, (2002). The study showed the potential of banana and orange peels as adsorbents for removal of

Cu<sup>2+</sup>, Zn<sup>2+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup>, and Pb<sup>2+</sup> from water. Adsorption isotherms showed the relations between the amounts of metal adsorbed per unite mass of banana and orange peel (qe) and their remaining concentrations in the solutions (Ce). The adsorption ability decreases in the order Pb<sup>2+</sup> > Ni<sup>2+</sup> > Zn<sup>2+</sup> > Cu<sup>2+</sup>>Co<sup>2+</sup> under comparable conditions The Langmuir equation was also used. The adsorption capacities are 7.97 (Pb<sup>2+</sup>), 6.88 (Ni<sup>2+</sup>), 5.80 (Zn<sup>2+</sup>), 4.75 (Cu<sup>2+</sup>), and 2.55 mg/g (Co<sup>2+</sup>) at an equilibrium pH of around 5.4–5.8 using banana peel; and are 7.75 (Pb<sup>2+</sup>), 6.01 (Ni<sup>2+</sup>), 5.25 (Zn<sup>2+</sup>), 3.65 (Cu<sup>2+</sup>), and 1.82 mg/g (Co<sup>2+</sup>) at an equilibrium pH of about 4.8–5.0 using orange peel. The banana and orange peels appeared to be useful in the removal of trace metals from synthetic solutions. This research seeks to identify the adsorption ability of sodium metasilicate of dissolved metals in waste and drainage waters which may find application for irrigation.

## II. MATERIALS AND METHODS

The sample bottles were first cleaned up with dilute HNO<sub>3</sub> for tightening. The samples were collected at different locations of Agbara, which were labeled A to D using necessary materials. Clean cups were used to collect each sample. For each sample, the geographical

information was recorded. The samples collected were kept in the refrigerator till they were needed for analysis. The waste water samples were filtered to obtain a clear solution. 225ml of each sample were measured into the beakers which were properly labeled. 10g of sodium metasilicate (adsorbent) were added to each sample and stirred continuously for 12 hours at 20 °C. Then, the pH of the samples was measured using pH meter. After achieving equilibrium sorption, the slurry was centrifuged at 18,000 rpm for 10 minutes with Beckman Coulter Optima™ MAX Series Benchtop Ultracentrifuge, and the supernatant recovered. The concentration the metal ions remaining in the supernatant of each sample were determined for the using AAS (Atomic Absorption Spectroscopy) analysis. The amount of metal adsorbed was calculated for the differences between the initial and final aqueous concentration of the metal. Each experiment was performed in duplicate (Ali Awan *et al.*, 2003). The same method was used for the prepared metal salts of zinc, copper, cadmium, nickel and iron. The working pH of the all samples was in alkaline region, having the pH range of 12.00-12.58. The samples were analyzed using an AAS Buck Scientific (BUCK 210 AAS).

## Results

The surface adsorption of some heavy metals ions in waste and underground water within Agbara industrial estate using sodium silicate has been carried out and the results are as shown:

**Table 1.** Results for analysis of the prepared salt before and after adsorption.

Metal salts	Initial Conc.(ppm)	Final Conc.(ppm)	Adsorbed Conc. (ppm)	% Absorbed
ZnSO <sub>4</sub>	977.5	919.800	57.700	0.0590
CuSO <sub>4</sub>	998.7	940.500	58.200	0.0583
CdCl <sub>2</sub>	984.9	916.135	68.765	0.0698
NiCl <sub>2</sub>	903.2	843.290	59.910	0.0663
Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	999.7	961.500	38.200	0.0382

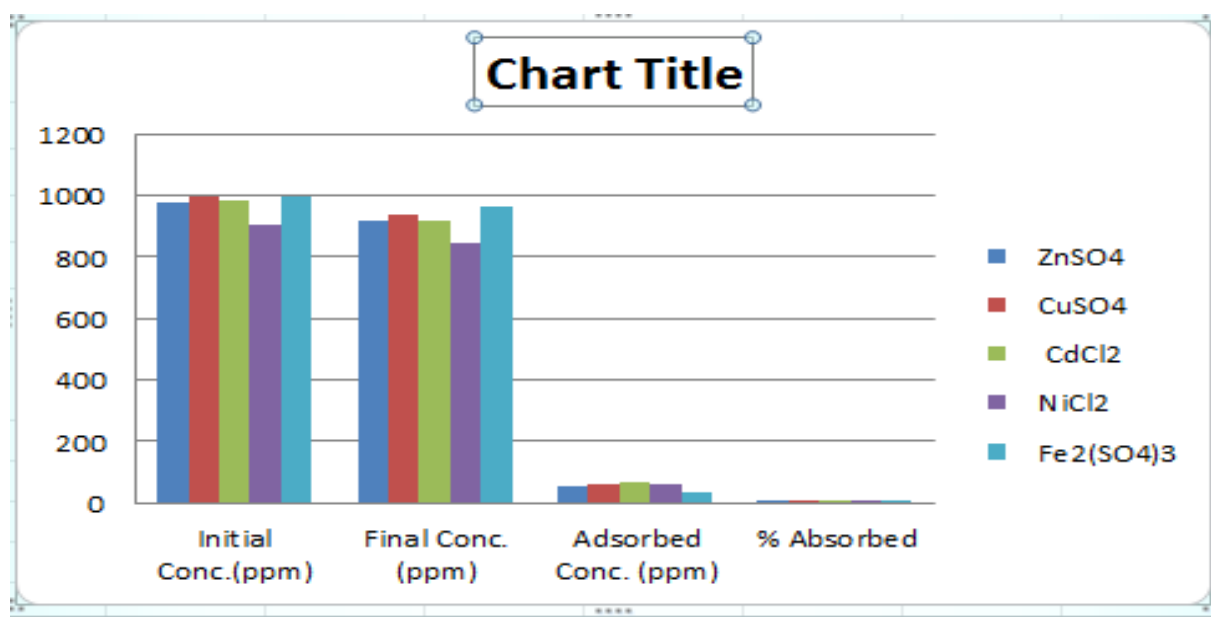
**Table 2.** Results for analysis of the waste water before and after adsorption with sodium metasilicate.

Samples	Zinc (ppm)		Copper (ppm)		Cadmium (ppm)		Nickel (ppm)		Iron (ppm)	
	Initial	Final	Initial	Final	Initial	Final	Initial	Final	Initial	Final
A	1.055	0.701	2.055	1.550	1.204	0.786	1.024	0.776	2.476	1.768
B	2.405	1.120	2.405	1.910	1.248	0.802	0.966	0.658	2.664	1.988
C	1.740	1.190	1.740	1.320	0.968	0.642	0.982	0.664	2.462	1.798
D	1.465	0.960	2.065	1.602	1.046	0.654	0.968	0.588	3.056	2.265
E	1.064	0.576	1.760	1.258	0.984	0.568	0.994	0.684	3.102	2.224

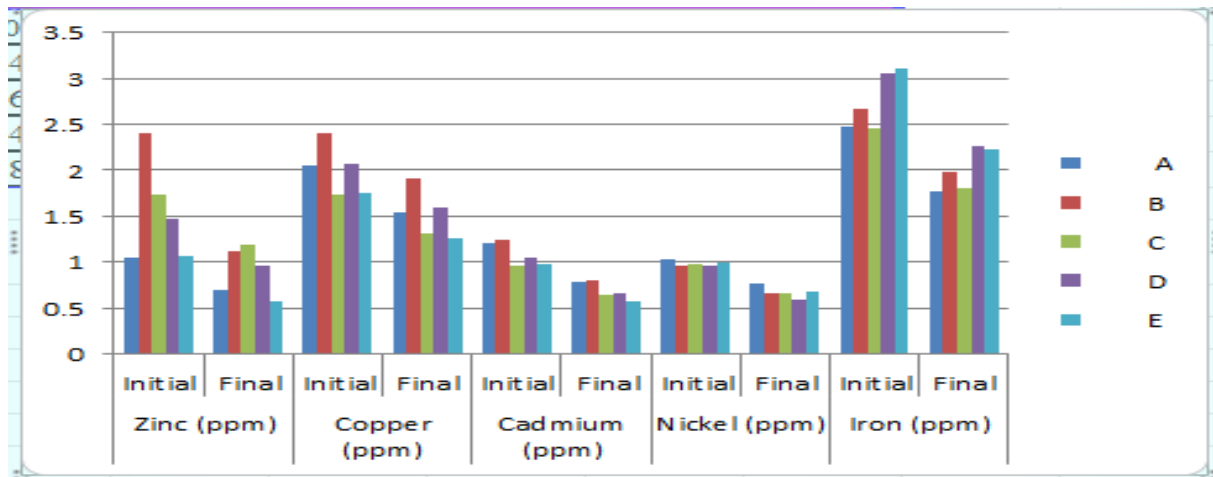
**Table 3.** Results showing adsorbed concentration and adsorption coefficient of the metasilicate Adsorption

$$\text{Coefficient} = \frac{\text{adsorbed concentration}}{\text{initial concentration}}$$

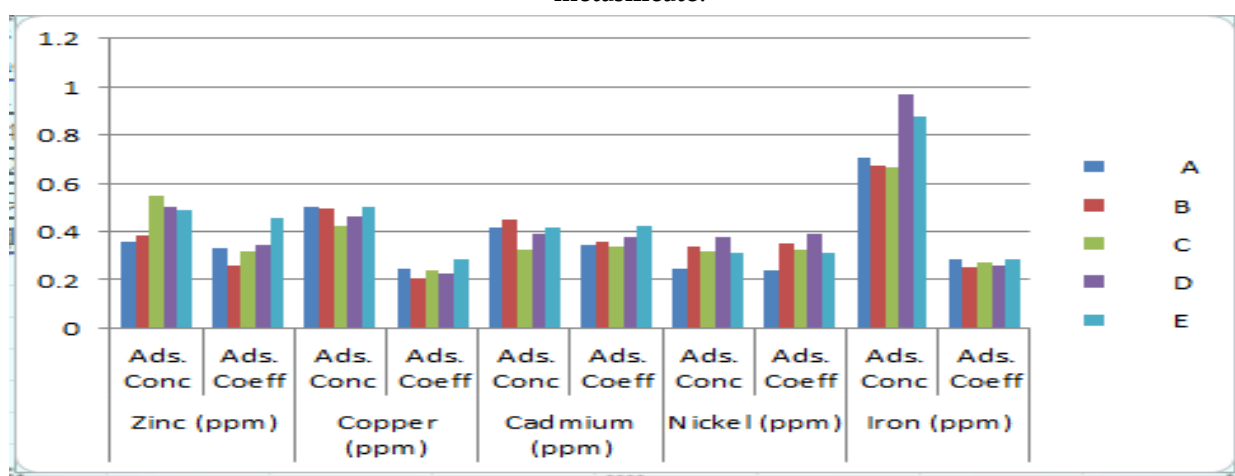
Samples	Zinc (ppm)		Copper (ppm)		Cadmium (ppm)		Nickel (ppm)		Iron (ppm)	
	Ads. Conc	Ads. Coeff	Ads. Conc	Ads. Coeff	Ads. Conc	Ads. Coeff	Ads. Conc	Ads. Coeff	Ads. Conc	Ads. Coeff
A	0.354	0.334	0.505	0.246	0.418	0.347	0.248	0.242	0.708	0.286
B	0.385	0.256	0.495	0.206	0.446	0.357	0.338	0.350	0.676	0.254
C	0.550	0.316	0.420	0.241	0.326	0.337	0.318	0.324	0.664	0.270
D	0.505	0.345	0.463	0.224	0.392	0.375	0.380	0.393	0.971	0.259
E	0.488	0.459	0.502	0.285	0.416	0.423	0.310	0.312	0.878	0.283



**Figure 1.** Bar chart showing results for analysis of the prepared salt before and after adsorption.



**Figure 2.** Bar chart showing results for analysis of the waste water before and after adsorption with sodium metasilicate.



**Figure 3.** Bar chart showing results of adsorbed concentration and adsorption coefficient of the sodium metasilicate.

### III. DISCUSSION

The surface adsorption of some heavy metals ions in waste and underground waters in Agbara industrial estate using sodium silicate has been investigated by examining the extent of adsorption of prepared metal salts of zinc, copper, cadmium, nickel and iron. Results show that the percentage of metal ions adsorbed by the sodium metasilicate from prepared salts were least in iron Fe 0.0382 % (38.20 ppm), followed by copper Cu 0.0583 % (58.20 ppm). This was closely followed by zinc Zn 0.0590 % (57.70 ppm), nickel Ni 0.0663 % (59.91 ppm) and finally cadmium Cd 0.0698 % (68.765 ppm). Five different waste and underground water samples were investigated for the metal ions present in them. These waste water

samples were subjected to the Results of the adsorbed concentration and adsorption coefficient of the metasilicate on the waste water samples showed that the value for zinc ranged from 0.354 ppm amounting to adsorption coefficient of 0.334 to 0.550 ppm amounting to an adsorption coefficient of 0.316, copper ranged from 0.420 ppm equivalent to a coefficient of 0.241ppm to 0.505 ppm equivalent to a coefficient of 0.246. The values for cadmium ranged from 0.326 ppm to 0.446 ppm equivalent to adsorption coefficient of 0.337 and 0.357 respectively. Nickel had values ranging from 0.248 ppm to 0.380 ppm equivalent to adsorption coefficient of 0.242 and 0.393 respectively while iron had the highest values ranging from 0.664 ppm to 0.878 ppm equivalent of an adsorption coefficient of 0.270 and 0.283 respectively.

#### IV. CONCLUSION

The chemo-remediation of heavy metal contaminated soil and water bodies may be approached through organic reduction process in which the metal is converted to a more stable oxidation state (Madu et al, 2017) or via surface adsorption. Analysis has shown that metasilicates and indeed any other silicate can act as veritable substrates in surface adsorption for metal ions especially heavy metals and so can be a pathway to the chemo-remediation of soil and water bodies contaminated by sludge and effluents from industrial wastes. The results revealed that though the initial concentration of the metal ions in the effluents was much lower than the metal salts as compared in the research, the absorption coefficients for the effluents were reversibly much higher, ranging from 0.316 to 0.535 as against 0.04 to 0.07 for the metal salts.

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