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REMOVAL OF Mn(II) & Zn(II)IONS USING SOIL COLLECTED FROM A POND IN TIRUCHIRAPPALLI, INDIA

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ABSTRACT

Water pollution due to the presence of toxic metal ions is a major task, since they cause toxic effects on all living organisms. In the present work, the adsorptive removal of Mn(II) & Zn(II)ions using soil (collected from a pond in Tiruchirappalli) was carried out after regeneration with NaCl solution. The process parameters like pH of the medium, size of the adsorbent, contact time etc., were varied and their effects on the removal of Mn(II) & Zn(II) ions were determined. The instrumental data (FT-IR and SEM EDX) of the adsorbent before and after the adsorption process confirm the removal of Mn(II) & Zn(II) ions. Desorption of the metal ions, was maximum when 0.5N HCl solution was used.

KEYWORD: Mn(II) & Zn(II)ions.

1. INTRODUCTION

The existing technologies for waste water treatment have major problems. Costs involved in the construction of waste water treatment plants are un-economical, it consumes lot of space, and commercially they are unattractive and have disposal problems. The technologies are divided into three types namely biological, chemical and physical.[1]

Manganese is a very common compound that can be found everywhere on earth. Groundwater is a main source of drinking water and the soluble Mn(II) and Zn(II) often exceeds WHO standard. In the present work, the adsorption of Mn(II) and Zn(II) on the natural clay was studied.[2]

2. EXPERIMENTAL

Natural clay(~500g) from a pond in Uttamarceli, Tiruchirappalli (~ one foot from the surface – during June 2013) was collected, washed well with water and filtered. Then, the material was stirred well with ~1N HNO_3, filtered and washed repeatedly with distilled water (filtrate checked with litmus paper). Then, the clay material was filtered, washed well with double distilled water, dried, sieved to different sizes and kept in airtight glass containers. The clay thus obtained is abbreviated as LPC (Lotus Pond Clay).

2.1. BATCH EQUILIBRATION METHOD

All experiments were carried out in batch mode. Batch mode was selected because of simplicity and reliability. In many applications, the preliminary evaluation program may take the form of simple feasibility study where capacities of adsorbents for the removal of chosen adsorbates are determined by simple batch experiments in laboratory. This study together with the knowledge of similar operating may provide sufficient capacity and design information to proceed with full scale design. In other cases considerable effort may be required for full scale implementation. Keeping this in view batch experiments were done in different ground joint glass bottles of 100 ml capacity Prior to each experiment a predetermined amount of absorbent was added to each flask. The stirring was kept constant (100rpm) for each run through to ensure equal mixing. Each bottle was filled with 50ml of sample was withdrawn from the shaker at the predetermined time interval, filtered and the residual concentration of the sample was measured concentrations of metal ions before and after adsorption was measured using a photocolorimeter.

All experiments were conducted by following the batch mode adsorption technique in a 100 ml reagent bottles by varying the parameters *viz.*, particle size (<75 µm to425µm -500 µm), initial concentration of synthetic Mn^{2+} solution (25 mg/l -200 mg/l), contact time (5 min - 50 min), pH (3 - 7) and temperature (27ºC-47ºC). The optimized size for LPC was first examined followed by varying contact time, initial concentration, pH and temperature.[3]

The metal ion retained in the adsorbent phase, q_e (mg/g) was calculated using.

$$q_e = \frac{(C_i - C_e)}{m} V$$

Where V= Volume (ml) of the equilibrated solution,

m= Mass of the adsorbent (g),

C_i = Initial concentration of synthetic Mn^{2+} and Zn^{2+} solution (mg/l),

C_e = Mn(II) at equilibrium (mg/l).

The percentage removal (%) of Mn^{2+} and Zn^{2+} ions was calculated using the following equation

$$\text{Removal (\%)} = \frac{(C_i - C_e)}{C_i} X100$$

2.1.1. EFFECT OF ADSORBENT PARTICLE SIZE

Experiments were conducted using LPC to evaluate the influence of adsorbent particle size for a constant weight on the removal of manganese ions. The removal of Manganese ions at different particle sizes *viz.*,< 75 µm, 75 µm -150 µm, 150 µm -250 µm, 250 µm -300 µm, 300 µm – 355 µm, 355 µm -425 µm and 425 µm -500 µm were done. The results obtained with the variation of adsorbent particle sizes and the percentage of removal was graphically represented in Fig. 1 & 2. The high adsorption efficiency was shown by the particle size of <75 µm. The presence of a large number of smaller particles provides the sorption system with a larger surface area available for manganese and zinc ion removal and it also reduces the external mass transfer resistance in addition to ion exchange.[4]

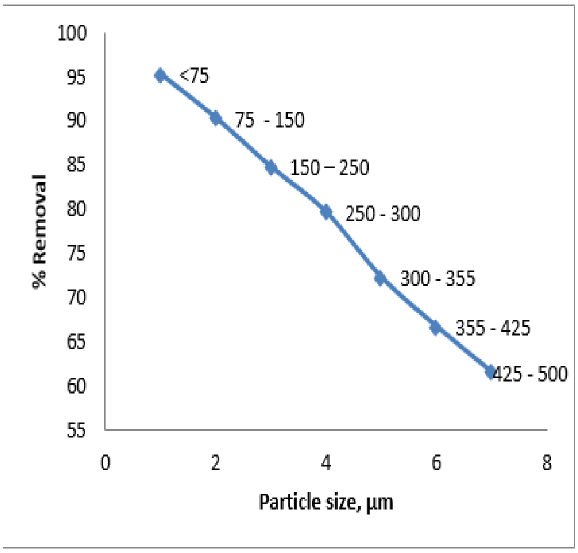


Fig. 1 Variation in % removal of Mn(II) with Particle size.

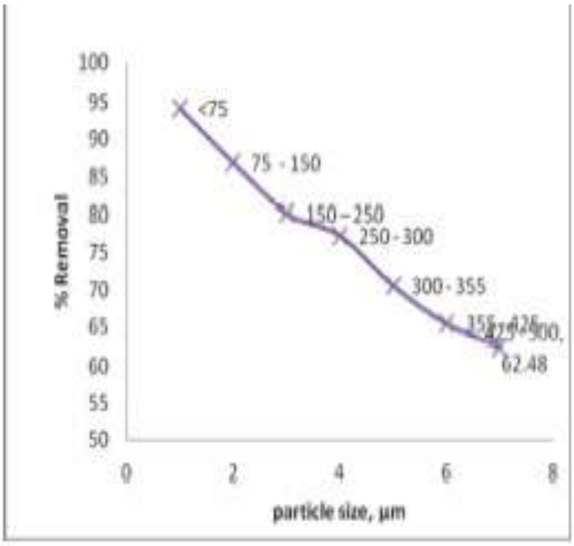


Fig. 2 Variation in % removal of Zn(II) with Particle size

2.1.2-EFFECT OF ADSORBENT WITH CONTACT TIME

The variation of percentage metal ions removal by each adsorbent with contact time was determined. The percentage of metal ions removal approached equilibrium within 30 min. for the adsorption of Mn^{2+} and Zn^{2+} by LPC. The fast adsorption may probably due to the initial concentration gradient between the adsorbate in solution and the number of vacant sites available on the surface of the adsorbent at the beginning. The progressive increase in adsorption and consequently the attainment of equilibrium may be due to limited mass transfer of the adsorbate molecules from the bulk liquid to the external surface of adsorbents.

2.1.3-EFFECT OF ADSORBENT WITH CONCENTRATION

In general, the adsorption capacity increases as the metal ion concentration increases from 25 to 200 mg/l which must be due to the progressive increase in the electrostatic interaction between the metal ions and the absorbent active sites. Moreover, this can be by the fact that more adsorption sites were being covered as the metal ion concentration increases and higher initial concentrations lead to an increase in the affinity of the metal ions towards the active sites.

2.1.4-EFFECT OF ADSORBENT WITH DOSAGE

The initial increment in adsorption capacity with increase in adsorbent dosage was expected, because, as the number of adsorbent particles increased, the surface area available for metal ions attachment also increased. The study revealed that as the adsorbent dose was increased from 0.25 g to 2.25 g there was an increase in the adsorption of metal ions on to the surface of the adsorbents. It is plausible that with higher dosage of adsorbent, there would be greater availability of active/exchangeable sites for the Mn^{2+} and Zn^{2+} ions.

2.1.5-EFFECT OF ADSORBENT WITH SPEED

The agitation speed less than 150 rpm favored the maximum removal of metal ions by LPC. Maximum removal of Mn^{2+} ions by LPC occurred at 50 rpm. For the removal of Zn^{2+}, the optimum agitation speed required was 100 rpm by LPC. The high agitation speed may shift the equilibrium process of adsorption and desorption towards the desorption.[5]

3. DESORPTION STUDIES

Desorption studies help to elucidate the nature of adsorption and recycling of the spent adsorbent and the metal ions. Various reagents used for the desorption studies were water, acetic acid (0.5N), hydrochloric acid (0.5N) and sulphuric acid (0.5N). The results indicate that the desorption of the metal ions was maximum when 0.5N HCl solution was used. The reason must be the higher solubility of Mn^{2+} and Zn^{2+} ions as chlorides in aqueous medium when compared to the other desorbents.

4. CHARACTERIZATION OF ADSORBENTS BEFORE AND AFTER ADSORPTION

4.1 FT-IR spectra

Adsorption of Mn(II)/Zn(II) ions on LPC[6]

The FT-IR spectra obtained for LPC before and after the adsorption of Mn(II)/Zn(II) ions are shown in Fig 3-5. The IR spectrum of clay material shows a sharp peak with high intensity at 1078.80 cm-1. This strong vibration is assigned to the Si-Al-Si asymmetric stretching vibration (1250 cm-1 – 950 cm-1) which represents the presence of substituted Al atoms in the tetrahedral forms of silica. A sharp band at 462.19 cm-1 can be assigned to the Si-Al-O bending mode (420 cm-1 - 500 cm-1). It is observed that the band recorded at 691.72 cm-1 is assigned to the Si-Al-O symmetric stretching (720 cm-1 -650 cm-1). Like zeolites, the clay material shows two IR bands characteristic of the water of hydration. In zeolites, the water molecules are associated with cations and to some extent hydrogen bonded to the oxygen ions of the framework.[7] The broad band observed at 3427.66 cm-1 is the characteristic of OH, hydrogen bonded to the oxygen ions of the framework. The IR spectra of the clay material before and after the adsorption process has not shown any significant change. From the recorded peak values, it may be concluded that the Si–O framework is rigid without any distortion even after the adsorption process.[8]

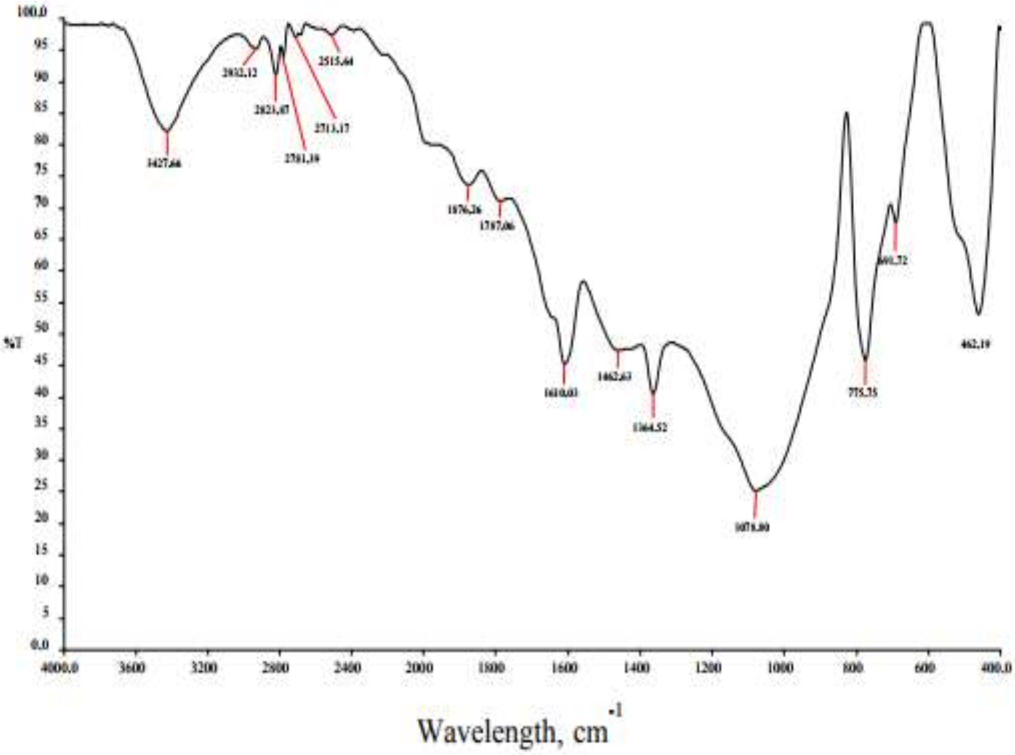


Fig.3: FT-IR spectrum of LPC before adsorption.

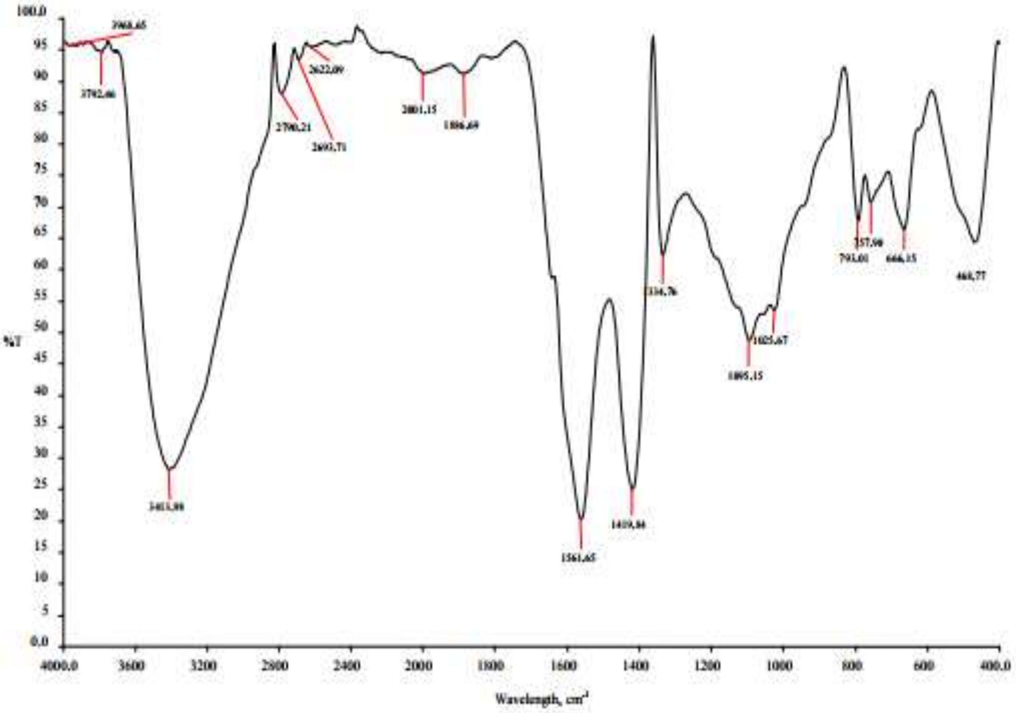


Fig.4 FT - IR spectrum LPC after adsorption of Manganese.

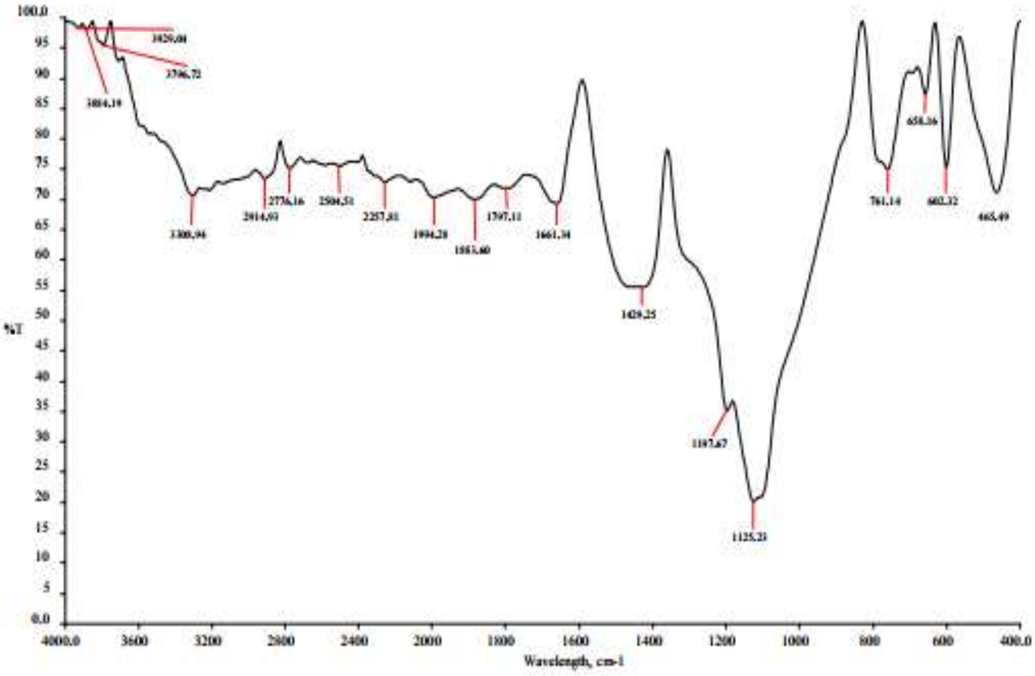


Fig.5. FT - IR spectrum LPC after adsorption of Zinc.

5. SEM –EDX Study

5.1. Adsorption of Mn(II)/Zn(II) ions on LPC[9]

The lotus pond clay (LPC) before and after sorption of Mn^{2+}/ Zn^{2+} ions is imaged using SEM at high magnification to understand the differences in surface morphologies. Mn^{2+} ions sorption result in a comparatively smooth surface similar to the plain LPC. But Zn^{2+} ions sorption results in a rough amorphous-like surface morphology with a few crystalline areas.[10]

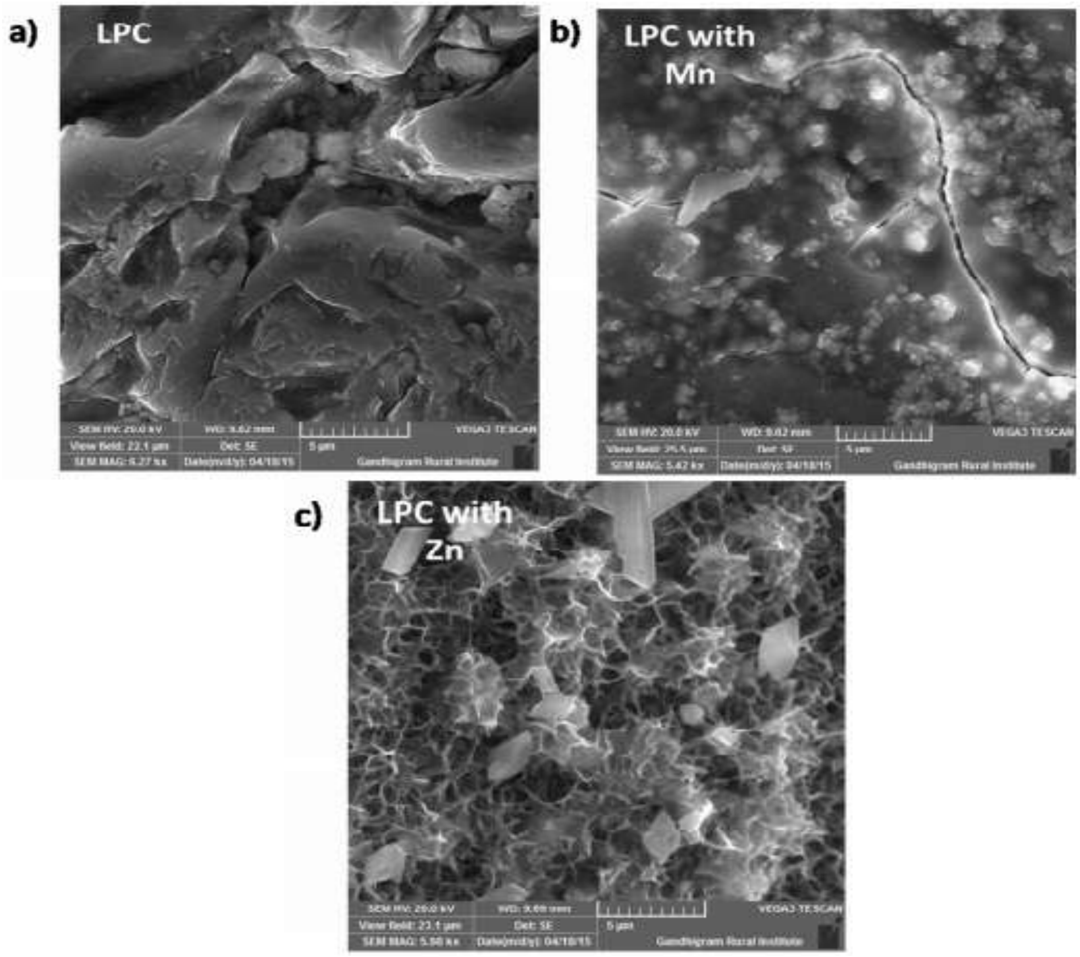


Fig.6. SEM EDX Study for LPC before and After Adsorption.

The sorption of Mn2+/ Zn2+/Cd2+ ions on LPC is confirmed using EDS spectroscopy

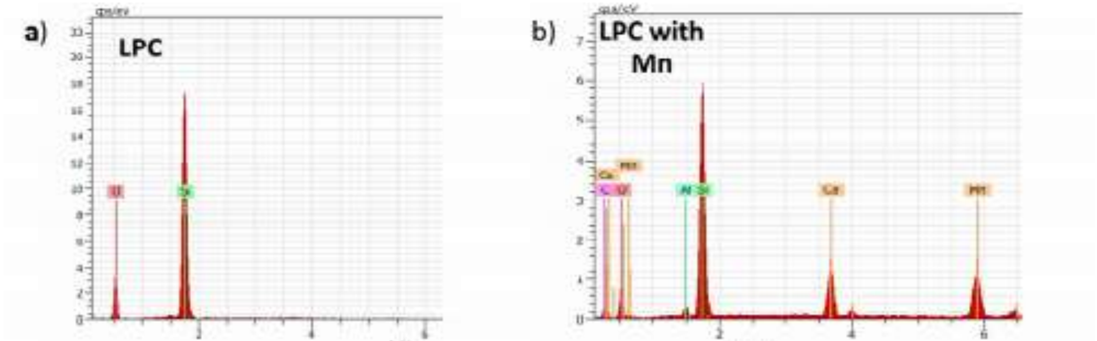
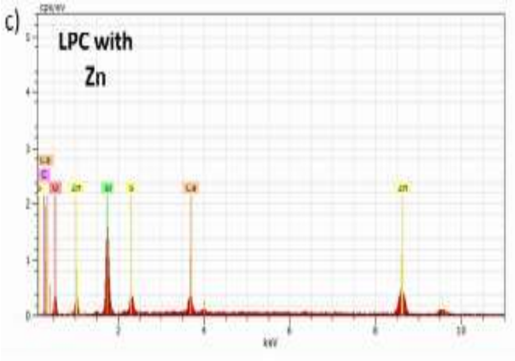


Fig.7.EDXspectra of a) LPC **b) LPC with Mn^{2+}ions,**



c) LPC with Zn^{2+}

CONCLUSION

In the present study, groundwater pollution due to heavy metal ions, viz., Mn^{2+} and Zn^{2+} ions is considered. Though many methods like precipitation, ion exchange, reverse osmosis, electro dialysis etc., are available for the removal of heavy metal ions, adsorption is found to be an easy, effective and economical process.The qualitative analysis carried out for the groundwater samples collected from the residential areas near Kodungaiyur waste dumping yard (North Chennai) indicate the presence of many metal ions, viz., lead, tungsten, copper, cadmium, manganese, chromium, iron, cobalt, nickel, zinc, calcium, magnesium and lithium. The reason must be the dissolution of these metals (from the electrical and electronic wastes dumped in the dumping yard) and their percolation into the ground by rain water.

The amount of Mn^{2+} and Zn^{2+} ions in the groundwater samples were estimated following the standard procedure using Atomic Absorption Spectrometer. The results indicate the presence of these metal ions beyond the permissible limit (WHO) in some of the groundwater samples collected from the study area. The data obtained confirmed the application of natural clay as a effective adsorbent on the removal of manganese and zinc ions.

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