



Removal of Mn^{+2} and Fe^{+3} ions from waste water and underground water using Calcium Silicate (CS)

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ABSTRACT

The determination of heavy metal ions are limited by two difficulties, very low concentration of heavy metal ions which may be lower than the detection limit of many traditional analytical techniques such as atomic absorption spectrometry, colorimetric, and voltametry. And the interfering effects of the matrix. Calcium silicate (CS) is obtained as mentioned in the literature, This synthesized material, which have many applications in various walks of life will be under study in this research. In a new area of the most important areas of life and the environment, a water treatment and removal of some heavy ions such as Mn^{+2} and Fe^{+3} ions present in waste water and underground water were efficiently removed by (CS).

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Introduction

Determination of heavy metals became one of the important water quality control measurements; human beings cannot deal with the surrounding environment safely without affirmative information about the level of different hazards. This is attributed to the harmful effects caused by the accumulation of heavy metals in human tissues through daily contact with the polluted environment [1].

Iron removal from water is mostly carried out in drinking water preparation, because mineral water contains high amounts of iron ions. These influence water color, odour and turbidity.

Iron is present in all wastewaters. Iron removal from wastewater may be achieved by oxidation of binary iron to tertiary iron. Hydrolysis subsequently causes flake formation, and flakes can be removed by sand filtration. Oxidation may be achieved by adding oxygen or other oxidants, such as chlorine or potassium permanganate. The reaction rate depends upon pH values, and is slower under acidic than under alkalic conditions. To speed up the reaction under acidic conditions, the water may be aerated for carbon dioxide removal and pH recovery. The total reaction causes acid formation and thereby diminishes itself. Iron is often reduced together with manganese. Applying ion exchangers for iron trace removal from drinking water and process water is another option, but this is not very suitable for removing high iron concentrations. Iron compounds are applied in wastewater treatment, usually as coagulants. One example is iron sulphate application in phosphate removal [3 - 6].

Calcium silicate is a known material and has many uses and diverse in many areas of life, for example Rice husk ash when ground with hydrated lime is being successfully used as mortar. Activated carbon and furfural are the two important chemicals which can be derived from rice husk [7].

A literature survey on the uses of the ash remained after firing agricultural residues showed that the following are the most abundant uses all over the world [8-12].

- As aggregate for insulating and light weight concretes.
- In making light weight, refractory and heat – insulating bricks.
- In rubber compounding (reinforcing fillers for rubber

compounds).

- Preparation of activated carbon and sodium silicate.
- Making hydraulic cements and glasses.
- As effective agent in disposing of oil spills.
- In insecticides as anticaking.
- Manufacture of silicon tetrachloride.
- Manufacture of silicon carbide and silicon nitride.
- As growing media and fertilizer.
- As moulds for molten steel ingots.
- As filter aid and filter media in water purification.

The following summarizes some technical commercial opportunities for agricultural residues, ash and char utilization.

Pure silicon used for making semi-conductors is yet another expensive material, which can be obtained from rice husk [13].

Silicon carbide and, silicon nitride are also very costly and useful materials obtainable from rice husk [14]. Rice husk can also be used for production of acetic acid, propionic acid, and phenol, cresol...etc by destructive distillation or xylos and glucose through hydrolysis [15]. preparation of CSH by the reaction between pure silica and calcium hydroxide had been extensively studied [16, 17]. On the other hand preparation of CSH from the ash remained after firing rice straw or other agricultural wastes [18].

The aim of the present work was to use calcium silicate to remove heavy metals ions from waste water and underground water

Experimental

Underground water samples were collected from different locations within the Delta region. All samples were filtered off and acidified with concentrated HCl to pH2 then introduced into plastic vessels at a temperature of 20-25 °C. Suspended matters were determined by filtering 1000 cm³ of the untreated water sample using a sintered glass G4 and weighing the residue after drying at 120 °C for 2 hrs.

Dissolved oxygen (DO) was determined by Winkler method [19]; dissolved oxygen was stabilized in field using manganese sulfate solution in presence of ammonia buffer.

The compound formed was treated with H_2SO_4 and KI and the liberated iodine was titrated against $K_2S_2O_8$.

Total alkalinity (mg $CaCO_3/L$) was determined according to the method described by Strickland and Parsons.

Total Dissolved Salts (TDS) of the water samples were determined by weighing the residue left after complete drying of 100 cm^3 of the water sample at $120\text{ }^\circ\text{C}$ for 2 hrs.

The reactivity of the produced material (CSH) towards heavy metals removal from aqueous solutions was also assessed. This was accomplished as follows: 100 mg of CSH was added to 100 ml of the tested water sample and the pH value was again controlled. The sample was stirred for 30 min. and filtered off. The filtrate was subjected to atomic absorption spectroscopy and determining the concentrations of Fe^{3+} and Mn^{2+} ions.

Results and Discussion

The main water quality properties was examined before treatment with CSH and the results were TDS (3.090 g dm^{-3}), (0.106 g dm^{-3}), DO ($4.49\text{ mg O}_2\text{ dm}^{-3}$), and total alkalinity determined ($153.5\text{ mg CaCO}_3\text{ dm}^{-3}$) respectively. This reveals that treatment with CSH has no appreciable effect upon the main water properties. The allowed concentrations of iron, and manganese are 200 and $50\text{ }\mu\text{g/l}$ respectively, according to health related guide level (HRGL) [20].

CSH was used for the treatment of waste water and underground water to remove Mn^{2+} and Fe^{3+} as examples for divalent and trivalent metal ions. The results for this treatment are shown in tables (1, 2 and 3).

Tables (1 and 2) give the removal of Fe^{3+} ions from water by using rice straw ash, CSH prepared from silica gel, and CSH from RSA. From these tables we could observe that the removal of Fe^{3+} ions from water by the prepared CSH was very efficient as almost 99.8 % from the initial amount of the metal ion in the solutions were removed.

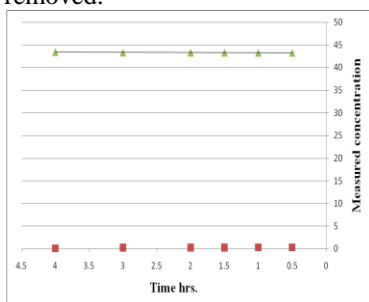


Fig. 1. The relation between time (hrs.) and the removed concentration of Fe^{3+} ions

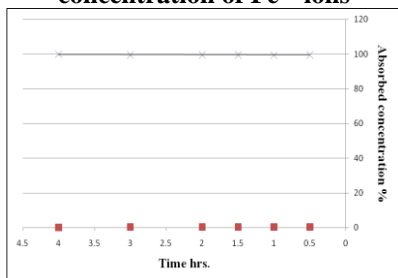


Fig. 2. The relation between time (hrs.) and the percent of the removed concentration of Fe^{3+} ions

Table 3. includes the data for the removal of Mn^{2+} ions from water using rice straw ash, CSH prepared from silica gel, and CSH from RSA. The results show that the removal of Mn^{2+} ions from water by the prepared CSH is very efficient as almost 99.85 % of the initial amount of the metal ion in the solutions were removed.

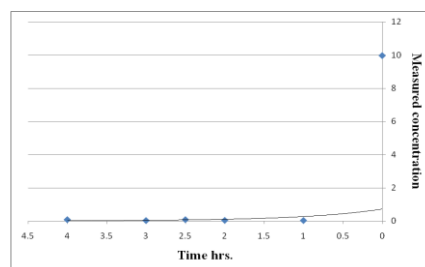


Fig. 3. The relation between time (hrs.) and the removed concentration of Mn^{2+} ions

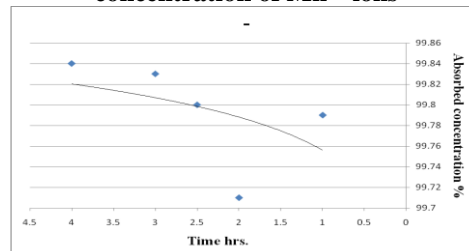


Fig. 4. The relation between time (hrs.) and the percent of the removed concentration of Mn^{2+} ions

Results Illustrated by the last tables and figures:

- Using calcium silicate to overcome the acidity of the waste water since adding calcium silicate acidic pH jumped from 1.9 to 11.8.
- Calcium silicate removed both Fe^{3+} and Mn^{2+} ions and that is obvious when the treatment time 0.5 hr and in spite of we continued to four hours of treatment to determine whether the adsorption process is a reversible.
- A comparison between the raw material (ash remaining after burning) and materials prepared (calcium silicate) to determine the effectiveness of each of them in water treatment has been shown that the effectiveness of calcium silicate in the removal of both Fe^{3+} and Mn^{2+} ions are very high (99.8) and that could be explained as follows:

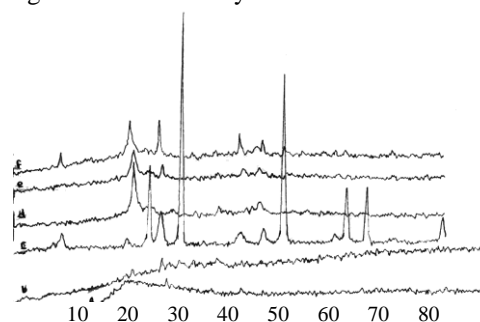
Two mechanisms of the removal of the ions from water using calcium silicate.

- the very clear and known one is the adsorption on the surface of the used materials.
- the second one the effect of the used calcium silicate on the PH of the medium which assist the ions to be hydrolyzed and found surrounded with OH^- ions.

X-Ray Diffraction analysis (XRD)

The XRD measurements for three samples of (CSH) prepared from heap fired RSA and obtained under different conditions were carried out in order to investigate the changes occurring due to their formation reactions.

Figure (I) shows the result of these measurements. There are two forms of CSH, these two forms have chemical composition as CSH (I) ($0.8-1.5\text{ CaO} \cdot \text{SiO}_2 \cdot 0.5-2.5\text{ H}_2\text{O}$) and CSH (II) ($1.5-2.0\text{ CaO} \cdot \text{SiO}_2 \cdot 1-4\text{ H}_2\text{O}$) [21]. natural plumbierite is closely similar but gives no basal X-ray diffraction.



20 : deg.

Fig. 5. XRD patterns for CSH samples; 1, 2 ash samples, 3 CaO sample, 4, 5 CSH samples and 6 CSH with Fe³⁺

The crystal form Crumpled foils (semi-crystalline) and basal spacing of CSH (I) varies with both water content and Ca / Si ratio hence several varieties exist. Powder data relate to fibber bundles. Some other varieties give powder patterns close to that of CSH (1) . The basal spacing, if it occurs , is always about 10 Å [22]. From fig.(1) and CSH (II) were formed and also the two forms are convertible. This is due to two main factors, the water content, and Ca / Si ratio.

Conclusion

Removal of divalent (Mn²⁺) as well as trivalent (Fe³⁺) ions on the surface of calcium silicate was found to be very efficient; the percent of uptake reached 99.84 % of Fe³⁺ from waste water and most of that present in underground water. The amount from Mn²⁺ ions removed from waste water samples reached about 99.85 %, and most of that present in underground water.

In this research there was a comparative study between four types of materials to be used in water treatment; Pure calcium silicate (CSH free from carbon and other insoluble matters in NaOH solution), Calcium silicate in presence of carbon and other insoluble matters in NaOH solution), Pure calcium silicate (CS prepared from silica jel) and Ash remained after burning of rice straw (active carbon and amorphous silicon oxide). It was clear through the results in the previous tables and graphs indicated that the samples from all four materials were effective in this field, as was expected.

Calcium silicate in presence of carbon and other insoluble matters in NaOH solution) gave the best results and appeared the most efficiency, as a result of this paper the use of residue for the manufacture of paper in the preparation and detail the material used for water treatment, gave this high efficiency.

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Table 1. Removal of Fe³⁺ ions by CSH

Time hr	pH	Meas. conc.	Abs. conc.	%abs.
0	1.9	43.55	-	-
0.5	11.25	0.25	43.3	99.46
1.0	11.24	0.26	43.29	99.4
1.5	11.15	0.21	43.34	99.5
2.0	11.24	0.21	43.34	99.5
3.0	11.23	0.23	43.32	99.47
4.0	10.8	0.07	43.48	99.84
For underground water				
4.0	11.72	Nil	5	100 %

Table 2. Removal of Fe³⁺ ions by ash and CSH from silica gel

Ash				
Time hr	pH	Meas. Conc.	Abs. conc.	%abs.
0	1.9	50.0	-	-
0.5	2.33	16.17	27.38	62.87
4.0	2.15	0.40	43.15	99.08
CSH from silica gel				
4.0	11.25	0.19	43.36	99.56

Table 3. Removal of Mn²⁺ ions by CSH

Time hr	pH	Meas. Conc.	Abs. conc.	% abs.
0	8.52	9.958	-	-
1.0	11.74	0.021	9.937	99.79
2.0	11.62	0.029	9.929	99.71
2.5	11.44	7.21	21.11	74.5
3.0	11.61	0.017	9.941	99.83
4.0	10.8	0.07	43.48	99.84
For underground water				
4.0	11.72	0.017	0.033	99