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RESEARCH ARTICLE

A PRELIMINARY STUDY OF EXTRACTION OF SULPHUR AND CALCIUM FROM EGGSHELL WASTE

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ABSTRACT

Background: Egg shells take a year to decompose but are known to keep pests at bay. They contain many basic amino acids like cystine in reasonable quantities. Cystine being a dimer of cysteine contains a disulphide bond. This could be used as a source of sulphur. **Objective**: Our aim was to extract sulphur and carry out various tests to check the presence of both sulphur and calcium in egg shells. Using this knowledge the efficacy of calcium and sulphur as fungicides could be postulated. **Methods**: Egg shells were treated with 40% sodium hydroxide and lead acetate giving lead sulphide which confirmed the presence of sulphur in eggshell. Eggshells were then treated with 40% sodium hydroxide once again followed by treatment with 16 N nitric acid which led to the formation of sulphur powder. Further by testing we confirmed the presence of sulphur in the final powder. We also performed various reactions to check if calcium carbonate could be converted to calcium chloride and calcium hydroxide. **Results**: Maximum % concentration of sulphur (4.45%) was obtained when the volume of sodium hydroxide to nitric acid used was in the ratio of 3:2 and least % concentration (0.13%) was obtained when the ratio was 2:1. **Conclusion:** The method developed could be worked on to get more % concentration of sulphur and cannot be used alongside the industrial method of obtaining sulphur. However, obtaining calcium from egg shells shows a promising future.

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INTRODUCTION

Egg shells are that part of food based waste that do not decompose easily but have extensive uses in the pharmaceutical industry. Many applications of egg shells have been thought over but our idea of using it as a fungicide sprung up from its chemical composition and its foul odour. Certain bacteria in the absence of oxygen reduce sulphur to hydrogen sulphide. Other bacteria reduce sulphur to hydrogen sulphide from sulphur containing amino acids (Skovgaard, 2012). But decomposition of egg shells which leads to the formation of hydrogen sulphide takes several months to yield results. The aim of our research was to figure out whether egg shells contain sulphur in its native form or as a compound in abundant amounts and if so, can it's presence be brought to fruition by extracting and using it as a fungicide. Lime of sulphur also known as a fungicide could be generated from egg shell as it was found to intrinsically contain both the compounds sulphur and calcium, calcium being present in magnanimous quantities. The calcium chloride obtained on processing egg shells could be used to improve the quality and shelf life of figs (Kardum, 2004), apples (Hafez, 2007), peaches (Arvind, 2012) and plums (Kirmani, 2013), this property of calcium chloride has been documented in literature. It also has the ability to improve shelf life of canned rambutan (Garnjanagoonchorn, 2007), bringing to light the fact that the calcium in egg shells if converted to calcium chloride could also be used as a preservative.

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MATERIALS AND METHODS

A thorough literature survey was done on sulphur fungicides. Their properties were studied in depth, thus understanding the mechanism of the active ingredients in sulphur fungicides. Chemical/Biochemical composition of egg shells was reviewed upon. Experiments to obtain sulphur from egg shells were performed with efficacy. The percentage concentration of sulphur was determined. Aliquots of the reactants taking part in the reaction were varied to find out the variation in concentration of sulphur obtained. Graphs were plotted based on experimental data. Conclusive results were noted down. Possible approach of utilizing the major component calcium carbonate was also reviewed over as an addendum. The raw materials used were finely ground egg shell powder in a mixer grinder model- Desire (230V AC, 550 W, 30 minutes rating), sodium hydroxide solution, solution of lead acetate and a Bunsen burner. All the lab reagents and chemicals used for

experimentation were purchased from Loba Chemie. First 0.1 g of egg shell powder was taken in a test tube to which 1 ml of 40 % sodium hydroxide solution was introduced. The mixture was then heated for a minute and lead acetate solution was added, the presence of sulphur containing amino acids was confirmed by this method, also referred to as the lead acetate test (Satyanarayana, 2017) for qualitatively analyzing the presence of sulphur containing amino acids in the sample of concern. Alkaline hydrolysis of cystine by treatment with 40% sodium hydroxide followed by heating for 1-2 minutes over a Bunsen burner was carried out. 16 N Nitric acid (HNO_3) was added to the reaction mixture. The volumes of sodium hydroxide (NaOH) and HNO_3 were varied from 10-30 ml to obtain the optimal ratio of NaOH to HNO_3 that gives the maximum % concentration of sulphur. Distilled water was then introduced in this mixture to separate the formed sulphur precipitate from sodium nitrate solution, since water preferentially dissolves sodium nitrate and does not dissolve sulphur. Distinct layers of sulphur and water containing sodium nitrate were formed. Subsequently filtration was carried out using a Whatman filter paper (Ash less, pore size 42, circle diameter 110 mm diameter) whereby, the sulphur powder was collected and sodium nitrate filtrate stored to test the presence of sulphur in it. Egg shells were also subjected to treatment with dilute HCl and concentrated sodium hydroxide in which there was an immediate formation, of white precipitate of calcium hydroxide. The analysis of the sulphur containing powder collected, was done at Geochem Laboratories Private Limited, Mumbai, India, wherein the sulphur estimation was done as per Indian Standard Specification for Sodium Sulphate Anhydrous (Technical Grade) .REF.IS:255-1982 and the calcium testing was done as per the Indian Standard Chemical Analysis of Limestone, Dolomite and Allied Materials .REF. IS: 1760(PART 3) - 1992.

Reactions involved in the extraction of sulphur

Reaction 1):

$C_6H_{12}N_2O_4S_2$ + 40% NaOH → Na_2S (desired product)
Cystine Sodium Hydroxide Sodium Sulphide

Reaction 2):

Na_2S + 16N 4HNO_3 → 2 NO_2 + 2 $NaNO_3$ + 2 H_2O + S↓
Sodium Sulphide Nitric Acid Sodium Nitrate Sulphur

Reactions for testing if calcium carbonate in egg shells could be easily converted to calcium chloride and calcium hydroxide

Reaction 1):

$CaCO_3$ + dilute 2 HCl → $CaCl_2$ + H_2O + CO_2
Calcium Carbonate Hydrochloric acid Calcium Chloride

Reaction 2):

$CaCl_2$ + Concentrated 2 NaOH → $Ca(OH)_2$ + 2NaCl
Calcium Chloride Sodium Hydroxide Calcium Hydroxide

RESULTS

From Table 1 and Figure 1 and 2 it could be noted that when 30 ml of sodium hydroxide and 20 ml of dilute nitric acid was added to egg shell powder, the maximum % concentration of sulphur (4.45%) was obtained. On varying the concentration of dilute nitric acid to 10 ml, only 0.13% of sulphur concentration was obtained, thus concluding that a ratio of 3:2 working volume of sodium hydroxide to nitric acid used gave the best results. Further, the proportion of calcium residue obtained was almost constant for all samples ranging between 24.77%-34.05% concentration. The powder obtained selectively gave only the sulphur test and did not give a positive response for the presence of sodium nitrate in it, whereas the filtrate gave only the test for the presence of nitrate ions. The reactions carried out between the egg shell powder and dilute HCl followed by the addition of concentrated caustic soda showed the characteristic white precipitate of calcium hydroxide. This conclusion made can be extrapolated to obtain pure calcium salts which can be used for fungicidal, agricultural and myriads of applications where calcium could be obtained from egg shell waste thus providing an excellent alternative of obtaining calcium which is today obtained from calcium ores.

Table 1. The table below depicts the % concentration of sulphur and volumes of NaOH and HNO_3 used

% concentration of sulphur	Volume of 40% sodium hydroxide added (ml)	Volume of 16N Nitric Acid added (ml)
0.9	10	20
1.62	20	20
4.45	30	20
0.13	20	10
0.41	20	30

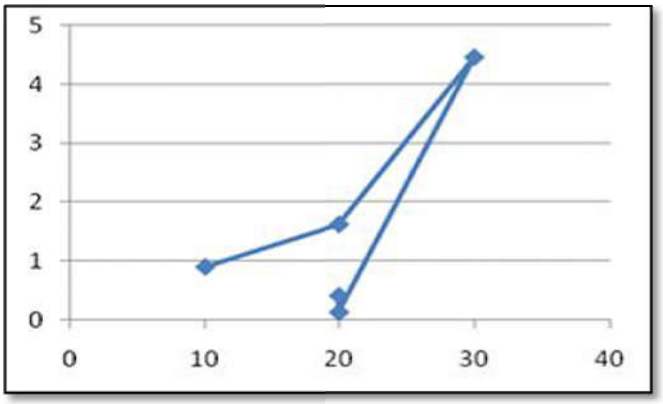

Figure 1. % concentration of sulphur V/s Volume of NaOH X-Axis represents the volume of NaOH and Y-Axis represents the % concentration of sulphur

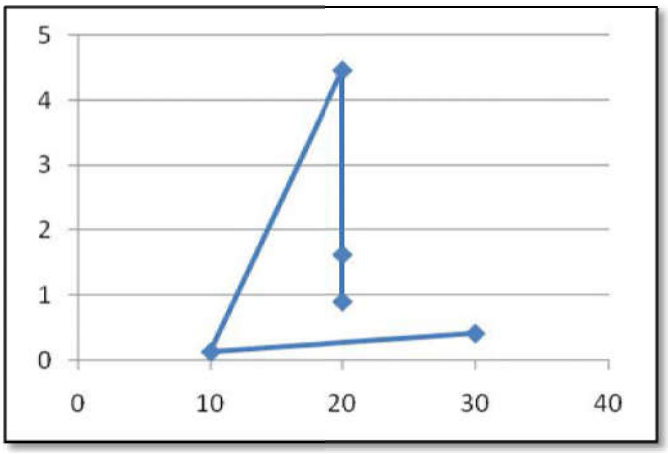

Figure 2. % concentration of sulphur V/s volume of HNO_3 X- Axis represents Volume of HNO_3 and Y-Axis represents % concentration of sulphur

DISCUSSIONS, CONCLUSION AND LIMITATIONS

From the above results it could be concluded that to obtain maximum concentration of sulphur, more amount of sodium hydroxide as compared to nitric acid must be used, the ratio of volume of sodium hydroxide to nitric acid being (3:2). Though the cost of obtaining sulphur isn't very high due to less concentration of sulphur being obtained, this process cannot be used alongside the industrial method of obtaining sulphur. Also the challenge of separating calcium which is obtained in much larger amounts poses a huge problem and the separation of these two compounds will increase the number of steps, thus increasing the cost of the process. Fungicides can also be made by using lime of sulphur where the presence of calcium carbonate in egg shells can be put to use (Lime Sulfur, 2014). Future scope on using calcium present in egg shells as a pesticide can be researched on. 0.4% calcium chloride has been used to increase shelf life of apples (Hafez, 2007). So conversion of calcium carbonate by treatment with hydrochloric acid could also yield results. Calcium Carbonate present in egg shells is almost 94% and can be converted to calcium chloride by treatment with dilute hydrochloric acid. The calcium chloride obtained from the first step can then be converted to calcium hydroxide by treatment with concentrated sodium hydroxide. Calcium Hydroxide is also used in Bordeaux powder which is also a fungicide alongside copper sulphate. A method suggested for the extraction of calcium chloride from egg shells by Wunwiboon Garnjanagoonchorn and Alongkot Changpuak using 4% (w/v) HCl solution for an extraction period of 3 hours yielded 87.38% of calcium chloride (Garnjanagoonchorn, 2007). Hence from the results of Wunwiboon et al it could be concluded that egg shells are a rich source of calcium chloride .Egg shells are non-toxic yet wholesome in terms of their chemical composition. The thermal stability of calcium carbonate in egg shells is higher having a decomposition temperature of about 771.5ºC whereas industrially its temperature is about 749.9º C. Hence though egg shell decomposition starts within 2 weeks, the entire procedure takes about 1-2 years minimum (Murakami, 2007). Further by chemical treatment the problem of waste can be solved. Hence, the farmers having a poultry business can use this simple technique for different fruits. In conclusion, this method if researched more could perhaps be a boon for farmers.

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Key Points

- Gave a preliminary method for the extraction of sulphur from eggshell.
- Studied the possibility of extraction of calcium in the form of its salts from eggshells.
- By referring to various literary materials a possibility of using these compounds as potential fungicides has been suggested.

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