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Reverse Osmosis Reject Brine as a Source of Struvite and Calcium Oleate

Annam Renita A.*, Kavitha V.[#], Lathasree S.[#] and Abdul rahman[$]

**Department of Chemical Engineering, Sathyabama University, Jeppiaar Nagar, OMR, Chennai*
[#]Department of Chemistry, Sathyabama University, Jeppiaar Nagar, OMR, Chennai-119
[$]Sri Sairam Engineering College, West tambaram, Chennai-44

ABSTRACT

Reverse Osmosis (RO) plants discharge concentrated brine to the environment which is detrimental to the receiving water bodies flora and fauna. This research paper aims at providing a cost effective solution by extracting calcium salts as calcium oleate and magnesium salts as struvite from reverse osmosis reject brine which cause water pollution. Calcium oleate was prepared by adding oleic acid to reject brine in a batch reactor with mechanical agitation. Struvite was prepared by reaction with ammonium hydroxide and phosphoric acid. Calcium oleate exhibited amorphous nature and struvite exhibited orthorhombic structure with average size of 75-80nm as characterized by x-ray diffractometer and Fourier Transformation Infra Red analyzer Calcium oleate finds application in cosmetic and food industries. Since struvite finds application as a slow release fertilizer it's potential as a fertilizer was tested for in-house cultivation of redbean plants. It was observed that there is an increase in plant height and leaf area for plants grown with struvite than with plants grown without addition of struvitefor a test period of 30 days. Hence this paper proposes an environmental friendly approach for reducing the waste load of reverse osmosis plants and the recovery of mineral salts.

Keywords: Reject brine; calcium hardness; magnesium hardness; struvite; calcium oleate

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INTRODUCTION

Popular among several desalination methods, reverse osmosis (RO) has received great attention in water and wastewater treatment because of its simplicity, high efficiency, low operating cost, less energy intensive and requires no or less pre-treatment procedures[1]. Despite its advantages, the method has major disadvantages as the rejects pose a major threat to environment as they increase the salinity, transition metal and heavy metal concentration to the receiving water bodies [2]. The urgent need to obtain potable water in many parts of the world made its associated environmental issues to be overlooked or an issue of secondary concern [3,4].Many treatment techniques like electro- fenton have been implemented [5]. Hence, treating the reject becomes a pre requisite in achieving zero discharge limits in RO treatments.

The disadvantages of reverse osmosis is increasing salinity in ground water as it affects the coastal flora and fauna ,extensive land use and low productivity[6].There is an increasing attention both in terms of environmental approvals and public perception in developed countries due to water pollution[7]. Using techniques like evaporation, precipitation, ion-exchange, solvent extraction, adsorption, membrane separation, researchers have extracted valuable end products which have market value so that the overall desalination cost can be reduced [8,9].Several researchers have reported the extraction of salts like NaCl, KCl, Mg and Bromide from sea water by evaporation

[10-12]. Dirach et al. [13] have isolated eight elements like Na, Mg, Rb, K,P, Indium, Cs and Ge from brines of nuclear desalination plants. Extraction of Rb and P from RO plant of 100,000 m^3/day of potable water capacity was studied by Jepessan et al. [14]. Most of the studies reported aimed on isolating or extracting the salts from rejects or brines and its potential application to industries was examined by few researchers like Reig et al. [15] and Eisaman et al.[16]. Struvite can be effectively used as a slow- release fertilizer at high application rate without the risk of damage to plants. In this work, the potential application of struvite as a fertilizer was examined on the growth of red beans. Calcium oleate finds application in food industries as food grease and in cosmetic industries as an ingredient for skin creams.

MATERIALS AND METHODS

2.1 Raw Materials

The reverse osmosis reject brine was collected from an inland desalination plant in Chennai, Tamilnadu, India. Triethylamine, ammonium hydroxide, phosphoric acid, potassium hydroxide, sodium hydroxide, oleic acid which was used for the experiments were of analytical grade.

2.2 Experimental method

All experiments were performed using a batch reactor with mechanical agitation. Reject brine had calcium hardness of 200 ppm and magnesium hardness of 30 ppm as tested by Tamilnadu water supply and drainage board. The reject brine was treated with oleic acid to extract the calcium hardness as calcium oleate wet scum at a pH of 8.5. 1N sodium hydroxide was added to maintain the pH of the solution. 25ml of oleic acid is added to 100 ml of reject brine sample at agitation speed of 1000 rpm. The formation of scum (calcium oleate) was observed according to equation 1.28 gm of wet scum formed was separated using centrifuge. Calcium oleate is unstable at room temperature. Calcium oleate was filtered and purified by washing in absolute alcohol .Stabilization by lyophilization and vacuum drying was carried out since calcium oleate can decompose to oleic acid at equilibrium conditions since it is a reversible process.20 gm of dry calcium oleate was stored in containers stoppered with parafilm in order to avoid reaction with atmospheric carbon dioxide. As Magnesium hydroxide (MgOH) is sparingly soluble in water, Mg present in the RO concentrate water can be easily precipitated. The Magnesium from reject brine is precipitated as magnesium hydroxide using potassium hydroxide solution which is added drop by drop at a pH of 12,which is maintained by adding tri-ethylamine. 50 ml of sample water was reacted with 20 ml of potassium hydroxide. Tri-ethylamine was added to ensure that pH was maintained at 12.The magnesium hydroxide precipitate is then agitated with ammonium hydroxide and ortho-phosphoric acid for the production of struvite. MgOH precipitates out as a white precipitate by a centrifuge and thus separated. This is further was reacted with ammonia and phosphoric acid at a pH of 12 and struvite was obtained. Extracted calcium oleate was analysed by powder x-ray diffractometer . Struvite was analysed by Fourier Transformation Infra Red analyzer and Powder x-ray diffractometer .Struvite was used for in house cultivation of red beans and the growth was monitored to validate its effectiveness as a fertilizer.

RESULTS AND DISCUSSION

The stabilized calcium oleate was subjected to XRD analysis to investigate the crystalline nature of the compound using Powder x-ray diffractometer, scanned from 3 to 80 degree in continuous mode using Cu-Kβ radiation (0.154°A). Extracted struvite was subjected to XRD and Fourier Transformation Infra Red analyzer using potassium bromide (KBr) pellets. The absorbance spectra was scanned from 400 to 4000cm^{-1}. X-ray diffraction was used for characterization and assessing the size of the prepared compounds, calcium oleate and magnesium struvite and are shown in Figure 1 and 2. The XRD patterns for magnesium struvite is a series of sharp peaks indicating crystalline nature. The crystal structure of magnesium struvite is orthorhombic with prominent peaks indexed as 111, 210,212. The lattice dimensions for magnesium struvite is a=6.56, b=6.84 and c=11.49. Magnesium struvite structure matched well with standard Magnesium struvite JCPDS no 71-2089. The average crystalline size of magnesium struvite obtained by Debye-Scheerer formula was found to be 75-80nm. The XRD pattern for Calcium oleate is broad indicating its amorphous nature with peaks at 2θ values of 19.3, 21.3 and 25.9.

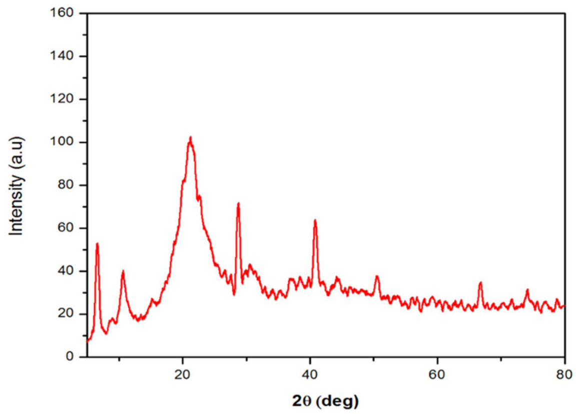


Fig. 1: X-ray diffraction image of calcium oleate

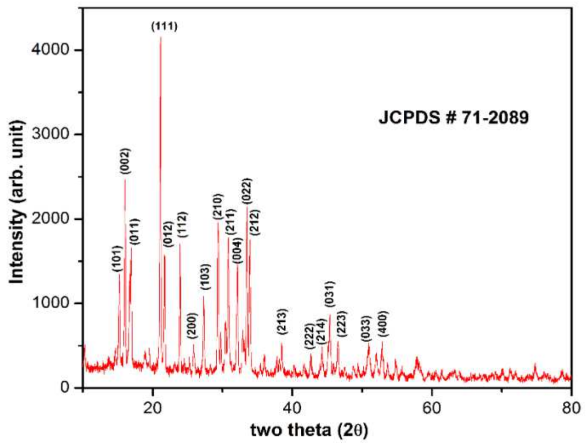
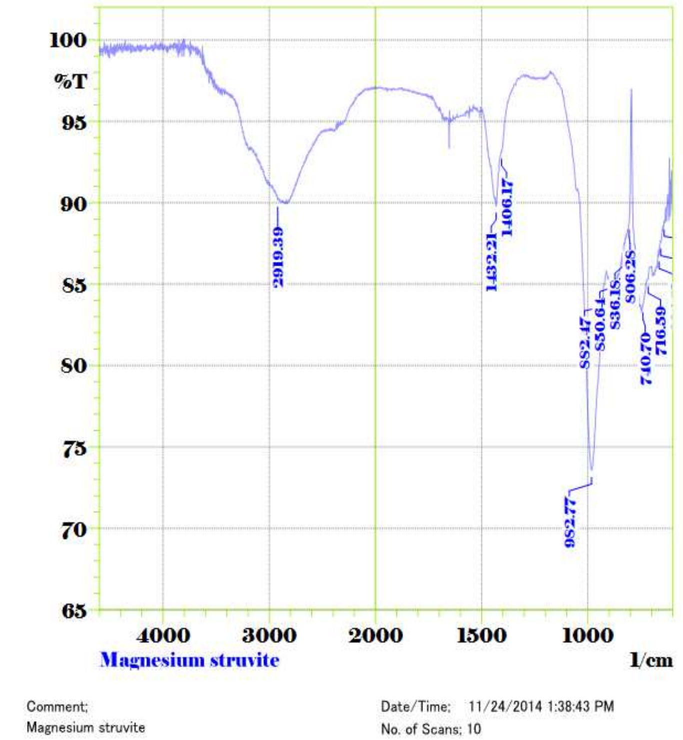


Fig. 2: X-ray diffraction image of struvite

FTIR spectrum of magnesium struvite is presented in figure 3. It has characteristic bands due to vibrations of NH_4^+, tetrahedral $PO_4^{3-}$and Mg-oxygen bonds. The peak at 2919 cm^{-1} corresponds to symmetric stretching vibration of N-H bond in NH_4^+ unit while peak at 1432 cm^{-1} indicates the asymmetric bending vibration of N-H bond in NH_4^+ unit. The absorption peaks at 982 cm^{-1} is due to symmetric stretching frequency of PO_4^{3-} while the peak at 474 and 519 cm^{-1} corresponds to symmetric and asymmetric bending frequencies of PO_4^{3-} unit. The metal-oxygen vibration frequency is seen at 640 cm^{-1}.

3.1 Plant growth analysis

Leaf area is an important physiological component of crop yield[17].Leaf area (LA) plays an important role in plant growth analysis. McKee [18], Pearce et al.[19] and Dwyer and Stewart[20] cited Montgomery's[21] general equation to estimate individual leaf area of maize : Leaf area(LA) = L × W × A where LA, L, W, and A are leaf area, leaf length, leaf maximum width and a constant (A = 0.75), respectively for non-destructive determination. The plants were raised in pots of diameter 10 cm with a growing medium of 1:1 mixture by volume of soil and sand. Two seeds were planted in each pot manually and thinned out to one plant at the 2-leaf stage for uniform planting density. The plants were watered twice a day. The prepared struvite was added to five plants and the growth was measured as GS and the other five plants were grown without adding struvite and their growth was designated as G. Biometric measurements like mean plant height and mean leaf area were determined for a period of 30 days. Mean plant height was noted for a period of 30 days with intervals of 5 days. Leaf area was determined by Montgomery's non destructive formula for a period of 30 days with intervals of 10 days. Leaves from five plants were used for the research each with G and SG. Length(base to tip) and width (broadest point at the base) were measured in individual lobes for each plant using LI 300 portable metre.



	Peak	Intensity	Corr. Int	Base (H)	Base (L)	Area	Corr. Are
1	340.45	55.32	85.04	342.38	339.49	0.53	0.7
2	381.92	50.79	46.89	384.82	375.17	1.12	1.17
3	398.32	64.33	37.29	400.25	396.39	0.42	0.45
4	413.75	71.02	18.78	420.5	412.78	0.68	0.56
5	425.32	62.92	64.67	427.25	421.46	0.47	1.08
6	449.43	42.97	81.54	453.29	445.58	0.46	1.07
7	458.11	54.52	53.22	461.97	456.18	0.56	0.79
8	466.79	53.16	64.99	468.72	462.94	0.42	0.9
9	474.51	46.01	70.68	477.4	469.69	1.18	1.58
10	491.87	55.04	45.43	493.8	488.98	0.6	0.63
11	510.19	67.12	41.79	512.12	507.3	0.45	0.52
12	519.84	43.81	72.3	521.77	517.91	0.51	0.8
13	545.88	69.76	7.79	548.77	542.98	0.73	0.1
14	558.42	71.72	6.02	561.31	556.49	0.62	0.09
15	567.1	70.75	6.69	569.99	565.17	0.63	0.1
16	573.85	77.17	2.68	575.78	570.95	0.51	0.05
17	640.39	88.77	0.24	641.36	633.64	0.39	0.01
18	656.79	87.58	0.15	657.75	649.07	0.48	0.01
19	664.51	86.79	0.43	666.43	658.72	0.46	0.01
20	716.59	85.28	0.24	718.51	711.76	0.46	0
21	740.7	83.66	0.23	742.63	721.41	1.55	0.01
22	806.28	88.74	0.72	807.24	795.67	0.43	0.07
23	836.18	86.91	0.13	837.14	830.39	0.4	0.01
24	850.64	85.79	0.16	851.61	837.14	0.92	0.01
25	882.47	84.6	0.15	884.4	877.65	0.49	0
26	982.77	73.55	14.87	1047.39	913.33	12.3	5.03
27	1406.17	93.1	0.14	1407.13	1377.23	0.7	0.01
28	1432.21	89.79	0.73	1435.1	1408.1	1.03	0.03
29	2919.39	90.15	0.19	2923.25	2913.6	0.43	0

Fig. 3 Fourier transform infrared spectroscopy of prepared struvite

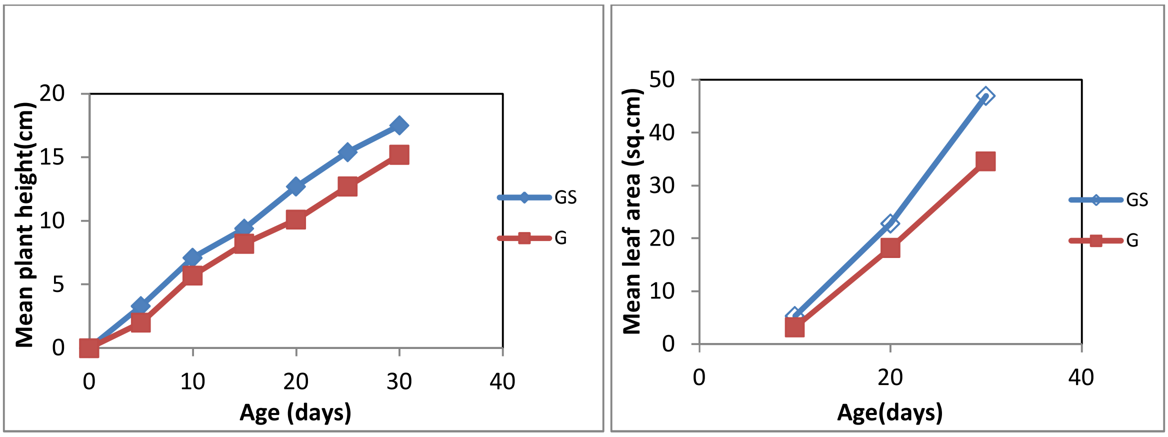


Figure 4 (a) Mean plant height vs Age (b) Mean Leaf area vs Age

From the graphs shown in figure 4 (a) and (b) , it can be inferred that there is an increase in plant height and leaf area for plants grown with struvite (GS) than with plant grown without addition of struvite(G).Only preliminary work was done and future experiments will be carried out for other growth measurements.From the studies, it can be inferred that struvite extracted from reverse osmosis reject has potential application as a fertilizer which is environment friendly.

CONCLUSION

Calcium oleate and struvite was extraced from reverse osmosis reject brine.RO rejects are usually dumped in water bodies which increases the chemical load on water bodies and thus leads to pollution. This research aims in producing valuable end products and thus decrease pollution of water bodies. Calcium oleate finds application in cosmetic and food industries.Struvite was validated as a fertilizer by the experiments and finds application in agricultural sectors. There are more value added salts in reverse osmosis brine which will be further estimated in future studies.

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