

INFLUENCE OF FLOW RATES AND COPPER (II) IONS ON THE KINETICS OF GYPSUM SCALE FORMATION IN PIPES

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(Received: February 2013 / Revised: June 2013 / Accepted: July 2013)

ABSTRACT

Experiments were performed in a piping system to examine the effects of flow rates and Cu^{2+} , a common metal ion in wastewater, on the kinetics of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) scale formation. The scaling was monitored by measuring the decrease in Ca^{2+} concentrations, $[\text{Ca}^{2+}]$, of the scaling solution. AAS analysis shows that $[\text{Ca}^{2+}]$ reduces progressively after a certain induction time, during which time the concentration remains steady. Thus, the gypsum precipitation which leads to scaling in pipes does not occur spontaneously. Higher impurity concentrations (0 to 10 ppm Cu^{2+}) result in longer induction time (26 to 42 min), which indicate that Cu^{2+} could inhibit the scale formation. Impurity concentrations and the scale mass generated are negatively correlated. Reduction in scale mass was as high as 61% depending on impurity concentrations and flow rates. Data of $[\text{Ca}^{2+}]$ versus time were used to calculate the reaction rate of the gypsum precipitation which led to scaling. It was found that the reaction follows a first order kinetics with respect to $[\text{Ca}^{2+}]$, with rate constants ranging between 5.28 and 7.37 per hour, which agree with most published values for mineral scale formation.

Keywords: Crystallization; Cu^{2+} ; Gypsum; Kinetics; Wastewater

1. INTRODUCTION

One of the main components of scale is crystals of calcium sulfate minerals, which exist in three different phases: calcium sulfate dihydrate ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), calcium sulfate hemihydrate ($\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$), and anhydride calcium sulfate (CaSO_4). At moderate temperatures, up to 50°C , the dihydrate phase ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), commonly known as gypsum, is prevalent; while at elevated temperatures the other two forms are commonly found (Li & Demopoulos, 2005). Gypsum crystallizes as white plate-like crystals according to the following reaction (Ang et al., 2011):



Gypsum crystals tend to agglomerate and form scale on equipment surfaces. The problem of gypsum scaling is well recognized in chemical and related industries, especially in units involving heat and mass transfer. Gypsum scaling entails operational consequences such as resistance to heat and mass transfer, contamination of products, corrosion, and metal fatigue (Ang et al., 2011).

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Permalink/DOI: <http://dx.doi.org/10.14716/ijtech.v5i1.117>

Consequently, extensive research has been conducted on gypsum scaling, even as early as in the 1950s (McCartney & Alexander, 1958). Basically, research on gypsum scaling falls into two areas: the kinetics of scale formation, and effects of external factors such as hydrodynamics. Impurities and ions in solution play an important role in the kinetics of gypsum crystallization (McCartney & Alexander, 1958; El-Shall et al., 2002; Dogan et al., 2004; Shakkthivel & Vasudevan, 2007; Hoang et al., 2009), whereas external factors such as flow velocity affect the scale formation and growth (Hoang et al., 2009; Najibi et al., 1997). Extensive gypsum research has been conducted to investigate the effects of organic impurities, mostly of organophosphorus compounds and carboxylic groups (Dogan et al., 2004; El-Shall et al., 2002; Hoang et al., 2009 and references therein), however similar research on the effects of metal ions is limited to a few studies (Yehia et al., 2011; Hamdona et al., 1993).

Copper (Cu^{2+}) is one of the common impurities in water and wastewater (Singh et al., 2012). It enters the water through wastage that originates from a variety of industries such as automobiles, electric and electronic manufacturing, electroplating, mining, and petroleum. At trace amounts, copper is vital to life. However, it turns toxic and is detrimental to human health at concentrations of about 10 to 12 ppm (Figueira et al., 2000). It has been confirmed that metal impurities such as zinc ions retarded mineral scaling effectively (Lisitsin et al., 2005), but the effect of copper ions on gypsum scale formation in a flowing system has not been documented in the literature. The work reported herein investigates the effect of Cu^{2+} on gypsum scaling in pipes where fluid flows in a laminar manner with the intention to gain a better understanding of the effects of flow rates and copper ions on gypsum scale formation and the related kinetics.

2. METHODOLOGY

Analytical grade reagents (Merck™ or equivalent) were used for the experiments without further purification. The gypsum solution was prepared by dissolving separately CaCl_2 and Na_2SO_4 crystals in distilled water, then mixing the two solutions in equimolar amounts. Cu^{2+} as impurities were provided by dissolving trace amounts of CuCl_2 crystals in a certain volume of solution taken from the CaCl_2 stock solution. The resulting solution was then put back into the CaCl_2 stock solution. Given that the amount of the crystals dissolved was less than one gram for each dilution, the volume of the CaCl_2 solution was considered unchanged. The experiment was done with a rig built in-house (Figure 1), of which the main components are: two vessels (1 & 2) to store the gypsum solutions, two pumps (3 & 4), and a test pipe section (5) wherein the scale develops. The test pipe section consists of a pipe, inside which four pairs of semi-annular coupons made of copper were inserted. The coupons were thoroughly cleaned, dried and weighed before being inserted into the test section.

Eight liters each of 0.1 M CaCl_2 and Na_2SO_4 solutions at predetermined concentrations were separately placed in the two bottom vessels (Figure 1, no 1 & 2) until they reached the equilibrated room temperature. Then the two pumps (Figure 1, no 3 & 4) were simultaneously activated to transport these solutions into the test pipe section to form scale. The liquor exiting the test pipe section was collected at intervals for up to four hours, and stored for atomic absorption spectrophotometry (AAS) analysis. Flow rates and Cu^{2+} concentrations were varied to investigate their effects. At the end of the experiment, the test pipe was disconnected and left hanging in place until no more dripping of solution was seen. Then, the coupons were removed from the test section and placed in an oven overnight at 60°C. The next day the coupons were removed from the oven, left to cool and weighed. The scale attached to the coupons was carefully removed, placed in vials for SEM, EDS and XRD analysis. The scale mass was taken as the difference in the weight of the coupons before and after the experiment.

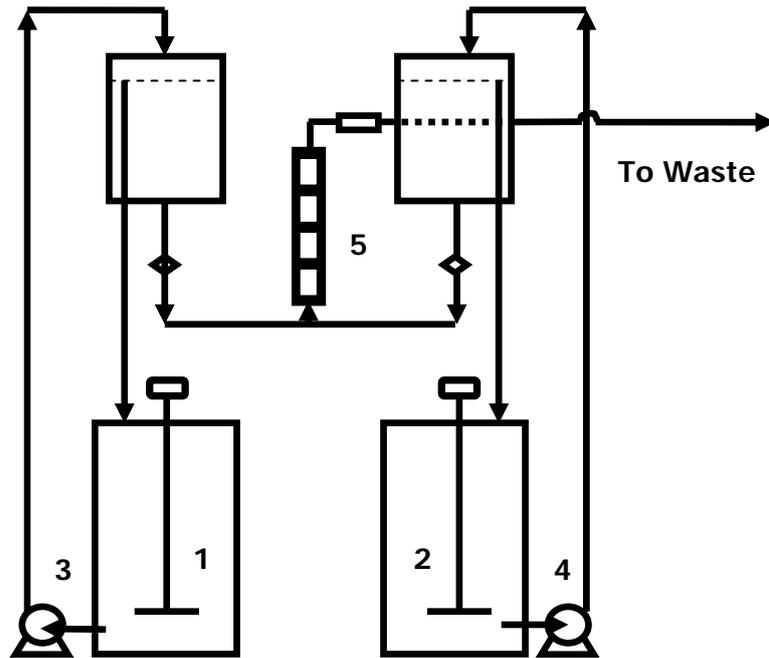


Figure 1 Schematic representation of the rig used for the gypsum scale experiment

3. RESULTS AND DISCUSSION

Gypsum crystallization which leads to scaling in pipes would result in the decrease of $[Ca^{2+}]$ in the solution (see Equation 1). AAS analysis shows that $[Ca^{2+}]$ decreases progressively after a certain induction time, during which time the $[Ca^{2+}]$ remains steady (Figure 2). Thus, the gypsum crystals which lead to scaling in pipes do not form spontaneously. Higher impurity concentration and lower rate (10 ppm Cu and 30 mL/min) (see Figure 2) result in longer induction time (~ 42 min) which indicates that Cu^{2+} may inhibit the scale formation.

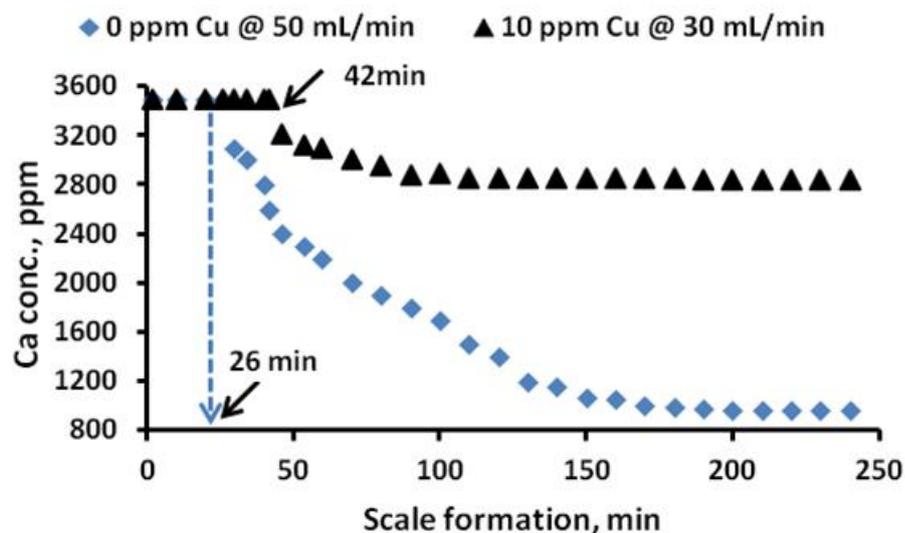


Figure 2 Sample graph of the decrease in $[Ca^{2+}]$ showing different induction times

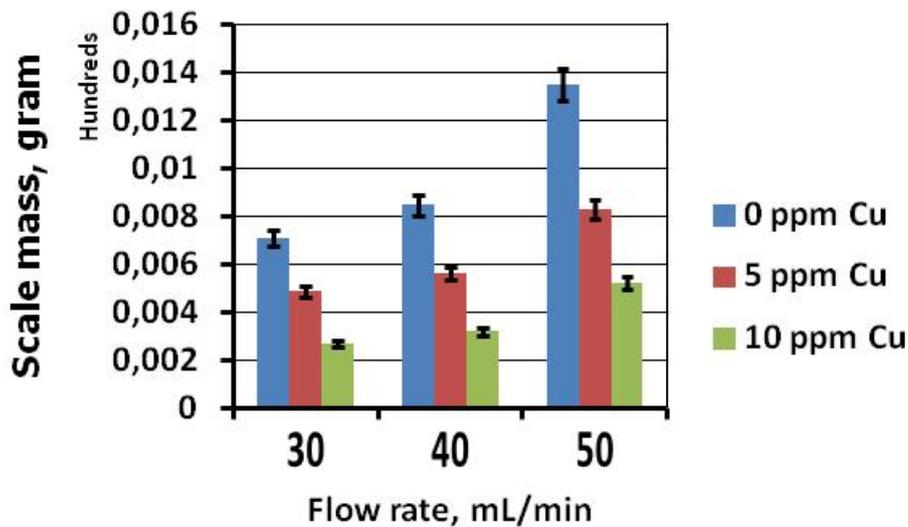


Figure 3 Mass of the gypsum scale at different Cu^{2+} concentrations and flow rates

For all experiments, the higher the impurity concentrations (from 0 to 10 ppm Cu^{2+}) the less the scale mass generated (Figure 3). On the other hand, within the three flow rates tested, the higher the flow rates the more the scale mass formed. This is consistent with the previous findings (Quddus & Allam, 2000; Najibi et al., 1997). It can be inferred from Figure 3, that the maximum reduction in scale mass can be as high as 61% (comparison between 10 ppm Cu^{2+} at 30 mL/min and 0 ppm Cu^{2+} at 50 mL/min). Data of $[\text{Ca}^{2+}]$ versus scale formation time (Figure 2) were used to calculate the reaction rate constants. The kinetic constants were assessed by fitting a modified first order kinetic model, which has a linear form as follows (Nelson et al., 2003):

$$\ln(c - c_{eq}) = -kt + \ln(c - c_0) \quad (2)$$

where in this case:

C : $[\text{Ca}^{2+}]$ at any time, t; C_{eq} : $[\text{Ca}^{2+}]$ at equilibrium;
 C_0 : initial $[\text{Ca}^{2+}]$ at time zero, (t = 0); k : reaction rate constant;
 t : scale formation time, minutes.

The crystallization reasonably follows a first order kinetics with respect to $[\text{Ca}^{2+}]$, with rate constants ranging between 5.28 and 7.37 h^{-1} (Table 1), which reasonably agree with the values reported for mineral scale formation (Rahaman et al., 2008; Nelson et al., 2003). Sample graph for this calculation is shown for 50 mL/min and 10 ppm Cu^{2+} (Figure 4).

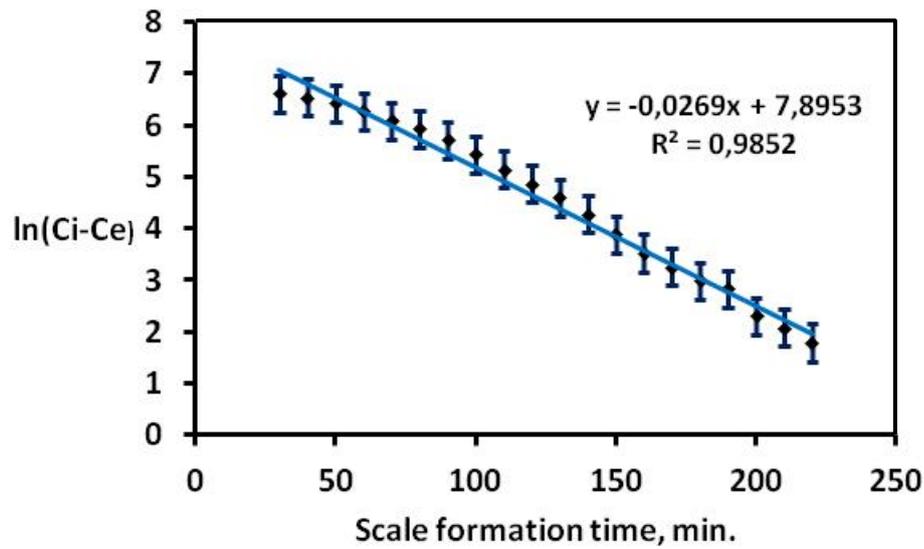


Figure 4 Sample graph for the reaction order determination (50 mL/min & 10 ppm Cu²⁺)

Table 1 First-order kinetic data for the gypsum scale formation

Cu ²⁺ ,(ppm)	Flow rates, (mL/min)	Regression equation	rate constant, (hr ⁻¹)	R ²
0.00	30	y = -0.0268 x + 7.8381	6.43	0.954
0.00	40	y = -0.0300 x + 8.0699	7.20	0.965
0.00	50	y = -0.0307 x + 7.9504	7.37	0.987
5.00	30	y = -0.0245 x + 7.6181	5.88	0.965
5.00	40	y = -0.0243 x + 7.9145	5.83	0.972
5.00	50	y = -0.0273 x + 7.6644	6.55	0.993
10.00	30	y = -0.0220 x + 8.1171	5.28	0.941
10.00	40	y = -0.0241 x + 8.1605	5.78	0.923
10.00	50	y = -0.0259 x + 7.8953	6.46	0.985

Through SEM imaging, it can be seen that the scale formed inside the pipes consists of overlapped plate-like crystals, mixed with fractured crystals of different sizes (Figure 5). The plate-like crystals seem to arrange in a certain direction (see the white arrow), which is most likely the direction of the fluid flow inside the pipes. Thus, it could further support the assumed first order kinetics of the crystallization, i.e. a transport-controlled process. The associated EDS analysis (Figure 5, right) corresponds to that of gypsum (Abdel-Aal et al., 2004; Liu and Nancollas, 1973). The X-ray diffraction (XRD) analysis (Figure 5, bottom) confirms that the scale is crystalline with signals that match up to the powder diffraction data for gypsum (ICDD - PDF#70-0982). With the addition of trace amounts of Cu²⁺, the mass of the scale decreases (Figure 3), but there seems to be no significant changes in the morphology of the crystals that agglomerate to form the scale.

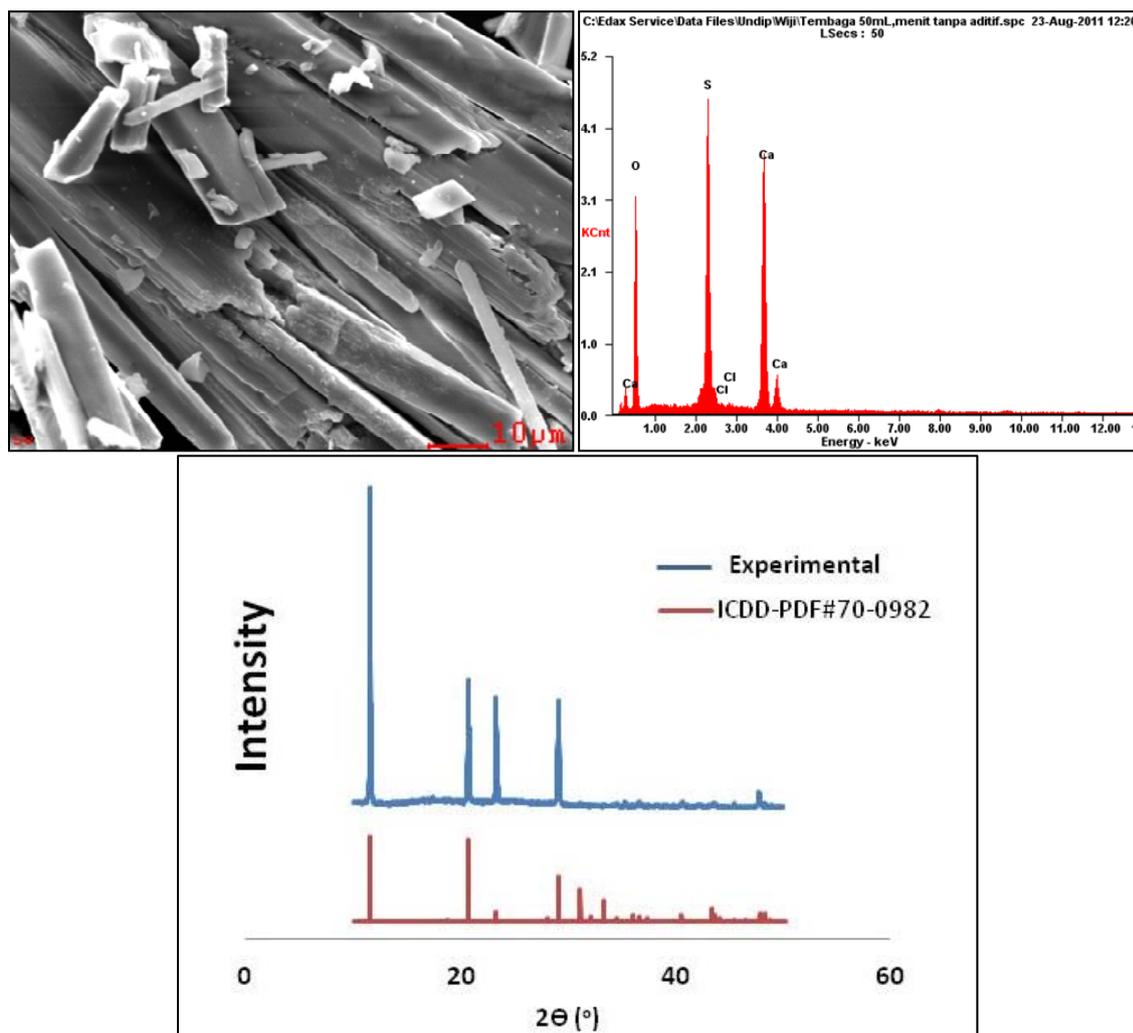


Figure 5 SEM, EDS, and XRD of the gypsum scale inside the coupon (@50 mL min⁻¹)

4. CONCLUSION

A laboratory rig was built and successfully used to investigate gypsum scaling in a flowing system. The crystallization of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) which led to scaling was not instantaneous, but was preceded by induction times (26 to 42 min). Depending on the flow rates and the Cu^{2+} concentrations as impurities, the gypsum scale mass generated can be reduced by up to 61%. The gypsum scaling reaction in pipes reasonably follows a first order kinetics with respect to calcium concentrations, with rate constants ranging between 5.28 and 7.37 per hour.

5. REFERENCES

- Abdel-Aal, E.A., Rashad, M.M., El-Shall, H., 2004. Crystallization of Calcium Sulfate Dihydrate at Different Supersaturation Ratios and Different Free Sulfate Concentrations, *Crystal Research and Technology*, Volume 39(4), pp. 313-321.
- Ang, H.M., Muryanto, S., Hoang, T.A., 2011. Gypsum Scale Formation Control in Pipe Flow Systems: a Systematic Study on the Effects of Process Parameters and Additives, in *Chemical Engineering Methods and Technology: Gypsum: Properties, Production and Applications*, Sampson, D.H. (Ed.), New York: Nova Science, 2011, pp. 1-33.
- Dogan, Ö., Akyol, E., Öner, M., 2004. Polyelectrolytes Inhibition Effect on Crystallization of Gypsum, *Crystal Research and Technology*, Volume 39(12), pp. 1108-1114.

- El-Shall, H., Rashad, M.M., Abdel-Aal, E.A., 2002. Effect of Phosphonate Additive on Crystallization of Gypsum in Phosphoric and Sulfuric Acid Medium, *Crystal Research and Technology*, Volume 37(12), pp. 1264-1273.
- Figueira, M.M., Volesky, B., Ciminelli, V.S.T., Roddick, F.A., 2000. Biosorption of metals in brown seaweed biomass, *Water Research*, Volume 34, pp. 196-204.
- Hamdona, S.K., Nessim, R.B., Hamza, S.M., 1993. Spontaneous Precipitation of Calcium Sulfate Dihydrate in the Presence of Some Metal Ions, *Desalination*, Volume 1(94), pp. 69-80.
- Hoang, T.A., Ang, H.M., Rohl, A.L., 2009. Effect of Organic Additives on Calcium Sulfate Scaling in Pipes, *Australian Journal of Chemistry*, Volume 62, pp. 927-933.
- Li, Z., Demopoulos, G.P., 2005. Solubility of CaSO₄ Phases in Aqueous HCl + CaCl₂ Solutions from 283 K to 353 K, *Journal of Chemical and Engineering Data*, Volume 50, pp. 1971-1982.
- Lisitsin, D., Yang, Q., Hasson, D., Semiat, R., 2005. Inhibition of CaCO₃ Scaling on RO Membranes by Trace Amounts of Zinc Ions, *Desalination*, Volume 183, pp. 289-300.
- Liu, S.T., Nancolas, G.H., 1973. The Crystal Growth of Calcium Sulfate Dihydrate in the Presence of Additives, *Journal of Colloid and Interface Science*, Volume 44(3), pp. 422-429.
- McCartney, E.R., Alexander, A.E., 1958. The Effect of Additives upon the Process of Crystallisation. I. Crystallisation of Calcium Sulfate, *Journal of Colloid and Interface Science*, Volume 13, pp. 383-396.
- Najibi, S.H., Müller-Steinhagen, H., Jamialahmadi, M., 1997. Calcium Sulfate Scale Formation during Sub-cooled Flow Boiling, *Chemical Engineering Science*, Volume 52(8), pp. 1265-1284.
- Nelson, N.O., Mikkelsen, R.L., Hesterberg, D.L., 2003. Struvite Precipitation in Anaerobic Swine Lagoon Liquid: Effect of pH and Mg:P Ratio and Determination of Rate Constant, *Bioresource Technology*, Volume 89, pp. 229-236.
- Quddus, A., Allam, I.M., 2000. BaSO₄ Scale Deposition on Stainless Steel, *Desalination*, Volume 127, pp. 219-224.
- Rahaman, M.S., Mavinic, D.S., Ellis, N., 2008. Effects of Various Process Parameters on Struvite Precipitation Kinetics and Subsequent Determination of Rate Constants, *Water Science and Technology*, Volume 57(5), pp. 647-654.
- Shakkthivel, P., Vasudevan, T., 2007. Newly Developed Itaconic Acid Copolymers for Gypsum and Calcium Carbonate Scale Control, *Journal of Applied Polymer Science*, Volume 103, pp. 3206-3213.
- Singh, L., Pavankumar, A.R., Lakshmanan, R., Rajarao, G.K., 2012. Effective Removal of Cu²⁺ Ions from Aqueous Medium using Alginate as Biosorbent, *Ecological Engineering*, Volume 38, pp. 119-124.
- Yehia, N.S., Ali, M.M., Kandil, K.M., El-Maadawy, M.M., 2011. Effects of Some Parameters Affecting the Crystallization Rate of Calcium Sulfate Dihydrate in Sodium Chloride Solution, *Journal of American Science*, Volume 7(6), pp. 635-644.