



KINETIC STUDY OF NANO-MAGNESIUM OXALATE PRECIPITATED FROM BITTERN

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ABSTRACT

One of the methods to prepare nano-crystals metal oxide (MgO) is by using a precipitation method. Magnesium oxalate as a valuable chemical almost produced in pure grade from seawater bittern by precipitation process. In this paper, kinetics of magnesium oxalate precipitation from sea bittern was studied. The rate constants determined at different temperatures, Molar ratios and pH. The activation parameters were also calculated. Sea bittern from salt production unit of El-Mex saline company is containing about 85.7 g.L⁻¹ Mg²⁺. Detailed characterization involving XRD, TEM and TGA was investigated. The results show that The precipitation of magnesium oxalate from sea bittern is first order with respect to the concentration of magnesium oxalate at pH=4, MR=1:1 and temp.=25 °C Also, The rate constant doesn't strongly affected by increasing temperature so the optimum operating reaction temperature is 25 °C. The spherical Magnesium oxalate with uniform diameter of about 0.5 µm was obtained with purity higher than 98%.

Keywords: magnesium oxalate, precipitation, sea bittern, kinetics, first order.

1. INTRODUCTION

In the previous decade, the production of magnesium has enormously expanded. Canada US and focused on magnesium generation during the 1990's. However, since the late 90's, the industrial revolution in China has seen that country become the main producer of magnesium metal [1]. Magnesium is one of super-strong and light weight metal. Following iron and aluminum applications, magnesium is mainly used in aluminum alloys, die-casting (alloyed with zinc), and removing sulfur in the production of iron and steel. Magnesium was used as one of the main aerospace construction metals in German military aircraft in World War I and also for German aircraft in World War II [2]. Because of the importance of fuel economy nowadays, magnesium alloy uses in aerospace is increasing. Six Framework Programs of the European Community runs three R&D magnesium projects in the Aerospace priority [3]. As magnesium, is readily available and relatively nontoxic, it has a variety of uses. Magnesium is flammable, burning at a temperature of approximately 3,100 °C and the auto ignition temperature of magnesium ribbon is approximately 473 °C. It produces intense, bright, white light when it burns and its high combustion temperature makes the process a useful tool for starting emergency fires. Materials such as termite that require a high ignition temperature can be ignited by magnesium[4]. Magnesium is used as a reducing agent to separate uranium and other metals from their salts, and as a sacrificial (galvanic)

anode to protect boats, underground tanks, pipelines, buried structures, and water heaters. Many aluminum-magnesium alloys are used for beverage cans, sports equipment such as golf clubs, fishing reels, and archery bows and arrows[5]. Many car and aircraft manufacturers have made engine and body parts from magnesium [6]. New technologies for alloy development with lower costs made magnesium competitive with aluminum increased the future of automotive applications [7]. In this work, we required, to prepare highly pure magnesium oxide from bittern through magnesium oxalate precipitation process. The effect of different parameters on Mg oxalate precipitation was studied too. The parameters varied included MR, pH and reaction temperature. The work resulted highly pure Mg oxalate which facilitates production of highly pure Mg-metal. The magnesium metal is separated from magnesium oxide through breaking the Mg-O bond using solar-powered laser process (the development of which is already well advanced) and is reused over and over again as green environmental fuel and produces renewable energy that can be converted to electricity[8].

2. MATERIALS AND METHODS

2.1 Materials

Liquid bittern (LB), as an inexpensive source of magnesium contains more than 80 g/L Mg used as magnesium source.

Table-1. Characteristics of liquid bittern used as source of Magnesium ions.

Element	TDS	Mg	Na	Cl	SO ₂	CO ₃	Bi.CO ₃	K	Br	I	Li	Conductivity
Value mg/L	292	85.7 g/L	21.7	218.6	3.2	0.5	9.81	1.73	12	5	0.3 1	583 mS/cm



All Chemicals used such as, Oxalic acid dehydrate, Sodium hydroxide, Magnesium sulfate (Heptahydrate) $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, Hydrochloric acid, Ammonium chloride, Calcium carbonate and EDTA were analytical grade.

2.2 Methods

2.2.1 Precipitation of magnesium oxalate

100 ml of bittern used in each experiment at different reaction temperature (15 to 80°C). Hot plate was set at constant stirring rate of 210 rpm; it was used to homogenize the solution. Oxalic acid added to the stirred solution and 6.25M NaOH was (slowly) added for controlling pH. Equal sample volumes were taken at interval time to evaluate steady state of reaction. The amount of sodium hydroxide added was evaluated through reaction to calculate the molar ratio of NaOH used with respect to Mg ions in bittern and oxalic acid in reaction media. After reaction completion, stirring was stopped and the precipitate was separate from residual liquid by a vacuum filtration. For further purification the solid was washed with distilled water several times. The final washed precipitate was dried at 100 °C for 2 hr before subjected to analysis and investigates the product (magnesium oxalate). It was also calcined at 650°C for 2 hrs. The residual solutions were subjected to chemical analysis by ICP-MS (AgilentA5500) and titration method for determinating the unreacted magnesium ions.

2.2.2 Different molar ratio study

The molar ratio of the reactants (magnesium to oxalic acid) greatly influences the rate of batch process. To obtain the optimum magnesium to oxalic acid molar ratio, the reaction was carried out at fixed temperature of 25°C, pH=4 and different RMR (1:1, 1:1.2, 1:1.4, 1:1.6 and 1:1.8). For each molar ratio the magnesium conversion was calculated and plotted versus time.

2.2.3 pH effect on product

The effect of pH was studied at constant MR (1:1) and constant reaction temperature at 25°C. Different pH was used (1, 3, 4 and 6). The Percentage of magnesium conversion was studied with time.

2.2.4 Study of temperature variation

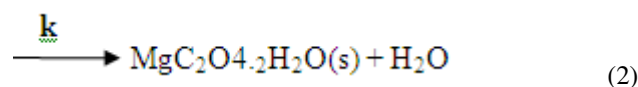
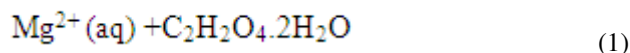
Influence of temperature on the batch process was achieved to obtain the optimum temperature which can provide the highest conversion. The batch process was carried out at MR=1:1, pH=4 and at various temperatures 15, 25, 60, and 80°. The reaction conversion was calculated and plotted versus time.

2.3 Studying the rate of reaction

2.3.1 Techniques for monitoring concentrations as a function of time

Mg Oxalate is produced through reaction (2.1) between Mg^{2+} (A) and oxalic acid dihydrate (B) giving Mg Oxalate (C) and water (W).

The following kinetic experimental results were studied.



The rate of reaction was assumed to be 1st or 2nd order for reactants. Firstly the 2nd order was checked due to assumption dependence of rate on both reactants concentration relying on reaction mechanism for different operating parameters.

This reaction (2) is assumed 2nd order, and therefore the rate of reaction will be given by:

$$r = -\frac{d[A]}{dt} = k[A][B] \quad (4)$$

where

[A]: is the concentration of magnesium ions presents in bittern solution during reaction progress at any time ($\text{g} \cdot \text{L}^{-1}$).

[B]: is the concentration of oxalic acid at any time ($\text{g} \cdot \text{L}^{-1}$).

K : is the rate constant of chemical reaction.

Since the initial concentrations of the two reactants are equal stoichiometrically: Equation (4) can be written as:

$$-\frac{d[A]}{dt} = k[A]^2 \quad (5)$$

Separating the variables and Integrating this for the boundary conditions at $t=0$, $[A] = [A]_0$ and at $t=t$, $[A]=[A]$ Equation. (5) may be rearranged for linearized data plotting as shown by Equation. (6), the slope will be K and the intercept will be $\frac{1}{[A]_0}$

$$\int_{[A]_0}^{[A]} \frac{d[A]}{[A]^2} = -K \int_{t_0}^t dt \quad (6)$$

$$\frac{1}{[A]} = Kt + \frac{1}{[A]_0} \quad (7)$$

In order to derive the rate constant for the pseudo first order reaction: The reaction (2) is assumed to be 1st order reaction, and therefore the rate of reaction will be given by:

$$r = -\frac{d[A]}{dt} = k[A] \quad (8)$$

Separating the variables and Integrating this for the boundary conditions at $t=0$, $[A] = [A]_0$ and at $t=t$, $[A] = [A]$.



$$\int_{[A]_0}^{[A]} \frac{d[A]}{[A]} = -K \int_{t_0}^t dt \quad (9)$$

$$\ln[A] - \ln[A]_0 = -kt \quad (10)$$

Where $[A]_0$ is the initial concentration of magnesium ions present in bittern solution. Converting Ln to log then the equation (10) becomes:

$$\log[A] - \log[A]_0 = -\frac{K}{2.3}t \quad (11)$$

Which is the integrated rate law for a pseudo-first order reaction. Equation.(11) can be rearranged for linearized data plotting as shown by Equation. (12), the slope will be $-\frac{K}{2.3}$ and the intercept will be $\log[A]_0$.

$$\log[A] = -\frac{K}{2.3}t + \log[A]_0 \quad (12)$$

2.4 Studying temperature dependency from Arrhenius equation

For many reactions, and particularly elementary reactions, the rate expression can be written as a product of a temperature-dependent term and a composition dependent term, or

$$r_i = f_1(\text{temperature}) \cdot f_2(\text{composition}) = k \cdot f_2(\text{composition}) \quad (13)$$

For such reactions the temperature-dependent term, the reaction rate constant, have been found in practically all cases to be well represented by Arrhenius equation.

$$k = k_0 e^{-E/RT} \quad (14)$$

Where k is the frequency or pre-exponential factor, E is the activation energy of the reaction and R is the universal gas constant. This expression fits experiment well over wide temperature ranges and is strongly suggested from various standpoints as being a very good approximation to the true temperature dependency. At the same concentration, but at two different temperatures, Arrhenius equation indicates that:

$$\ln K = \ln k_0 + \left(-\frac{E}{RT}\right) \quad (15)$$

The values of K for the precipitation reaction of magnesium oxalate at different temperatures were processed. By plotting $\ln K$ versus $1/T$, the slope will be $-E/R$ and the intercept will be $\ln K_0$ as shown in Figure (*).

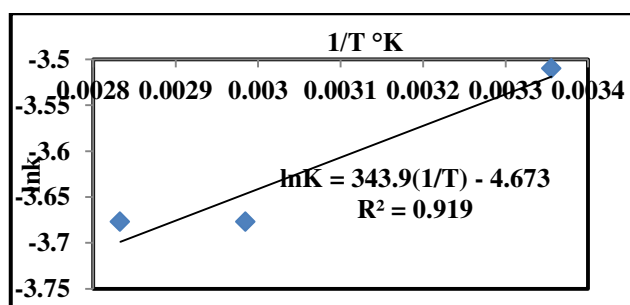


Figure (*) The slope ($-E/R$) and $\ln k_0$ from Arrhenius equation.

2.5 Experimental apparatus

2.5.1 Laboratory set-up

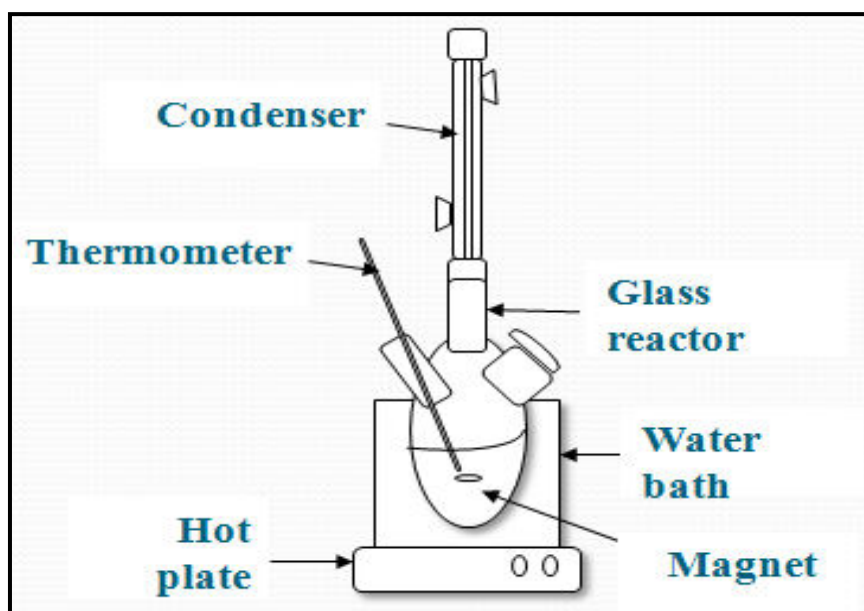
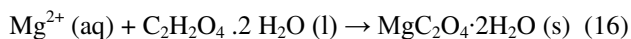


Figure-1. Laboratory experimental set-up for magnesium oxalate preparation.



3. RESULTS AND DISCUSSIONS

3.1 Liquid-liquid reaction



Oxalic acid was used in liquid state [9]. 100 ml bittorn, 1.095M oxalic acid at pH=4 were the reaction parameters. 6.25M NaOH was used for controlling pH.

210 rpm was used to stir the solution during the precipitation process. The precipitate was filtrated and washed by distilled water at temperature of 25°C. This process gives yield about 51.662 gm and conversion of 98.7%. The final precipitate was dried in at 100°C before being subjected to XRD analysis. Figure-2 illustrates the XRD patterns of magnesium oxalate, where all peaks could be clearly the basis for magnesium oxalate.

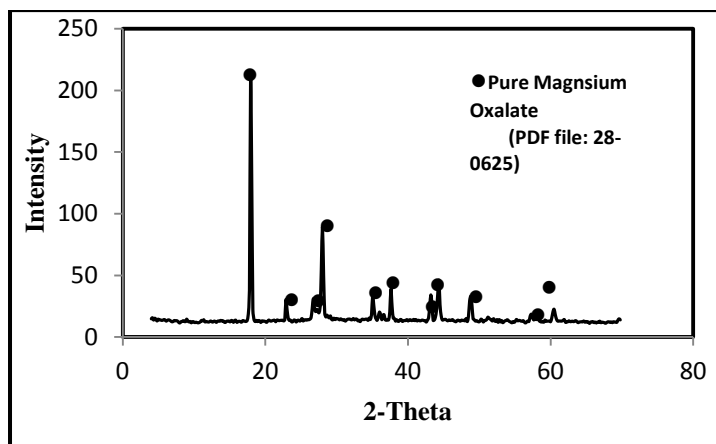


Figure-2. XRD patterns of produced Mg oxalate.

3.2 Determination of the rate law from experimental data

The kinetics of the reaction between Mg^{2+} and oxalic acid dihydrate is shown as a plot of $\frac{1}{[A]}$ vs time produces a curve and its linearization with correlation

coefficient of 0.671; therefore the reaction (2.1) is not obeying the 2nd order as described in Figure-3, which means that the concentration of two reactants are not controlling the rate but only one reactant.

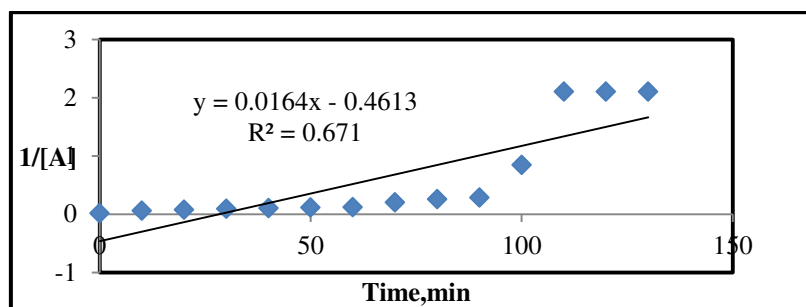


Figure-3. Pseudo - second order kinetics of magnesium oxalate precipitated.

But, a plotting of $\log [A]$ against time produces straight line with correlation coefficient

of 0.916; so the reaction (2.1) is obeying first order as shown in Figure-4.

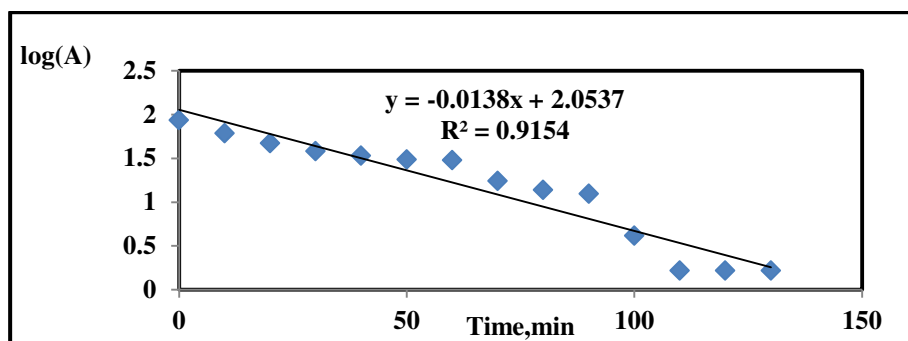


Figure-4. Pseudo - first order kinetics of magnesium oxalate precipitated.

It is clear from Figure-4 that the 1st order integrated rate equation will be $-\log [A] = 0.015 t - 1.654$ with $R^2 = 0.916$. Then $\frac{k}{2.3} = 0.015 \text{ min}^{-1}$ at optimum reaction condition.

Figures 3 and 4 show a linearity for second order plot and first order reaction respectively using liquid phase magnesium concentration in Equation. (6) and Equation. (11) for the precipitation of magnesium oxalate by using oxalic acid. The linear plots of $\log [A]$ against time from the pseudo-first order rate law of correlation coefficients are greater than 0.9 for contact times of 120 min. This assumes that precipitation system is not a second order reaction and it is pseudo-first order reaction with providing the best correlation of the data.

3.3 Kinetics study at different molar ratio

Determining concentration of magnesium ions with time intervals at different molar ratio (MR), we obtained different straight lines and different regression factors shown from Figure-5 to Figure-9 with different values of $[A]^0$ and K (slope). Data shows fitting the pseudo first order reaction. The kinetics study of magnesium oxalate precipitation from bittern with rate constant at different molar ratio (1:1–1:1.8) of Mg with oxalate ions and at fixed (temp. =25°C and pH=4) are shown from Figure-5 to Figure-9. Table-2 shows; that by increasing molar ratio of oxalic acid, the rate constant is stabilized from MR=1:1 to MR=1:1.4. A slight decrease from MR=1:1.6 to MR=1:1.8 was then achieved. Thus, kinetics study proved that MR 1:1 is the optimum molar ratio. The correlation coefficients for the plots of $\log [A]$ against time for the first order data fitted of MR from 1:1 to 1:1.8 is shown in Figure-5.

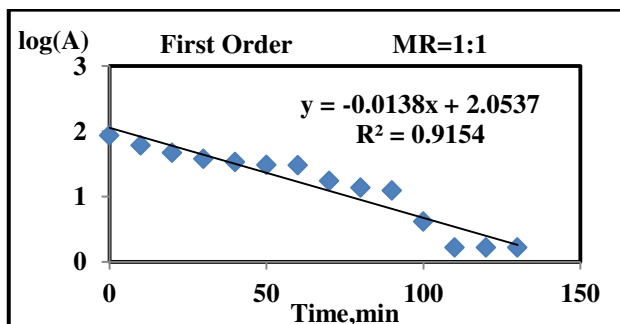


Figure-5. Pseudo first order kinetics at MR=1:1.

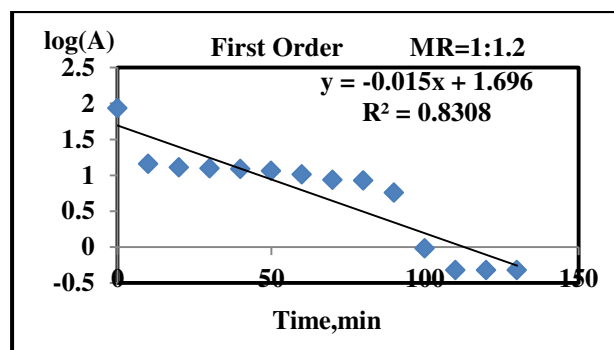


Figure-6. Pseudo first order kinetics at MR=1:1.2.

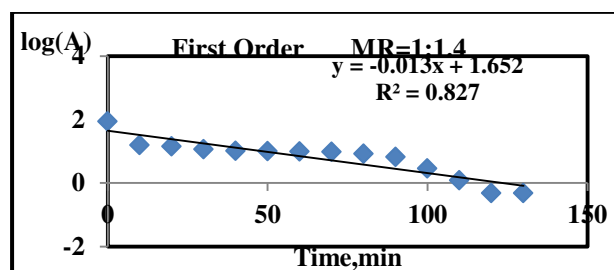


Figure-7. Pseudo first order kinetics at MR=1:1.4.

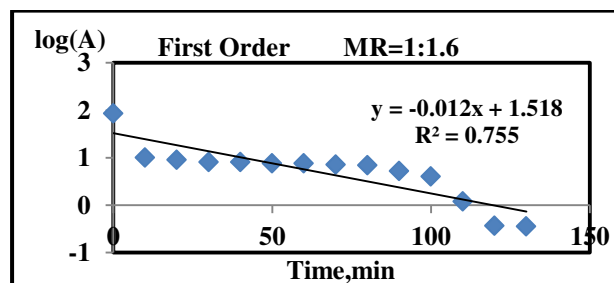


Figure-8. Pseudo first order kinetics at MR=1:1.6.

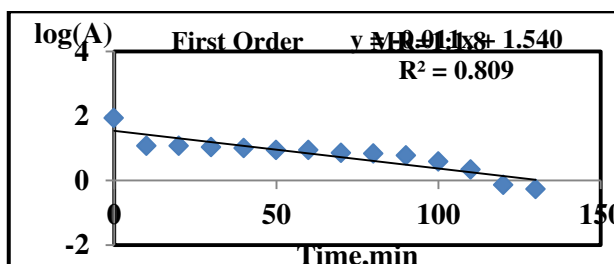


Figure-9. Pseudo first order kinetics at MR=1:1.8.



3.4 Kinetic study at different pH

Kinetics study at different pH (1, 3, 4 and 6) and at fixed (MR=1:1 and temp. =25°C) is shown from Figure-10 to Figure-13. The linear plots of log [A] versus time for the first order data fitted the pH from 1 to 6 as shown in Figure-10 to Figure-13. From a point of view of kinetic study, the correlation coefficient at pH=1 is more fitting to first order reaction as shown in Figure.(10) but magnesium oxalate is not precipitated as proved in analysis. pH is the significant factor as by increasing pH the K values increases as shown in Table-2 but at pH= 4 the highest purity of magnesium oxalate is reached. Figure-12 shows the best correlation of the data for magnesium oxalate precipitation from bittern at pH=4, (Pseudo first order kinetics).

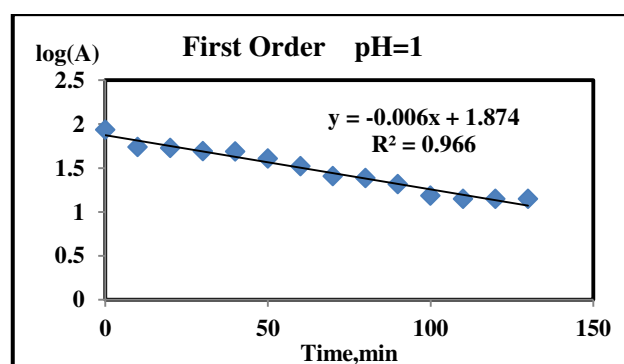


Figure-10. Pseudo first order kinetics at pH=1.

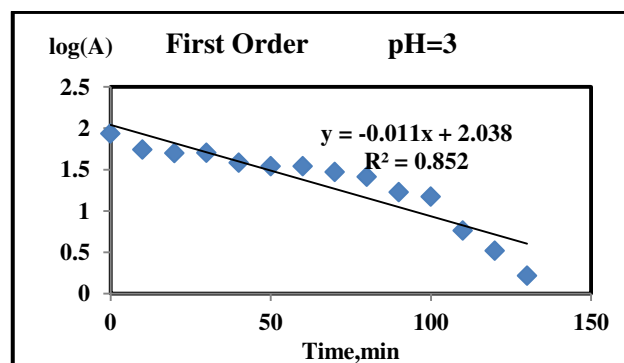


Figure-11. Pseudo first order kinetics at pH=3.

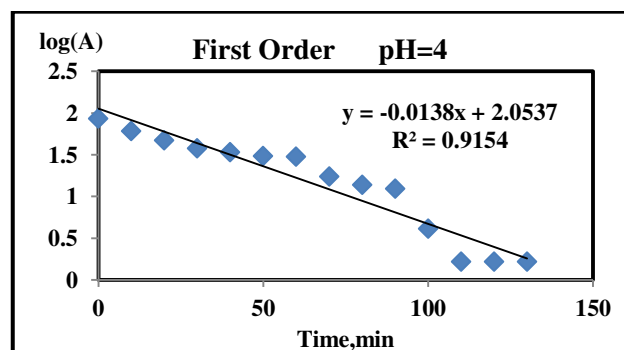


Figure-12. Pseudo first order kinetics at pH=4.

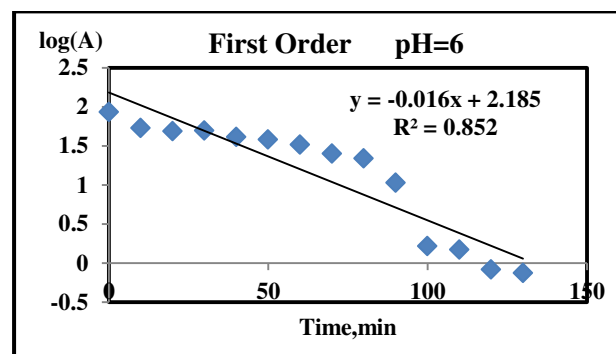


Figure-13. Pseudo first order kinetics at pH=6.

3.5 Kinetic study at different reaction temperature

The kinetics study at different temperatures (15, 25, 60 and 80°C) and fixed parameter (MR=1:1 and pH=4) as shown from Figure-14 to Figure-15 respectively were performed. The correlation coefficients for the linear plots of log [A] against time for the pseudo-first order data fitting of temperature from 15 to 80°C were shown from Figure-14 to Figure-17. The rate constant doesn't strongly affect by increasing temperature so the optimum operating reaction temperature is 25°C. Figure-15 provides the best correlation of the data for magnesium oxalate precipitation from sea bittern at temp. =25°C (pseudo first order kinetics).

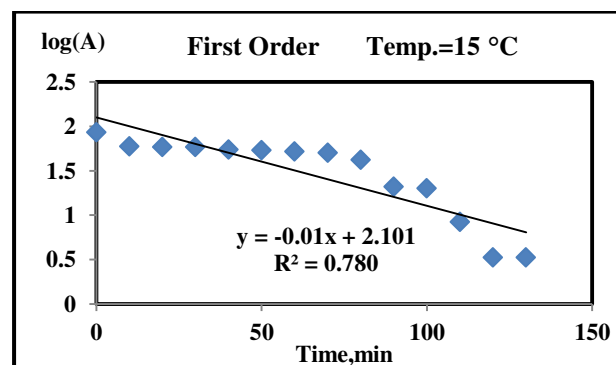


Figure-14. Kinetic at 15 °C.

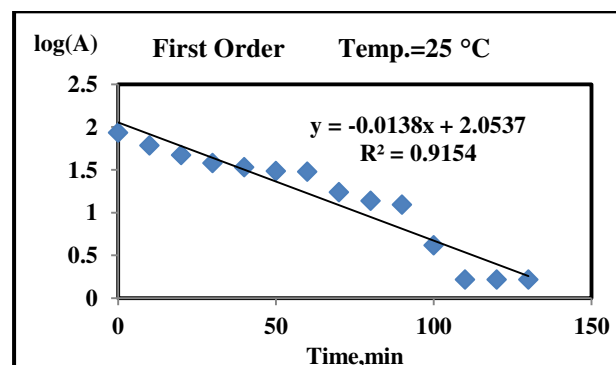


Figure-15. First order relation at 25 °C.

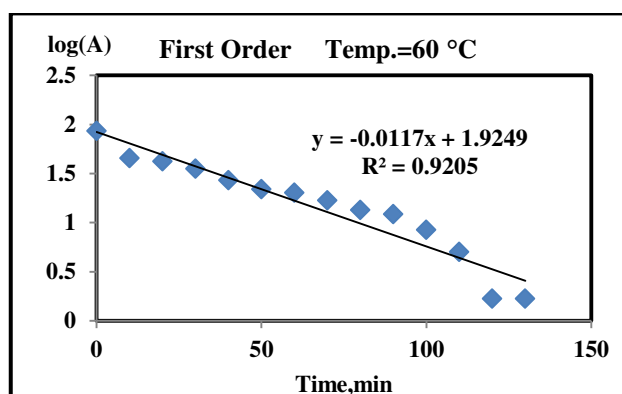


Figure-16. Relation at 60°. Pseudo first order kinetics Linear relations.

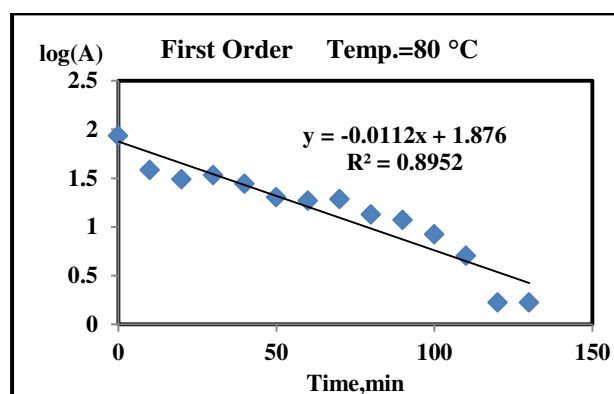


Figure-17. Linearity at 80°. Pseudo first order kinetics Linear relations.

3.6 Effect of different parameters on rate constant

From Table-2 k values shows a constant value from 1:1 till 1:1.4 and achieved slight decrease which confirms that stoichiometric ratio is an optimum. pH is the significant factor as by increasing pH the K values increases, but at pH= 4 the highest purity of magnesium oxalate is achieved. The rate constant is not affected by increasing temperature so the optimum operating reaction temperature is selected to be 25°C.

Table-2. Relationship between rate constant, K and various parameters.

Molar ratio, MR	1:1	1:1.2	1:1.4	1:1.6	1:1.8
Rate Constant, K	0.0299	0.0299	0.0299	0.0276	0.253
pH	1	3	4	6	
Rate Constant, K	0.0138	0.0253	0.0299	0.0368	
Temperature, °C	15	25	60	80	
Rate Constant, K	0.023	0.0299	0.0253	0.0253	

3.7 Temperature dependency from Arrhenius equation

By applying Equation. (14) on the experimental data, values of the rate constant (k) for the precipitation

reaction of magnesium oxalate at different temperatures were processed in the following Figure-18 (*).

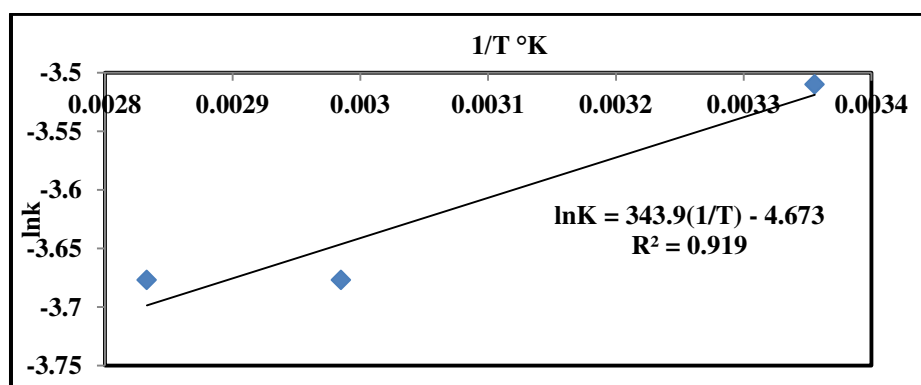


Figure-18. (*) The slope ($-E/R$) and $\ln k_0$ from Arrhenius equation.

It was deduced from Figure (*) that $-E/R = 343.9$ and so $E = -2859.18$ J/gmol. $= -2.859$ KJ/gmol. Also $\ln k_0 = -4.673$ and $k_0 = 93 \times 10^{-5} \text{ min}^{-1}$. The activation energy

obtained is negative, which means that the reaction slows down with increasing temperature and indicating an exothermic reaction.



4. CHARACTERIZATION OF MAGNESIUM OXALATE PRODUCT AT OPTIMUM CONDITION

It can be concluded that ideal working conditions for encouraging pure Mg oxalate are at MR=1:1, pH= 4, ambient temperature and time of response for 2 hr. The yield is 51.662 g with conversion 98.7% and evaluated by complex-metric titration. The results were affirmed by ICP and atomic adsorption analysis. Ideal calcinations temperature is 650°C which was close to the temperature obtained from TGA chart showing the calcinations temperature of MgO produced.

4.1 TGA and DTA analysis for magnesium oxalate

Figure-18 shows the TGA curves obtained for the magnesium oxalate prepared at optimum conditions, sample stability, pure sample of magnesium oxalate, and

no more $\text{Mg}(\text{OH})_2$ is present. Thus, TG analysis illustrated high purity of Mg oxalate prepared. TGA curve of the Mg oxalate shows number of weight loss in steps up to a temperature of 600 °C. These steps can be due to moisture loss about 26.62% at temperature <200 °C (24.32% theoretically), Mg oxalate decomposed from 400 °C to 500 °C with 48.78% weight loss. This weight loss is corresponding to formation of MgO due to the loss of CO and CO_2 (48.64% theoretically). The chart shows a continuous weight loss of 75.4% between 150-800 °C. After 600 °C, thus confirming formation of MgO. The difference between theoretical and observed mass loss at first step may be due to the incompleteness of the dehydration reaction within this temperature range. These results are in well agreement with publications [10].

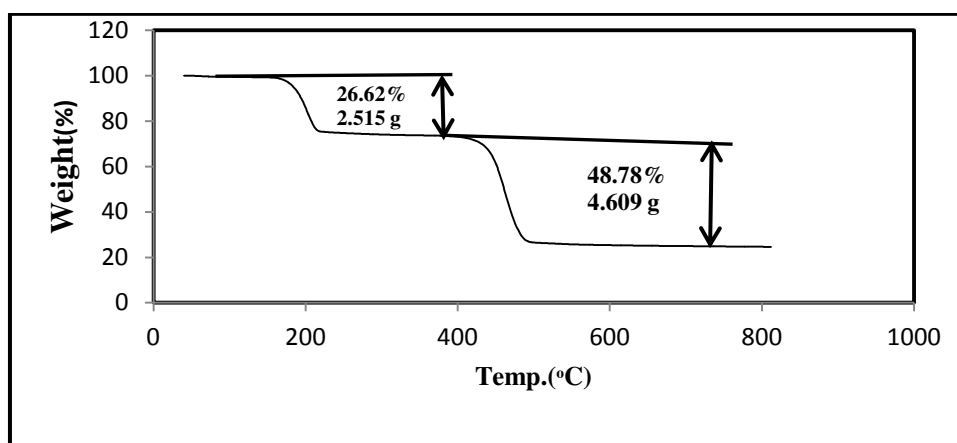


Figure-19. TGA analysis of magnesium oxalate prepared at optimum condition.

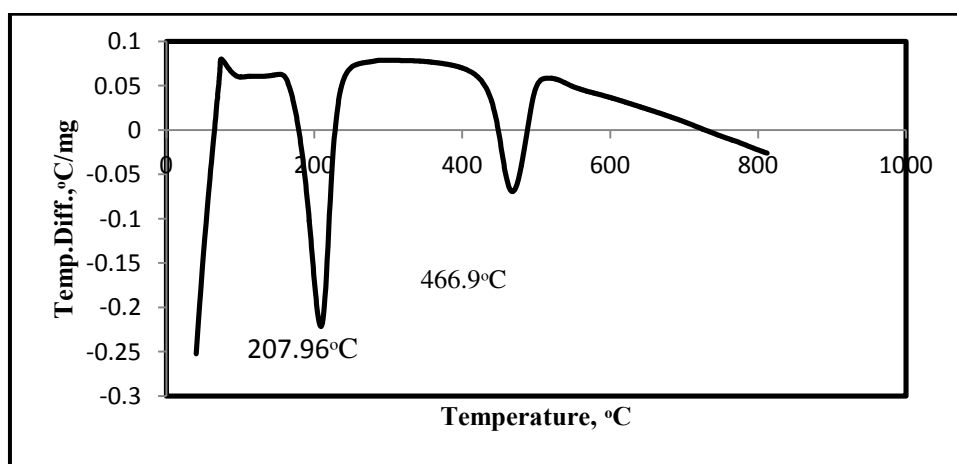


Figure-20. DTA analysis of magnesium oxalate prepared at optimum conditions.

From the DTA curves shown in Figure-20, clearly two sharp endothermic peaks related to dehydration process and to magnesium oxalate decomposition.

4.2 Transmission electron microscopy (TEM) analysis of MgO product

The synthesized MgO platelet was examined by Transmission Electron Microscopy (TEM) and illustrated in Figure-21a. The Selected Area Electron Diffraction (SAED) pattern confirms the structural nature of the synthesized platelet nano-MgO and supports the presence of MgO in cubic structure is shown in Figure-21b.

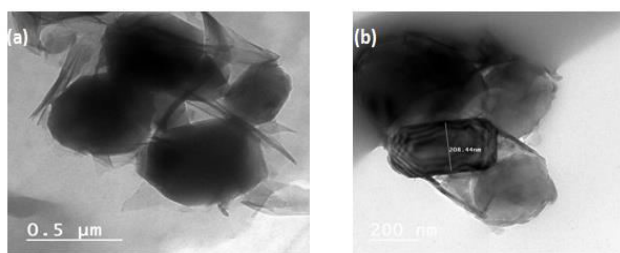


Figure-21_a and 21_b, Exhibits TEM image of the synthesized MgO.

5. CONCLUSIONS

TGA and DTA indicate the full production from magnesium oxalate to magnesium oxide. This method of preparation is found to be efficient for the large scale industrial production of fine magnesium oxide without any expensive chemical.

The precipitation of magnesium oxalate from bitters is first order reaction kinetics with respect to the concentration of magnesium oxalate. The rate constants were determined at different temperatures and activation parameters calculated.

Mg oxalate produced in pure form, can be a good precursor for MgO production.

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REFERENCES

- [1] Zang J.C. and Ding W. 2001. The Pidgeon Process in China and Its Future. Magnesium technology, Warrendale, PA, TMS. pp. 7-10.
- [2] Mordike B.L. and Ebert T. 2001. Magnesium Properties-applications-potential. Materials Science and Engineering. A302: 37-45.
- [3] Gray J.E. and Luan B. 2002. Protective coatings on magnesium and its alloys-a critical review. Journal of Alloys and Compound. 336(2): 88-113.
- [4] Das S. 2008. Primary Magnesium Production Costs for Automotive Applications. Journal of the Minerals, Metals, and Materials Society. 60(11): 63-69.
- [5] Mustafa K.K. 2008. Magnesium and its alloys applications in automotive industry. International Journal of Advanced Manufacturing Technology. 39(9): 851-865.
- [6] Muneer S. and Khairul A. I. 2014. Trends in the Global Automotive Sector. Australian Journal of Business and Management Research. 3(11): 1-5.
- [7] Jaroslav Č., Dalibor V. 2013. Properties of porous magnesium prepared by powder metallurgy. Materials Science and Engineering C, 33: 564-569.
- [8] Nancolls G.H. and Purdie N. 1961. Crystallization of magnesium oxalate in aqueous solution. Transactions of the faraday. 56: 278-284.
- [9] Behij S., Hammi H., Hamzaoui H. A. and M'nif A. 2013. Magnesium salts as compounds of the preparation of magnesium oxide from Tunisian natural brines. Chemical Industry and Chemical Engineering Quarterly CICEQUATION. 19(2): 263-271.