Tapping into the Ballast Potential of Sparingly Soluble Salts for Enhanced Floc Physiognomies in Algae Biomass Harvesting

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Abstract

Enhanced floc settling rates and reduced biomass volume were achieved when sparingly soluble salts of magnesium were used as ballast agent in the pH induced algae biomass harvesting operation. The floc characteristics of biomass harvested from non-ballasted pH induced system were compared with that of pH induced ballasted system that contained soluble ($MgCl_2$) and sparingly soluble salts (i.e., $Mg(OH)_2$ and $Mg(OH)_2$ nanoparticles ($NMg(OH)_2$)). The pH value for onset of coagulation was lower in soluble salt system (pH = 10.2) than in the sparingly soluble salt (pH =11.4). The floc generated from the ballasted $NMg(OH)_2$ system had the highest sedimentation rate (*K (L/mol/s)* = 1.0454), while that of the non-ballasted pH induced system had the lowest rate (*K (L/mol/s)* = 0.2155). The ballast agent enhanced the sludge volume index of the biomass by 66.04% and had no negative impact on the filterability. The values of the the specific cake resistance (α (m/kg)) and the resistance of the filter medium (R_m (1/m)) were within the same range. Both the growing and harvested biomass exhibited good strength and recovery factor (>90%). The evaluation of the effects of the ballast agents on the biomass viability showed that the ballast agent was not toxic to the harvested biomass.

Keywords: Algae, harvesting, coagulant aid, flocculation, ballast, sedimentation

1.0 Introduction

Coagulation-flocculation (CF) is an important procedure developed to aggregate algae cells for biomass harvesting. This is the first stage of a two-step process that involves the preconcentration of miniscule algae cells (< 30 μm), prior to the dewatering. The overall cost of the biomass harvesting greatly depends on the magnitude of the water removed during the CF stage (Jorquera, et al., 2010). In order to minimize the cost of this second stage (i.e. the mechanical dewatering), it is important that low algae biomass volume is produced from the CF stage (Danquah, 2009). Albeit, the production of small algae volume is important, but the overall harvesting rate is also vital. Consequently, an appropriate and sustainable algae biomass harvesting procedure should have high floc sedimentation rate. A CF procedure with high floc settling rate requires a smaller harvesting unit, thereby incurring lower investment costs. Granados et al., (2012) observed that studies on algae biomass harvesting rarely take into consideration the issue of floc volume or the floc sedimentation kinetics.

Considering the challenges synonymous with the use of conventional metal slats (i.e. aluminum and iron salts) for algae harvesting, pH induced autocoagulation procedure is now considered the preferred option for microalgae biomass harvesting. In the pH induced autocoagulation, the role (Vandamme, et al., 2012, Smith, et al., 2012, Schlesinger et al., 2012) and mechanisms (Brady, et al., 2014, Wua, et al., 2012, Branyikova, et al., 2018) of alkaline earth metals (i.e. Mg^{2+} and Ca^{2+}) have been documented. At present, no study has been reported on the influence of these metal salts on the characteristics of the flocs produced from the pH induced autocoagulation system. Premised on the importance of floc volume and the settling rate characteristics on the overall process economy of any algae harvesting procedure, the present study aimed at the determination of the role of bivalent metal salts, using Mg^{2+} as a case study, on the sludge volume produced from a pH induced autocoagulation system.

The use of coagulant aids in CF operations enhances the process efficiency and cost (Oladoja, 2016). Flocs produced from such systems are stronger and settle faster and a reduction in the required optimum primary coagulant dosage and sludge volume is achieved (Jessey and Sydney, 1971). In order to enhance the settling kinetics of algae flocs, Jiménez et al., (1999) posited that apposite small-particle-size sand, as a ballast agent can be added to the CF procedure. It was postulated that the added sand particles serve dual roles: as seed grains at the onset of the CF process; and then as a weighting agent to boost the rate of floc sedimentation. In view of the extraneous nature of sand in algae medium, its use as a ballast agent complicates the subsequent stages of the processing, because of the need to separate it from the microalgae biomass matrix (Gorin et al., 2015). Consequently, Gorin et al., (2015) used the flocculated biomass of *Chlorella vulgaris* GKV1, as ballast agent, for its harvesting, with different primary coagulants (i.e. ferric alum, polyacrylamide and polyethylenoxide). Premised on the role of bivalent metal ions, which has been enunciated (Vandamme, et al., 2012, Smith, et al., 2012, Schlesinger et al., 2012), we hereby hypothesize that the ballast potential of sparingly soluble bivalent metal salt, which is a component of the culture medium, can be used to enhance the floc volume and the settling kinetics of harvested algae biomass.

Considering the report of Vandamme, et al., (2012) on the essential role of Mg^{2+}, as the most important bivalent metal ion in the pH induced autocoagulation of algae cell, sparingly salts of magnesium was chosen as the bivalent metal to be investigated. *Chlorella vulgaris* was selected as the targeted algae cell because it is an auspicious algae species that is being intensively studied for the production of microalgae biomass for food and biofuel (Feng et al., 2011). Different magnesium salts ($MgCl_2$, $Mg(OH)_2$, and Nano($Mg(OH)_2$ particles) of varying solubilities were used in a pH induced algae biomass harvesting. The optimum Mg^{2+} salt dosage was determined

for the algae biomass harvesting and the sedimentation rate parameters of the harvested biomass were determined, using different kinetic equations. The floc characteristics (surface architecture, settleability, filterability, size, strength and breakage factors) were determined and the influence of the ballast agent on the viability of the harvested algae biomass was also evaluated.

Materials and Methods

2.1. Preparation and characterization of magnesium salts

The appropriate $MgCl_2$ salt solution and $Mg(OH)_2$ suspension were prepared from Laboratory grade salts. The nano magnesium hydroxide ($NMg(OH)_2$) was prepared as previously described (An, 2009 and Oladoja et al., 2015) viz: Sodium hydroxide (NaOH) (2.0 M) solution was added into a preheated (50 ℃) 1.0 M magnesium chloride ($MgCl_2$) solution (50 mL) at a discharge rate of 3 mL/min. The suspension was allowed to age for 2 h in the mother liquor, while vigorous stirring was ensured. The precipitate produced was filtered, washed with deionized water and dried at 80℃ to obtain the $Mg(OH)_2$ nanoparticles. The features (i.e. elemental and mineralogical composition, BET surface areas, and the surface functional groups) of the $NMg(OH)_2$ were reported in an earlier treatise (Oladoja et al., 2015).

2.2. Algae cultivation and harvesting

The Marine *Chlorella* (GY-H6) sample was purchased from the Institute of Hydrobiology, Chinese Academy of Sciences, Wuhan, China. The cultivation and inoculation procedures previously described (Jin et al., 2015) was adopted in the present study.

The magnesium solution/suspension that contained 0.01g Mg^{2+}/mL was prepared from the respective magnesium salt in deionized water. The algae harvesting was conducted in a jar test apparatus (ZR3-6, Zhongrun Water Industry Technology Development Co. Ltd., China), using a 200mL of the algae suspension in a 500 mL beaker, mixed with a predetermined dosage of the

magnesium suspension or solution. The pH of the mixture was gradually corrected with 1M NaOH solution until the onset of coagulation. The mixture was stirred at 200 rpm for 1 min, then 50 rpm for 10 min and the flocculating algae biomass was allowed to settle for 30min before an aliquot was withdrawn for the determination of the optical density (OD).

The OD, measured at λ_{max} = 750nm, of the supernatant was determined and compared with that of the raw algae suspension using UV/Visible spectrophotometer. The harvesting efficiency (HE%) was calculated as:

$$\text{HE (\%)} = \frac{OD_i - OD_f}{OD_i} \qquad (1)$$

Where, OD_i and OD_f is the optical density of the raw algae suspension and the treated algae suspension, respectively.

The optimum Mg^{2+} dosage for the pH induced algae cell harvesting was determined between the dosage that ranged between 100mg/L and 500mg/L.

The floc sedimentation rate parameters of the harvested biomass were determined with 500mL of algae suspension of cell concentration of 1.91g/L and the optimum Mg^{2+} dosage, within the sedimentation time that ranged between 0 and 60min. The time-concentration profile of each CF system was determined through a combination of gravimetric and UV spectrophotometric method viz: a fixed volume of serially diluted raw algae suspension was measured into a set of pre-weighed crucible in triplicate and dried to a constant weight in a drying oven. The OD value of each of the serially diluted samples was also measured using a UV spectrophotometer at λ_{max} = 750nm. The correlation of the algae cell OD value with the gravimetric values gave a linear correlation coefficient values (r^2) of 0.9993 (Supplementary Information Fig.1 (SIF. 1)). In order

to quantify the algae cell concentration (AC), the OD values of the cell suspensions were correlated with the algae cell weight (g/L) using the regression equation presented below:

$$AC = 7.1045OD_{750} + 0.0215 \quad ; r^2 = 0{:}9993$$

The time-concentration profiles of the residual concentration of the algae cell was fitted to different kinetic order equations to obtain the algae floc sedimentation parameters.

2.3 Determination of floc characteristics

The surface architecture and elemental composition of the harvested biomass were determined and compared using SEM-EDAX. The floc settleability was determined by adopting the procedure used for the determination of the sludge volume index (SVI, (mL/g)) (APHA, 1998) and the SVI values were calculated using Equation 2:

$$\text{SVI} = \frac{settled\ sludge\ volume\ \left(\frac{mL}{L}\right)\ x\ 1000}{mass\ of\ dried\ sludge(g)} \qquad (2)$$

In order to determine the filterability of the harvested algae flocs, the settled flocs were homogeneously mixed and the ensuing slurry was used accordingly. The filterability of the floc was determined via gravimetric analysis in a filter paper placed in a Buchner funnel. The slurry was filled up to 60% volume of the funnel and the volume of the filtrate collected in the graduated vertical cylinder was recorded at regular time intervals. Using differential equation, the force balance for gravity filtration in a filter paper placed on a Buchner funnel is as presented in Equation 3 (McCabe, 2001):

$$\frac{\Delta t}{\Delta v} = \frac{\mu}{A_f \Delta p}\left(\frac{\alpha C V}{A_f} + R_m\right) \qquad (3)$$

where Δt denotes the time interval of filtration (s); ΔV, the volume of the filtrate collected during Δt (m^3); V, the cumulative average volume of the filtrate collected up to the considered time

interval (m^3); *C*, the concentration of solids in the wastewater (kg/m^3); α, the specific cake resistance (m/kg); μ, the viscosity of the filtrate (Pa s); ΔP, the pressure drop across the filter (Pa); A_f , the area of filtration (m^2); and R_m, the resistance of the filter medium (1/m) (Mahesh, et al., 2006).

The floc size, strength and breakage were determined using a particle size analyzer (Mastersizer 3000) and the mean diameter, $d_{0.5}$, was used to estimate the algae floc size. The floc size was determined during the coagulation-flocculation stage in the particle size analyzer and floc size was monitored every 60s., at a flow rate of 1.5L/h. In order to study floc breakage and re-growth, the flocculating flocs were exposed to shear force at 200rpm for 1min and 50rpm for 10min, repeatedly, for three consecutive cycle. Floc sizes was monitored every 60second, at a flow rate of 1.5L/hour during the shear and slow mixing period. In order to compare the floc strength and recoverability the strength and recovery factors were calculated using Equations 4 and 5 (Jarvis, et al., 2005, Francois, 1987, Yukselen and Gregory, 2004):

$$\text{Strength factor} = \frac{d_2}{d_1} x\ 100 \qquad (4)$$

$$\text{Recovery factor} = \frac{d_3 - d_2}{d_1 - d_2} x\ 100 \qquad (5)$$

Where: d_1 is the average floc size of the steady phase before breakage or shear phase, d_2 is the floc size after the floc breakage period, and d_3 is the floc size after re-growth to the new steady phase.

In order to determine the floc strength of the harvested biomass, the floc breakage and re-growth factors of the harvested flocs, after 60min.settling time, were also determined consecutively at different shear rate 300, 400 and 500 rpm.

2.4 Determination of Viability of harvested algae cells

After the algae harvesting procedure, the supernatant and the flocs were separated immediately, to recover the harvested biomass. The biomass was used to cultivate algae using a fresh autoclaved culture medium. The algae cell viability was monitored as a function of the growth over time through the determination of the OD value at λ_{max} = 750.

3.0 Results and Discussion

3.1 Determination of optimum Mg^{2+} dosage and algae harvesting mechanism

The results of the determination of the optimum dosage for the different Mg^{2+} solutions/suspensions are presented in SIFig. 2. At the optimum dosage for each of the magnesium salt, high HE (%) value (range = 93%-98%) was achieved. Relative to the optimum dosage of the $MgCl_2$ salt (i.e., 200mg/L), lower dosages (100mg/L) of the $Mg(OH)_2$ and nano-$Mg(OH)_2$ were required to attain the optimum dosage. In a raw algae suspension of pH value of 9.64, the pH induced autocoagulation was achieved at pH value of 11.4. In the $Mg(OH)_2$ and nano-$Mg(OH)_2$ systems, the autoflocculation of the algae cell occurred at similar pH value range at which the pH induced autoflocculation occurred. Contrariwise, the autoflocculation was achieved at lower pH value (10.2) in the $MgCl_2$ system.

Thus far, controversy still rages on the underlying mechanism of pH induced autoflocculation of algae biomass. The role and mechanism(s) of the Mg^{2+} in pH induced autoflocculation are still debatable. Herein, if the difference in the pH values at which the autocoagulation was achieved in the presence of the soluble and sparingly soluble magnesium salts was considered, it could be assumed that different operating mechanisms were responsible for the algae floc formation in the two systems.

Taking into cognizance, the dosage of the Mg^{2+} added to the algae suspension (i.e. 200mg/L (0.017M), (the Mg^{2+} molar concentration range in the system was fixed at 0.00001M – 0.017M), the speciation of the Mg^{2+} in the algae suspension was elucidated using a hydrodynamic equilibrium calculation software, HYDRA and MEDUSA (Fig 1a and 1b). The speciation diagram (Fig. 1a) showed that the precipitated $Mg(OH)_2$ was the dominant species at this concentration, within the range of the pH value at which autocoagulation was observed. Although Mg^{2+} and $Mg(OH)^+$ were also present in the system, but the charge neutralization that is often touted as the possible operating mechanism (Wu et al., 2012, Semerjian and Ayoub, 2003, Vandamme et al., 2012) could not be justified. This is because the surface charges on these positively charged species (i.e. Mg^{2+} and $Mg(OH)^+$) were grossly inadequate to induce algae cell coagulation. Consequently, the autoflocculation in the presence of soluble magnesium could be said to have occurred through sweep coagulation during the precipitation of the $Mg(OH)_2$ in the system. In the sparingly soluble systems, the solubility of the $Mg(OH)_2$ salt was 0.0064g/L (i.e. 0.00053M). Therefore, the Mg^{2+} molar concentration range in the system was fixed at 0.00001M – 0.00053M). The speciation diagram (Fig. 1b) showed that similar magnesium species found in Fig. 1a were also present in the system. The pH value at which the formation of the insoluble $Mg(OH)_2$ was inducted differed from that of soluble magnesium system but the domineering specie still remained the insoluble $Mg(OH)_2$. The results resented in Fig 1a and 1b revealed that the sweep coagulation by the growing insoluble $Mg(OH)_2$ was the underlying mechanism of algae biomass harvesting but the difference in aqueous phase concentrations of the Mg^{2+} was responsible for the difference in the pH values at which the autocoagulation was initiated in the respective system.

The four identifiable underlying mechanisms of CF include: the double-layer compression; charge neutralization; bridging; and sweep coagulation. Considering the non-polymeric nature of the magnesium species present in the algae suspension, the algae harvesting process cannot occur through the bridging mechanism option. The influence of charge neutralization and double layer compression was not apparent, because no visible algae cell coagulation was observed in the presence of abundance of Mg^{2+} and $Mg(OH)^{+}$ prior to the formation of $Mg(OH)_2$ species. The speciation diagram (Fig. 2a and 1b) that showed the onset of formation of the $Mg(OH)_2$ that coincided with the pH value of induction of algae autocoagulation affirmed this postulate. The evidence of sweep coagulation was further attested to by the SEM image of the flocs derived from the centrifugation, pH induced autocoagulation and Mg^{2+} salt aided autocoagulation (Fig. 2). The surficial images of the flocs obtained from the different system showed that the biomass obtained from the centrifugation was totally different in the algae cell arrangement. In the image presented in Fig. 2[A], the cells were arranged adjacently to each other, without any extraneous material. In the images presented in Fig. 2[B-D], the algae cells were embroiled in a separate phase, which indicated the incorporation of the algae cell, by sweep coagulation, into the framework of the precipitating $Mg(OH)_2$. Despite the occurrence of the sweep coagulation mechanism in the $NMg(OH)_2$ system, the image presented in Fig. 2[E] showed that the algae cell were further encapsulated by the $NMg(OH)_2$ particles, which made it difficult to decipher a distinct algae cell physiognomies in the floc image (Fig. 2[E]).

3.2 Determination of algae floc sedimentation parameter

The time-concentration profiles of the floc sedimentations rate are presented in Fig. 3. The influence of the different Mg^{2+} salts on the sedimentation rate of the algae flocs varied and the settling rate could be arranged thus: $NMg(OH)_2$ >$Mg(OH)_2$>$MgCl_2$ > pH Induced. The flocs

obtained from both the $NMg(OH)_2$ and $Mg(OH)_2$ exhibited comparable sedimentation rate but that of $NMg(OH)_2$ was slightly faster. The sedimentation rate of the floc derived from the pH induced system was the least. In order to obtain the settling rate parameters, the data obtained from the time-concentration profiles were fitted to the kinetic equation that represents homogeneous chemical reactions (Richardson, et al., 2005). This kinetic equation is based on the solution concentration viz:

$$-\frac{d[C]}{dt} = k[C]^n \qquad (8)$$

Where: *C* is the concentration of reactant, *k* is the rate constant and, *n*, is the order of reaction. If the equation is integrated for the first order (Equation 9), second order (Equation 10), and third order (Equation 11), it yields the following integrated equations, respectively:

$$ln[C] = ln[C]_0 - kt \qquad (9)$$

$$\frac{1}{[C]} = \frac{1}{[C]_0} + kt \qquad (10)$$

$$\frac{1}{2[C]^2} = \frac{1}{2[C]_0^2} + kt \qquad (11)$$

The sedimentation rate was derived from the plots of the left-hand sides of the different kinetic equations against time (SIF4a-4c). The fitting of the kinetic equations to the algae floc sedimentation rate was evaluated from the value of the correlation coefficient (r^2) of the straight line obtained from the plots of the experimental data. The r^2 values presented in Table 1 showed that the processes of algae harvesting in all the systems were best described by the second order kinetic equation (r^2 value range = 0.9219-0.9925) (Table 1), but with the exception of the pH induced system that was described by the third order kinetic equation (r^2 = 0.9791). The trend in

the value of the second order rate constant (*k (L/mol/s)*) (range: 0.2155 and 1.0454) for the different harvesting system also followed the pattern exhibited in Fig. 3. The pH induced algae harvesting system had the lowest sedimentation rate 0.2155 (L/mol/s), while the $NMg(OH)_2$ exhibited the highest rate (1.0454(L/mol/s)). The higher sedimentation rate of the harvested biomass was ascribed to the ballast effect of the $Mg(OH)_2$ that enmeshed the algal cells.

3.3 Determination of floc settleability and filterability

The ability of the algae flocs harvested from the different procedure to settle and compact was determined by adopting the standard protocol for the evaluation of sludge volume index. The value of the SVI (mL/g) obtained from the different algae harvesting system varied (Table 2). The highest value was obtained in the pH induced system (4237.29) while the presence of $NMg(OH)_2$ greatly reduced the SVI value (1438.8), by 66.04%). The range of SVI values obtained for a particular sludge portend the settling characteristics and the compactness. It was posited that a very good sludge should have a value of 50 mg/g, while a value less than 80 mg/g is still considered good enough. The settleability of sludge with values greater than 120mg/g is considered poor (Gray, 1999). For the very high SVI values, as reported herein, it was attributed to, either a sludge that settles very slowly and compacts poorly, or filamentous sludge bulking. The filaments may be embedded within the floc, thereby producing a dispersed, open floc structure. Considering the peculiarity of the harvested algae biomass, the standard SVI criteria may not be viable for the assessment of the settleability of the harvested biomass but it provided a comparative analogy of the influence of the sparingly soluble salts on the settling and compactness of the harvested biomass.

The filterability of the harvested biomass derived from the different algae harvesting operations are presented in Fig. 4. In all the algae harvesting systems, the rate of filtration reduced over time

and all the harvested flocs showed similarities in the filtration potential. With the caveat that the change in the hydrostatic head is insignificant and the gravity filtration is assumed to be a constant pressure filtration process, as shown in Equation (3), the process of filtration is considered to have terminated when deviation is observed in the linear plot of $\Delta t/\Delta V$ versus V (Fig.4) (Ramavandi, and Farjadfard, 2014). The values of α (i.e. the specific cake resistance (m/kg)) and R_m (the resistance of the filter medium (1/m)) were derived from the slope and intercept of the linear portion of the plot of $\Delta t/\Delta V$ against V (SIFig. 4a-4d). The values of α and R_m for all the harvested flocs were close (α value range= 2.17 x 10^9 m/kg to 2.19 x 10^9 m/kg) and (R_m value range = 6.7 x 10^4 l/m, to 8.6 x 10^4). The similarities in the α and R_m values was ascribed to the similarities exhibited in the harvested biomass filtration (Fig. 4), which showed that the presence of the ballast agent in the harvested biomass had no influence on the filtration potential of the harvested biomass.

3.4. Determination of floc size and strength

In order to evaluate the influence of the ballast agents on the size and strength of the floc formation, the floc size and the values of breakage and recovery factors during the CF process were determined in three consecutive breakage/re-formation cycles. During the first stage of the system agitation at 200rpm fast rate and 50rpm slow rate, the average d_{50} floc size ranged between 42.1 and 49.8 for all the CF systems studied. The pH induced flocs had the lowest average size while the average size of the flocs derived from the $Mg(OH)_2$ system was the highest. The results presented in Fig.5a showed that much fluctuations were recorded in the size of the flocs produced from the pH induced system than the flocs produced from the other CF systems. The flocs produced from all the systems with enhanced Mg^{2+} dosages were relatively stable. In the pH induced flocs, the strength factor reduced from 48% to 35%, with increasing

cycle of perturbation. In other flocs, the strength factors remained almost the same (>90%) throughout the period of perturbation. The tendency of the floc to recover after the breakage cycle, expressed as the recovery factor (%) showed that the recovery of the flocs derived from the pH induced system reduced after the second cycle from 96% in the second cycle to 27% in the third cycle. Amongst all the flocs studied, the $MgCl_2$ flocs showed the poorest recovery factors (20% and 9%) and the recovery factor reduced with increasing number of cycles. The floc derived from nano $Mg(OH)_2$ system showed the best recovery factor of 216% and 150% in the second and third cycle, respectively.

The strength and recovery factor of harvested flocs that have been allowed to settled for a period of 60min, was determined at different shear cycle of 300, 400 and 500rpm. All the flocs showed appreciable strength and recovery factors after the 60min period of settling (Fig. 5b and Table 3). Within the agitation speed studied, the strength factor (%) of all the flocs ranged between 82 and 99. The recovery factors were very good and the values exceeded 100% in some cases.

3.5. *Determination of Viability of harvested algae cells*

The determination of the effects of the ballast agent on the viability of the algae biomass are presented in Fig. 6. A culture medium propagated with fresh algae cell, under the same condition, was used as the control. All the harvested biomass reused successfully propagated in the new culture medium. The growth progressions of all the algae system were faster in all the biomass harvested from both the ballasted and non-ballasted systems than the control system. Within the study period (i.e., 1^{st} day-10^{th} day), the rate of increase of the OD values of the algae suspension prepared from the harvested biomass was more than that of the control system. On the 10^{th} day, the OD values of all the reused biomass system were higher than that of the control

system. This is an indication that the harvested system contained higher algae density than the control system. The higher growth rate and algae cell density in the harvested system were ascribed to the possible enrichment of the culture medium with precipitated nutrient phase in the harvested algae biomass.

3.6 Practical implications and process sustainability

Amongst the strategies that have been developed for the optimization of CF operations is the incorporation of coagulant aids (CA). On the basis of the operational requirements to be augmented, the conventional CA include activated silica, weighting agents (e.g. bentonite clay, powdered limestone, and powdered silica) and polyelectrolytes (Oladoja, 2016). In algae biomass harvesting using CF procedure, the low floc sedimentation rate and the challenge of large harvested algae volume, which encumbered the process of dewatering has been an issue of grave concern that deserves attention. Consequently, the inclusion of ballast/weighting agent in the harvesting operation has been advocated as a leeway out of this challenge. In CF operations, the use of weighting agents, also known as ballasted flocculation, has been used to reduce the system footprint and hydraulic retention time (Jacobsen and Hong, 2002).

The kinetic analysis of the floc sedimentation rate of both the ballasted and non-ballasted pH induced harvesting operations showed that the harvested biomass from the ballasted flocculation procedure (i.e., $Mg(OH)_2$, $NMg(OH)_2$ and $MgCl_2$ systems systems) exhibited faster sedimentation rate than the flocs obtained from the non-ballasted systems (i.e. pH induced). The faster sedimentation kinetics of the ballasted coagulation system is a pointer to the fact that adopting the ballasted coagulation procedure described herein would greatly reduce the system

footprint, the hydraulic retention time and the overall process economy of the biomass harvesting operations.

A comparative analysis of the settleability of the flocs derived from the different procedures, using the SVI analysis revealed that the ballasted flocculation procedure enhanced the settleability and the compactness of the harvested biomass. The superior settling and compacted biomass would engender better biomass handling and processing during the dewatering process for other downstream operations. The assurance of an improved handling and processing of the harvested biomass from the ballasted flocculation operations was further provided by the better breakage and strength factors displayed by the biomass obtained from the ballasted system, relative to those obtained from the non-ballasted system. The use of ballast agent did not vitiate the filtration potential of the harvested biomass, since the parameters obtained for the determination of the filterability of the harvested biomass from both ballasted and non-ballasted operations were similar.

One of the shortcomings of the use of CA in CF operation is the contamination of the harvested biomass, which requires additional separation stage after the harvesting procedure. Considering the fact that the salts used were part of the nutrient in the culture medium, the presence in the harvested biomass is not considered a contaminant, therefore no further separation procedure is required. The negative impact of the CA material on the harvested algae biomass has also been one of the bottlenecks of ballasted flocculation. The determination of the impact of the ballast agents on the harvested algae cell, through the reuse of the harvested algae biomass for algae cultivation, showed that the ballast agents had no toxic effect on the harvested biomass. The confirmation of the non-toxicity of the ballast agents on the harvested biomass enhanced the sustainability potential of the entire ballasted biomass harvesting operations.

4.0 Conclusion

The use of sparingly soluble magnesium salts as weighting agent in ballasted flocculation operation enhanced the algae biomass harvesting efficiency, produced biomass with improved floc properties and lower biomass volume. The use of ballasted flocculation procedure enhanced the floc sedimentation kinetics, settleability and did not vitiate the filtration ability of the harvested biomass. The improved characteristics of the biomass obtained from the ballasted operation has provided a way forward for enhanced downstream processing and handling of biomass obtained from pH induced algae harvesting for industrial and agricultural applications.

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Conflict of Interest.

The authors declared no conflict of interest

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Figures

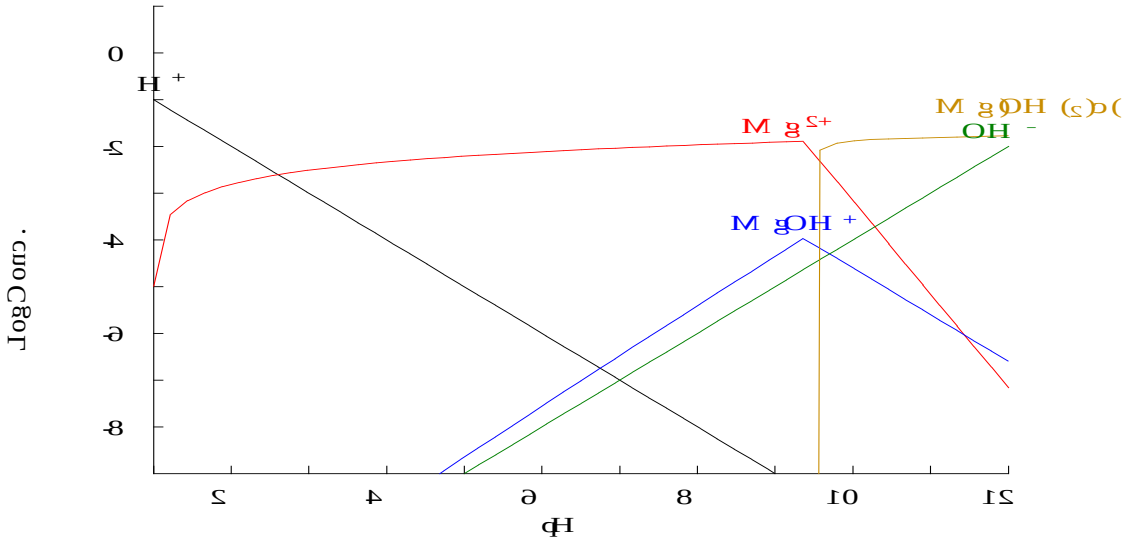


Figure 1a: Hydrochemical equilibrium diagram of $MgCl_2$ @ concentrations that ranged between 1.0 x 10^{-5}M – 0.017M

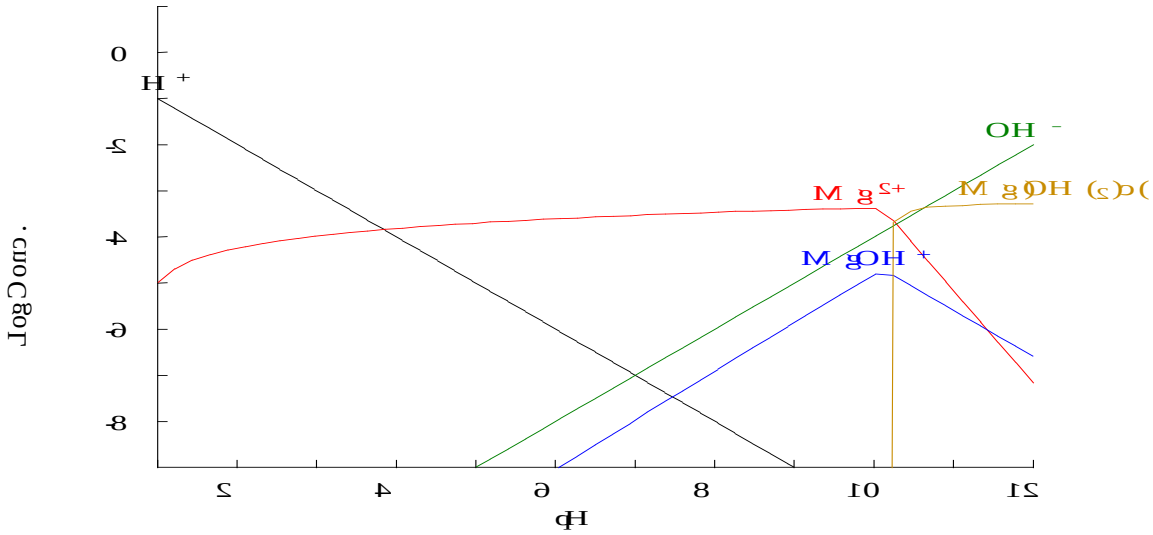
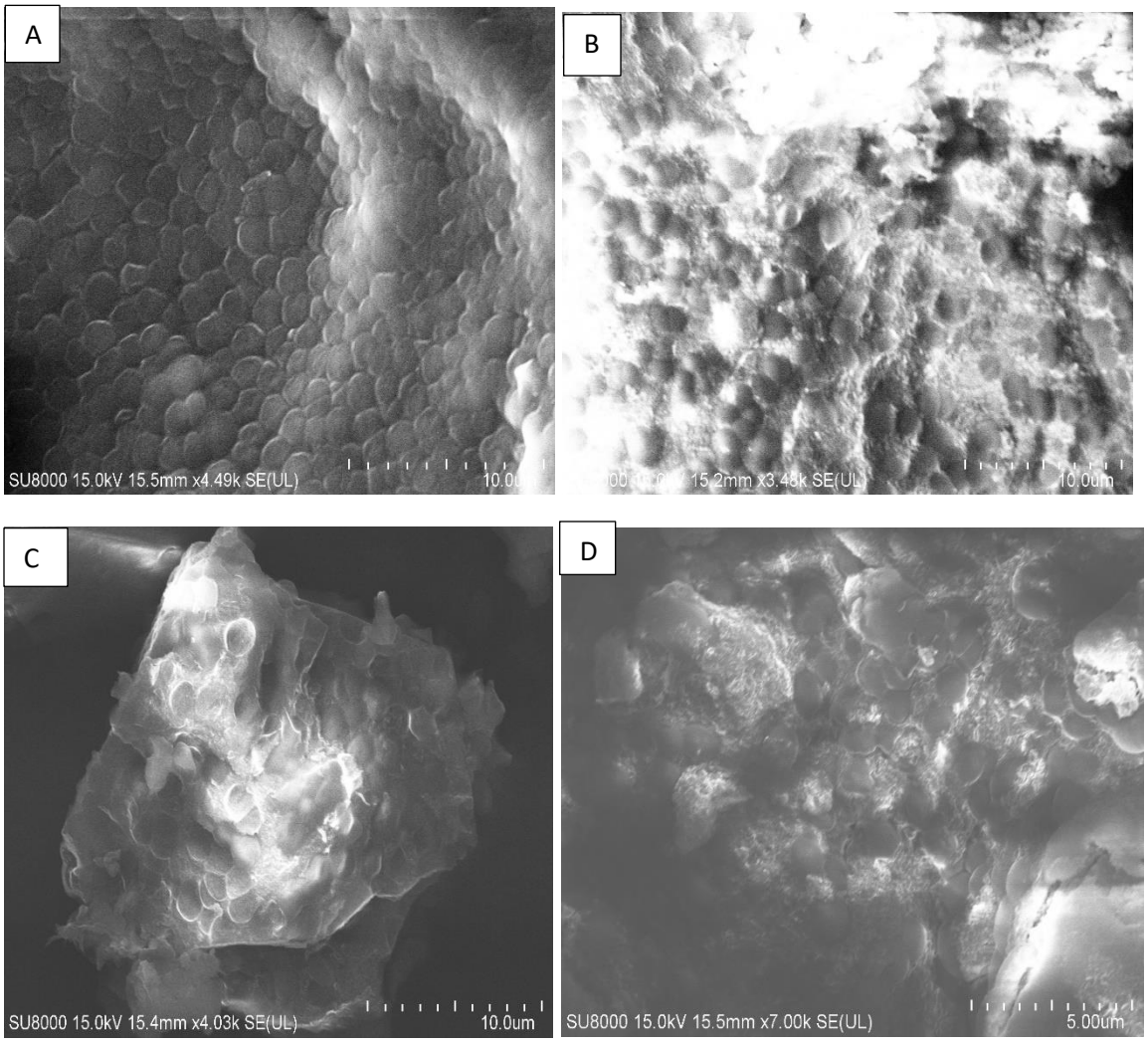


Figure 1b: Hydrochemical equilibrium diagram of Mg $(OH)_2$ @ concentrations that ranged between 1.0 x 10^{-5}M – 5.3 x 10^{-4}M



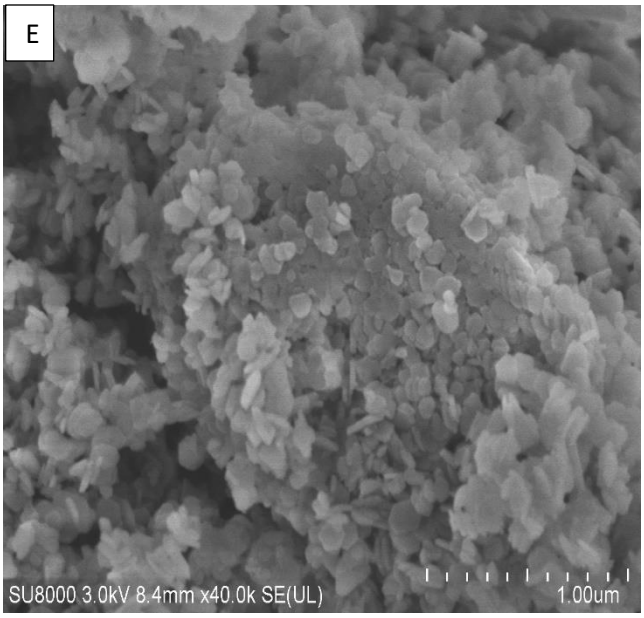


Figure 2: Surficial image of the algal flocs harvested from different coagulation procedure [A = centrifugation, B = pH induced, C= $MgCl_2$, D = $Mg(OH)_2$ and E = $NMg(OH)_2$]

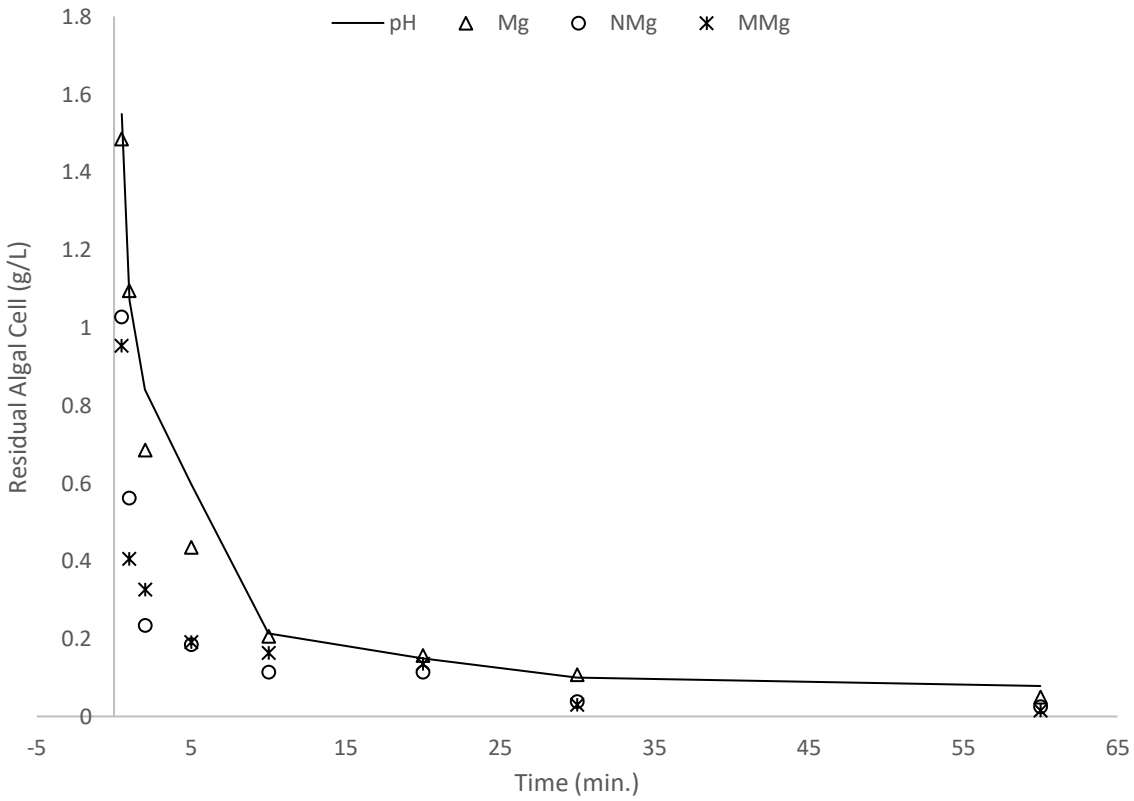


Figure 3: Time -concentration profile of the algae floc sedimentation in different Mg^{2+} system

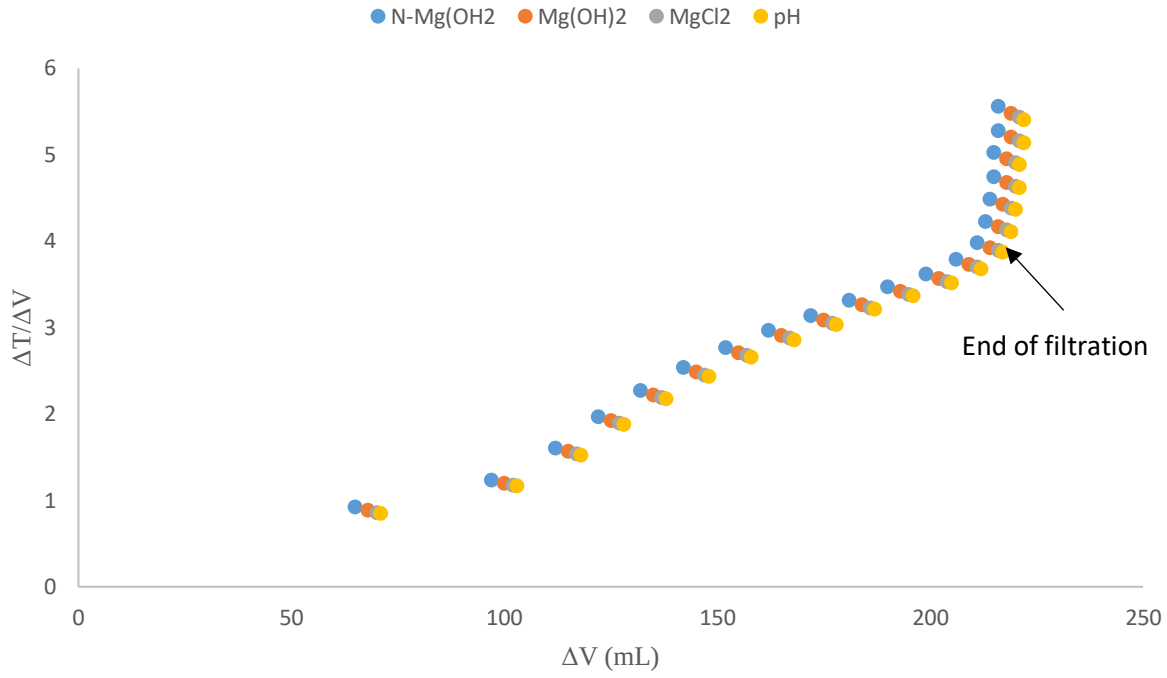


Figure4: Determination of the filterability of the harvested algal floc

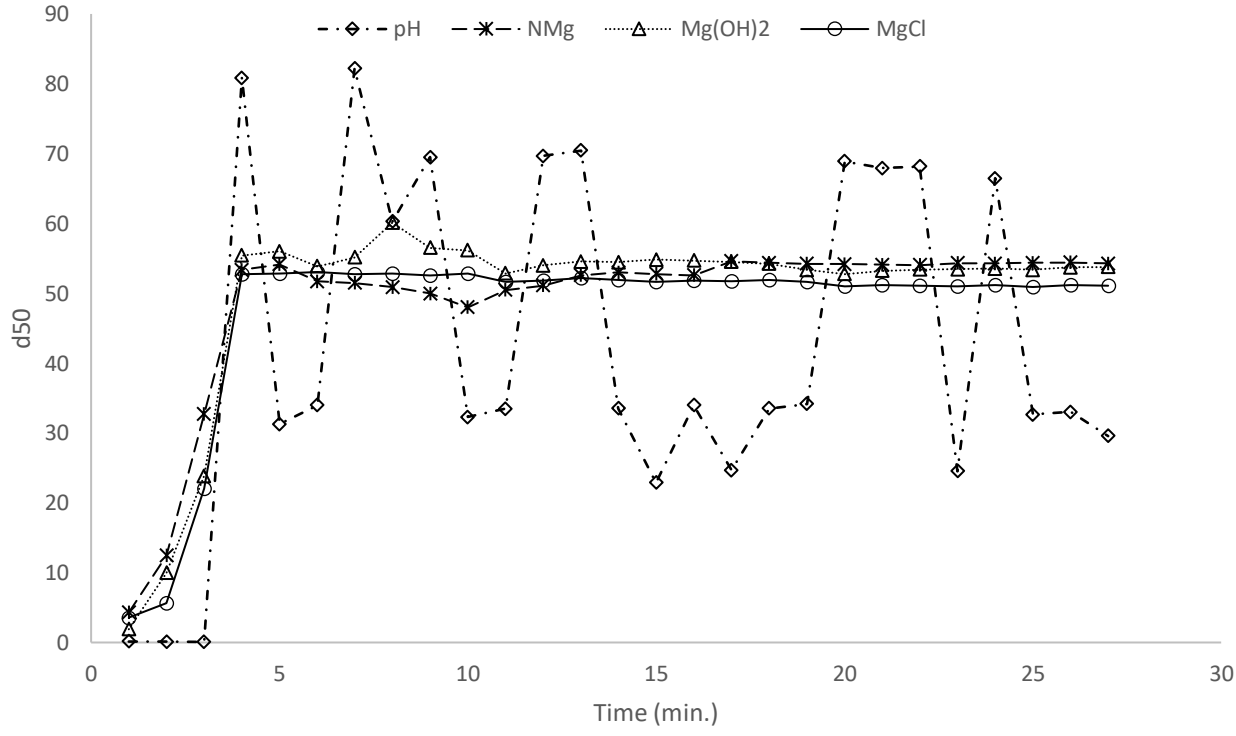


Figure 5a: Formation, breakage and re-formation of algal flocs in three consecutive cycles.

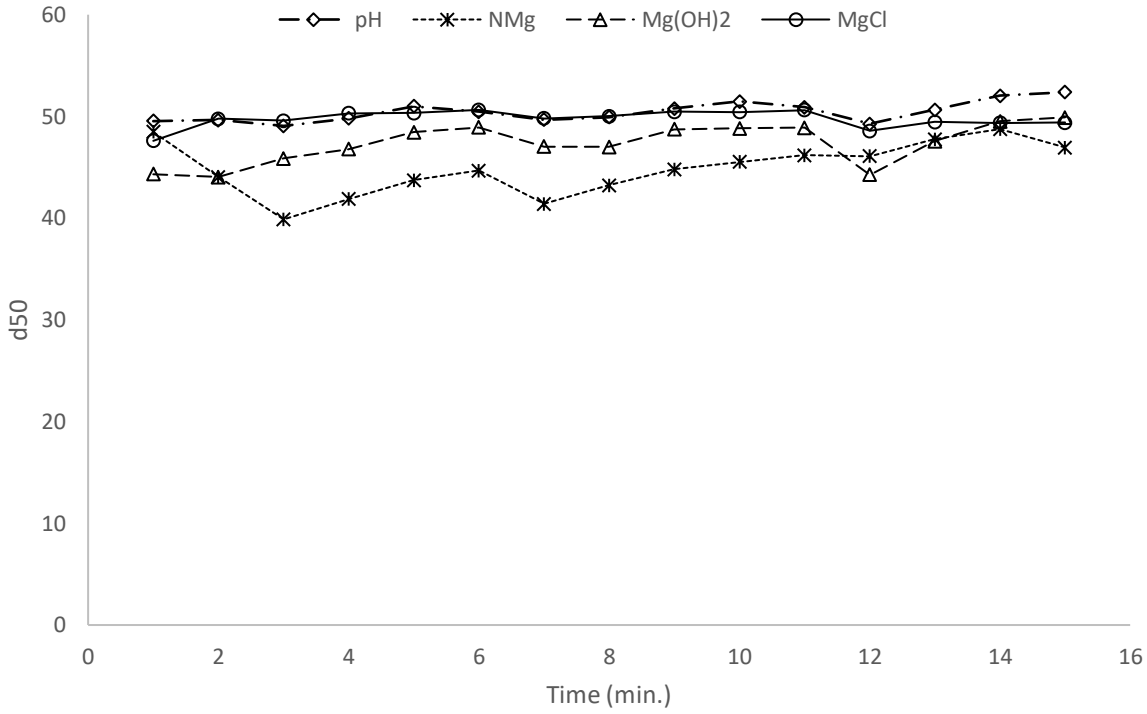


Figure 5b: Formation, breakage and re-formation of algal flocs at different shear cycle.

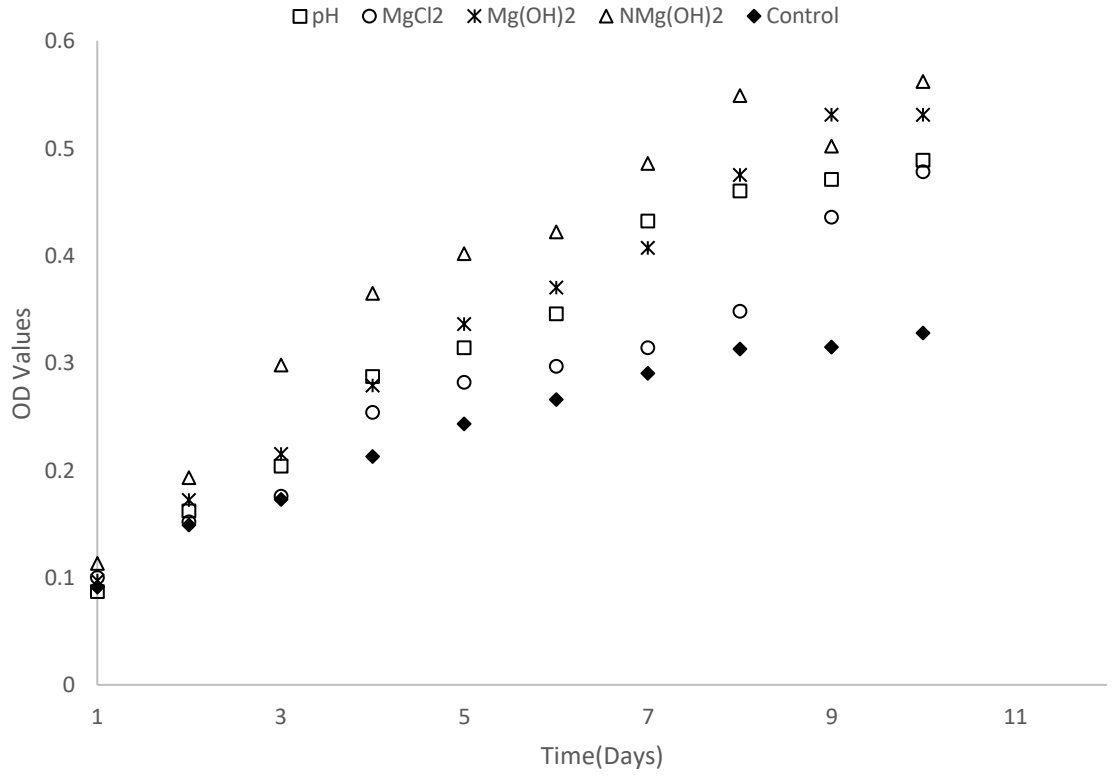


Figure 6: Determination of the effects of the ballast agents on algal cell viability

Tables

Table 1: Determination of the Kinetic Parameters for Algal Harvesting

Algal Suspension Sytem	***K* (s^{-1})**	**r^2**	***K* (L/mol/s)**	**r^2**	***K* ($L^2 \cdot mol^{-2}/s$)**	**r^2**
	Firts Order		**Second Order**		**Third Order**	
pH Induced	0.0478	0.7292	0.2155	0.9219	1.4389	0.9791
$MgCl_2$	0.0518	0.8038	0.3156	0.9925	3.1633	0.9028
$Mg(OH)_2$	0.0607	0.7437	0.6371	0.9503	12.648	0.9308
$NMg(OH)_2$	0.052	0.8542	1.0454	0.9441	32.544	0.8877

Table 2: The flocs settleability and filterability characteristics

Sludge type	**α (m/kg) x 10^8**	**R_m(1/m) x 10^3**	**SVI (mL/g)**
pH Induced	2.17	8.6	4237.3
$MgCl_2$	2.17	8.3	2284.3
$Mg(OH)_2$	2.18	7.7	1718.8
$NMg(OH)_2$	2.19	6.7	1438.8

Table 2: The values of breakage and recovery factors of fresh flocs from consecutive breakage/re-formation cycle.

Harvesting procedure	**Average floc size (nm)**	**Strength Factor (%)**		**Recovery Factor (%)**	
		2nd	**3rd**	**2nd**	**3rd**
pH Induced	42.1	48.14	35.96	96.25	27.38
$MgCl_2$	47.3	97.77	98.30	20.34	7.95
$Mg(OH)_2$	49.8	94.14	96.9	48.33	37.86
Nano-$Mg(OH)_2$	48.8	94.34	99.78	215.97	150

Table 3: The values of breakage and recovery factors of settled flocs at different hydrodynamic shear strength.

Coagulating System	**Strength Factor (%)**			**Recovery Factor (%)**		
	300	**400**	**500**	**300**	**400**	**500**
pH Induced	98.85	98.45	96.77	243.86	149.17	125.34
$MgCl_2$	95.56	98.32	95.99	509.52	97.64	42.86
$Mg(OH)_2$	99.37	96.10	90.51	1739.29	98.95	4772.73
Nano-$Mg(OH)_2$	82.26	92.19	99.76	55.81	146.18	1536.36