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Struvite Crystallization Applying Natural Flocculants

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Abstract
The study is focused on improving struvite crystallization by flocculation with natural products as chitosan, gelatine, pectin and zeolite aiming to form large crystals obtained. The best results reported when chitosan in dose of 2 mg/L as natural flocculant was applied to the crystallization process. The diameter of precipitated particles was 5.77 µm. Applying of other natural products as flocculants demonstrated heterogeneity in the diameter of the precipitated particles. Scanning electron microscopy (SEM) of precipitated products indicated some of typical orthorhombic long struvite crystal structures observed 43 days after crystallization.
The study demonstrated that struvite crystallization combined with flocculation by natural products improves the crystals particle growth and struvite precipitation process.
Keywords: *struvite, flocculants, improved crystallization, wastewater.*

1. Introduction

In recent decades, environmental protection is of great interest. Aiming to reduce usage of non-renewable resources, many researchers are seeking alternative sources of phosphorus and nitrogen. It is estimated that the phosphorus rocks will be depleted within 90 years. Agricultural production depends on the use of P, and so far, there are only a few alternative sources [1].
Some of industrial and domestic wastewaters, and manure are contaminated with multiplicity nutrients. Alternatively, the wastewaters containing significant amount of ammonia and phosphates could be applied for struvite precipitation. The product precipitated could be used as a slow release fertilizer [2].
Many studies review different factors affecting struvite precipitation and crystal growth such as initial ion concentrations; molar ratio between NH_4^+, PO_4^{3-} and Mg^{2+}; pH values; aeration rates; temperature; type of crystallization reactor etc. The molar ratio of PO_4^{3-}: Mg^{2+} is a main parameter. Some studies reported the optimum range of 1: 1 or 1: 1.2 [3, 4, 5]. Struvite crystal growth could be improved by coagulation process aiming destabilization of fine particles and agglomeration in macro phase. Different coagulants/flocculants such as metal ions and polymers applied in water and wastewater treatment process. The main products applying in industrials are different polymers such as polyacrylamides, copolymers between acrylamide-acrylate, dimethyldial-lylammonium ion and acrylamide etc. The advantage is forming of large, dense flocs, but, polymer and synthesis products could be potentially ecological problem due to toxicity and difficult biodegradation [6]. Natural products have gained great interest as biocoagulants/bioflocculants because of low cost, biodegradability, non-toxic of these biopolymers [7] such as chitosan, clay, alginate, zeolite etc. For example, chitosan is linear amino-polysaccharide and it is used as cationic biopolymer, also classified as green product [8]. Some advantages of chitosan usage are non-toxic product, less sensitive to Ph change compared to the conventional metal ions, successful application for water, wastewater and sludge treatment [9, 10] Latifian [11] studied application of chitosan, alginate and bentonite as natural coagulant/flocculant compared to polymeric Poly-DADMAC.
Gelatine is water-soluble protein originated from animal skin, bones etc [12] and it could be applied as natural flocculant contained both anionic and cationic groups (an amphoteric polyelectrolyte). Pectin contains complex matrix of various types of polysaccharides, protein and lignin and it could be classified as anionic polysaccharides [13]. Pectin and PAM are compared as flocculants on treatment in kaolin suspension [14]. The obtained results shown that pectin was successfully applied in ten times lower dose than PAM flocculant at pH=3, so natural products as pectin are effective coagulant/flocculant in a small amount.
Natural zeolite is known as adsorbent of different metal ions from water and wastewater [15].
The coagulant/flocculant addition could be applied in struvite crystallization process to improve crystals aggregation. Their role is aggregation on fine particles to suspension. Coagulants/flocculants addition affect the stability of the colloidal negatively charged particles and the added chemicals are generally positive charged [16, 17]. Le Corre [18] investigated addition of ferric and aluminium salts, calcium compounds, polyDADMAC and alginate aiming destabilising and coagulating struvite particles. The obtained results showed that the struvite have high negative zeta-potential between -17.5 and 27.6 mV and the optimal flocculant affecting to form greatest struvite crystals is Poly-DADMAC.

In the present study, the possibility of natural products as chitosan, zeolite, gelatine and pectin as flocculants to improve struvite precipitation process was carried out. The results obtained were compared to non-flocculant struvite crystallization process.

2. Material and methods

Waste sludge originated from Municipal Wastewater Treatment Plant (Burgas MWWTP) was applied as phosphorus and nitrogen source for struvite precipitation. In lab scale, the sludge was centrifugated (Centrifuge DLAB DM0412, 3000 rpm at 5 min). The supernatant obtained contained phosphate of 291 mg/L and ammonia ions of 1172 mg/L determined by cuvette tests (Hach Lange DR 3900).
Burgas WWTP has average wastewater flow of 1208800 m3/month. The phosphorus removal process in the municipal WWTP is performed with Chemical Phosphorus Removal (CPR) (dosing of FeCl3) and Biological Phosphorus Removal (BPR). The plant is conventional activated sludge system with Denitrification/Nitrification zones. Sludge stabilization is carried out in anaerobic open reactor and centrifugation is applied as dewatering technique. The balance of phosphorus in the Burgas - MWWTP is presented in table 1.

Table 1. Phosphorus balance in manicipal wastewater treatment plant (MWWTP) - Burgas

WWTP	Inlet P [kg P/d]	Outlet P [kg P/d]	P directed to dewatering system [kg P/d]	Solid waste [kg P/d]	Returned P load [kg P/d]
Burgas	**103**	**23**	**120**	**80**	**40**

Salt concentrated flow (sea brine) obtained from Pomorie Salt Lake containing 66.82 g Mg2+ /L and Calcium ions of 2.04 g Ca2+/L was applied as alternative magnesium source.
The supernatant (previously alkalized by Sodium Hydroxide solution, 1.5 %, pH=8.95) and sea brine were mixed in molar ratio P:Mg (1:2) and stirring for 15 minutes at 50 rpm.
Aiming better realization of struvite crystallization, the natural flocculants as chitosan, zeolite, pectin and gelatine in doses of 1 mg/L, 2 mg/L and 5 mg/L were applied to the precipitation process.
The zeta potential and size of formed particles/crystals were measured by Particle Size Zeta Potential Analyser (Nanotrac Wave II).
Scanning electron microscopy (SEMoscope IEM11) was applied to be observed crystals obtained by struvite precipitation process.

3. Discussion

The struvite precipitation process was carried out within 15 minutes. Therewith, the size and zeta potentials of precipitated particles were measured.
Some studies presented that struvite crystals have higher negative zeta potential (higher negative surface charge) which affect to particle aggregation and precipitation process [19, 20]. Higher negative zeta potential affects of crystals precipitated and no aggregation is observed at higher pH over 9.5 [21]. On the other hand, supersaturation of struvite particles is increasing with pH elevation. The process could be carried out of range 7.0-11.5, as optimal values is range 7.5 - 9.0 [22]. Aiming improved precipitation and aggregation process, the experiment was carried out at pH=9. Different natural flocculants were applied in the precipitation process with purpose better flocculation, reduce aggregation ability and higher positive potentials of particles precipitated and higher efficiency for struvite precipitation process.
The zeta-potential of suspended particles varies depending on the type and dose of applied natural coagulant. A negative potential of – 52.15 mV for control probe is reported. The series of experiments with flocculants indicated wide range of polarities of -124.8 mV to 123.1 mV according to type and dose of natural coagulant. The results presented that addition of 1 mg/l dose of all types of natural coagulants demonstrated negative polarities while doses of 2 mg/L and 5 mg/L indicated positive values, except dose of 5 mg/L of pectin. The zeta potentials obtained are presented in Figure 1.

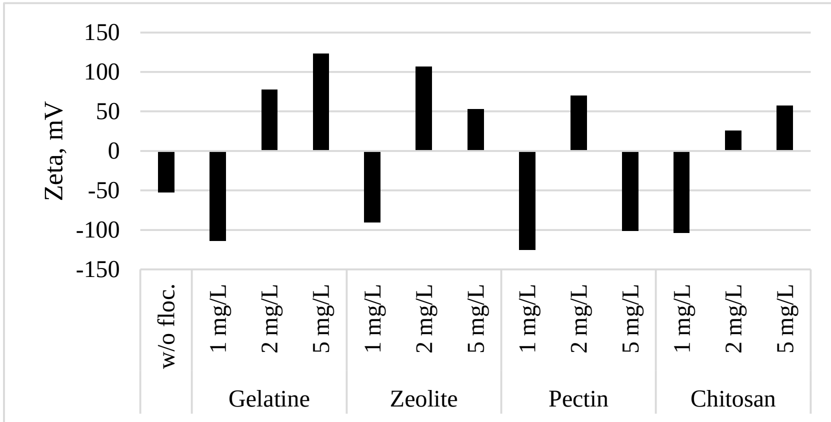

Fig. 1. Zeta potentials of precipitated particles applying different coagulants

Particle size of struvite crystals is important characterization when it would be applied as fertilizer – larger particles lead to higher soil retention effect of nutrients in the soil [23]. Forming of big crystals requires a long reaction time for the growth of particles. Some studies reported larger particle size of struvite crystals -350 µm (operation time of 1 hour) [24], 1000 µm (operation time of 5 days), or 2000 µm (operation time of 42 days) [25]. Le Corre [26] reported that particle sizes of 13.416 and 15.157 µm after 5 min of experiment when pure solutions were applied in struvite precipitation process. Smaller particle size corresponds to our results obtained with real wastewater. The diameter of particles was measured stirring process. The best results reported when chitosan in dose of 2 mg/L as natural flocculant was applied to the crystallization process. The diameter of precipitated particles was 5.77 µm. Applying of other natural products as flocculants demonstrated heterogeneity in the diameter of the precipitated particles. The flocculant addition improves the crystals particle growth. When the experiment is carried out without natural coagulant, the diameter of the most of crystals obtained was 1.71 µm. Chitosan and pectin in dose of 2 mg/L indicated larger struvite precipitated crystals than those obtained at non-flocculant experiment. When pectin is applying as natural flocculant, the positive polarity is reported at dose of 2 mg/L, and the diameter of precipitated particles is about 4.2 µm. Zeolite and gelatine indicated positive polarities when doses of 2 and 5 mg/L were applied. The largest amount of particle is reported in the maximum dose of 5 mg/L, size diameter of 1.058 µm for gelatine and 1.25 µm for zeolite, respectively. The sizes of struvite particles obtained at applied flocculants and non-flocculant experiment are summarized in Table 2.

Scanning electron microscopy (SEM) of precipitated products indicated some of typical orthorhombic long struvite crystal structures observed 43 days after crystallization. Figure 2 shows some of crystal aggregations when chitosan and zeolite as natural flocculant was applied. It was observed growth of crystals up to range of 18-54 µm.

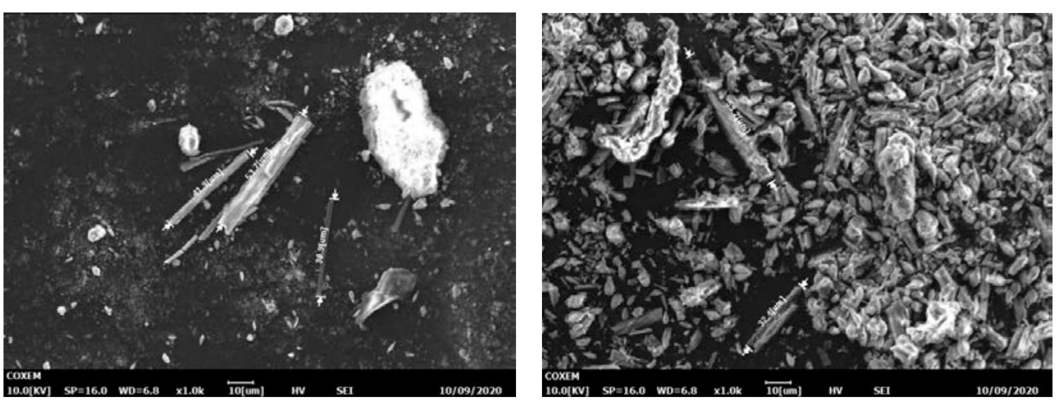

Fig. 2. Typical struvite crystals obtained when chitosan and zeolite were applied as flocculants.

Phosphate removal rates (%) applying different doses of natural flocculants and non-flocculant experiment (control probe) were studied. The precipitation rate of 66.2% for control sample was observed. When flocculants in different doses were applied, the phosphate precipitation rates at range of 77-87 % were achieved. The efficiencies (%) are shown in Figure 3.

Table 2. Diameter of precipitated particles in different experiments

Flocculant experiment						
param. / Flocc.	diam , µm			Vol %		
	1 mg	2 mg	5 mg	1 mg	2 mg	5 mg
Gelatine	4.31	5.75	5.76	57.5	11.4	20.7
	1.038	1.714	1.058	36.3	65.6	79.3
	0.322	0.554		6.2	23	
Zeolite	5.67	3.24	5.66	2.3	36.5	21.2
	2.54	1.074	1.248	84.5	63.5	78.8
	0.311			13.2		
Pectin	2.175	4.2	5.44	64.9	82.4	88.9
	0.56	0.518	0.802	35.1	17.6	11.1
Chitosan	5.75	5.77	5.09	27.7	100	68.9
	1.135		1	72.3		31.1

Non-flocculant experiment	
Diam, µm	Vol %
5.86	11.2
1.71	71.1
0.4	17.7

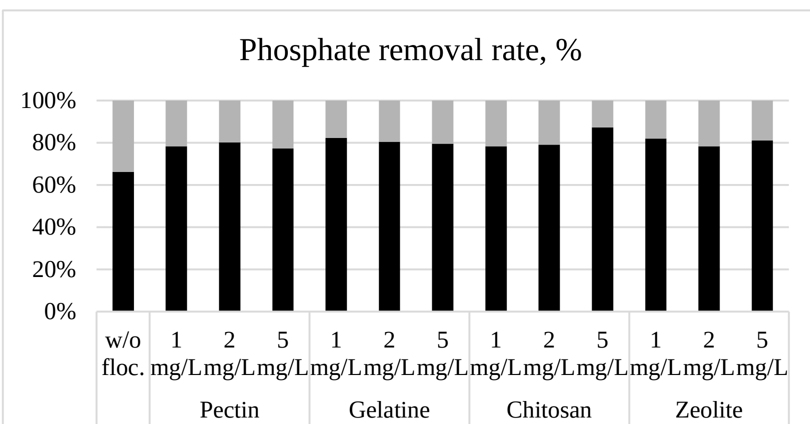

Fig. 3 Phosphate removal rates applying different doses of floculants

4. Conclusions

In recent years eco-friendly products are in great interest. Coagulation/flocculation processes are widely use of water/wastewater treatment. Main coagulants as polymers or chemical reagents cause pollution due to toxicity and difficult biodegradation. Alternatively, natural flocculants have gained great interest as biocoagulants/bioflocculants because of low cost, biodegradability, and non-toxic. One application of the natural products could be improving struvite crystallization process. The study demonstrates that chitosan, pectin, gelatin and zeolite are suitable coagulants contributing to form of large crystals.

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