

Correlations between floc physical properties and optimum polymer dosage in alum sludge conditioning and dewatering

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Abstract

This paper aims to examine the correlations between floc physical properties, such as size, density, structure (in terms of fractal dimension) and optimum dosage in an alum sludge conditioning with organic polymer and also dewatering using an air pressure plate apparatus. Initially, optimum dosage was evaluated by a modified specific resistance to filtration (SRF). Thereafter, floc size, density and structure were examined in greater detail by means of an image analysis system. The results of this investigation reveal that: (1) polymer conditioning of alum sludge can result in a significant increase of floc size with a plateau to be reached in higher dosages; (2) higher floc effective densities are associated with larger doses; and (3) increased fractal dimensions are associated with increased dose, particularly in small dosages, this reflecting the increased compactness of floc structure. However, no direct correlation was found between floc physical properties and optimum dose both in conditioning and dewatering except for the weak correlation in floc size and optimum dosage.

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1. Introduction

Alum sludge can be produced from many different water treatment systems with aluminium sulphate as the primary coagulant. A common view is that an alum sludge consists of bulk water together with a floc phase. The flocs form a three-dimensional network and are essentially a two-phase mixture of solid particles and interstitial water [1]. The particles can be thought as forming the skeleton of the floc while the interstitial water refers to water trapped within the crevices of the floc. Characteristics of alum sludge can be described in different categories, such as physical and chemical aspects, etc.

Floc size, density and fractal dimension characterise the sludge's physical properties. An accurate measurement of floc size is difficult because of its physicochemical nature. The methodologies for such sensitive measurements are prone to errors and can often be misleading. Three principal methods have been reported for floc size/size distribution measurement [2]. The floc density, more accurately the floc effective density, ρ_e , is defined by the density difference $\rho_e = \rho_f - \rho_w$ in which ρ_f and ρ_w refer to the density of the floc and water, respectively. Effective density and size are interrelated properties of the floc. Early studies [3,4]

have shown a size–density dependence for smaller flocs, in particular, the general trend showing a decrease in density as size increases. Now it is widely accepted that these two parameters are not mutually independent and tend to conform to a power-law type empirical relationship, as shown in Eq. (1) and known as size–density function:

$$\rho_e = Ad^{-n} \quad (1)$$

where d is a representative diameter of the floc, A and n are fitted constants. From humic flocs, n is generally found to be in the range 1.8–2.0 and parameter A is sensitive to the alum dose and pH [5]. The floc size and density data for flocculated sludges can provide information about the coagulant–particle interactions and its effects on the sludge performance. There are several experimental techniques available for the measurement of floc density, namely, sedimentation techniques, light scattering and other methods. A brief review of some of these techniques is provided by Gregory [6].

From Eq. (1), the non-linear relationship between floc density and size implies a change in floc porosity with size, i.e. causing changes in the floc mass. Meakin [7] deduced that floc mass (m_s) scaled with its size, such as floc diameter, in the form of:

$$m_s \propto d^{D_F} \quad (2)$$

where D_F is called the fractal dimension, strictly being a mass fractal dimension. It is a quantitative measurement of

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floc structure and a description of how the particles are organised with the floc interior. The higher the fractal dimension (maximum 3), the more compact the floc. Bache and Hossain [8] found that the humic flocs could be characterised by $D_F = 1.0$. Wu et al. [9] found the D_F of raw alum sludge to be 1.18. These generally suggest that raw alum sludge is characterised by a low degree of floc compaction. When $D_F \approx 1.0$, it implies that $m_s \propto d$, i.e. a chain formation which is sometimes referred to as ‘necklaces’ (structure). Since the mass of a floc (m_s) is related to the number (N) of primary particles within the floc by $m_s = Nm_0$ (m_0 refers the mass of primary particle), Eq. (2) can be expressed as:

$$N \propto d^{D_F} \quad (3)$$

For a floc made up of N particles, each of mass m_0 and volume v_0 , the volume fraction of solid ($1 - \varepsilon$) in the floc is:

$$1 - \varepsilon = \frac{Nv_0}{V_f} \quad (4)$$

where $V_f = \pi d^3/6$, is individual floc volume and ε refers to the porosity. By combining Eqs. (3) and (4), it follows that:

$$1 - \varepsilon \propto d^{(D_F-3)} \quad (5)$$

By comparing Eq. (5) and density function, n in Eq. (1) is related to D_F in terms of:

$$D_F = 3 - n \quad (6)$$

It is well known that sludge dewaterability can be improved by polymer flocculation. A number of studies have demonstrated that the floc size, density, structure, etc. play an important role in sludge dewatering. It has been reported that polymer conditioning can lead to the shift towards larger size aggregates of flocs [9–13]. However, Wen et al. [11] reported that the floc size does not always show a unique effect on sludge dewatering as they found no correlation between floc size and optimum dose determined on the basis of sludge dewatering. On the other hand, there is some evidence showing that higher densities are associated with higher doses [14,15]. However, concerning with floc effective density and compactness, Wen et al. [11] reported that the floc density and fractal dimension (D_F) of synthetic sludge were insensitive to the polymer doses. Yet, it appears that there is insufficient data in the literature to identify the change of floc properties to the addition of polymer. In addition, does the floc size relate directly with sludge dewaterability? What is the role of floc size in determination of the optimum polymer dosage? What is the relationship between floc structure and sludge dewaterability? These questions are still unclear and form the main focus of this study.

In this study, initially, alum sludge generated from the treatment of upland, low-turbidity, coloured water was conditioned with an anionic organic polymer (Magnaflow LT 25), and the optimum polymer dose was gauged by modified specific resistance to filtration (SRF) [16]. Thereafter, floc size, effective density and fractal dimension were examined

in greater detail using an image analysis system. Primary emphasis was placed on the response of such floc physical properties to varied polymer addition. It was followed by the dewatering tests using an air pressure plate apparatus for identifying the dewatering behaviour after conditioning. Finally, the study focuses on the discussion of seeking correlations between the optimum polymer dose and floc physical properties.

2. Experimental section

2.1. Sludge, polymer and generation of flocs

The alum sludge was collected from sludge holding tank of a waterworks receiving a low-turbidity, coloured water coagulated with aluminium sulphate. The sludge had an initial solids concentration of 4.595 mg/l and pH of 6.8. After collection, the sludge was stored at room temperature ($20 \pm 2^\circ\text{C}$) for the period not exceeding 2 weeks. The sludge was conditioned using Magnafloc LT25 (*Allied Colloids UK Ltd., now Ciba Speciality Chemicals Ltd.*), this being an anionic organic polymer with molecular weight in the range $(1.0\text{--}1.5) \times 10^7$ and charge density of 15–30%. A 0.01% stock solution was prepared using nanopure water and allowed to stand for 24 h prior to use. Thereafter, the stock solution was used within the next 24 h period before being discarded.

Polymer was added to 200 ml sludge samples with dosages in the range 0–30 mg/l. Following polymer addition, the sludge was subjected to 30 s of rapid mixing followed by 1 min slow mixing to promote flocculation. To estimate the modified SRF [16], conditioned sludge samples and resulting supernatant were subjected to filtration tests. These were performed on 100 ml sludge/supernatant samples in a Buchner funnel using standard procedures [17]. During the tests, the pressure differential was maintained at 760 mmHg and Whatman 1# filter paper was used as the filter medium.

2.2. Image analysis system

CCTV recordings and image analysis were used to measure the floc size and sedimentation rate. The components of the image analysis system are illustrated in Fig. 1.

Raw sludge was dosed with polymer LT 25 ranged from 0 to 20.0 mg/l, respectively. For each run, 50 ml of the concentrated suspension was diluted using 250 ml nanopure water and stirred slowly (speed at 13 rpm, $G = 6.5 \text{ s}^{-1}$) in the Jar test equipment which was held in a water bath at 20°C (see Fig. 1). The free-settlement column is a temperature-controlled Perspex column (cross-section of 121 cm^2) with a Perspex plate facing the JVC camera. Nanopure water is used as the settling medium. Since the fluid viscosity is sensitive to temperature and can have a significant effect on the experiment, the column was provided with a water jacket (see Fig. 1) to keep the temperature

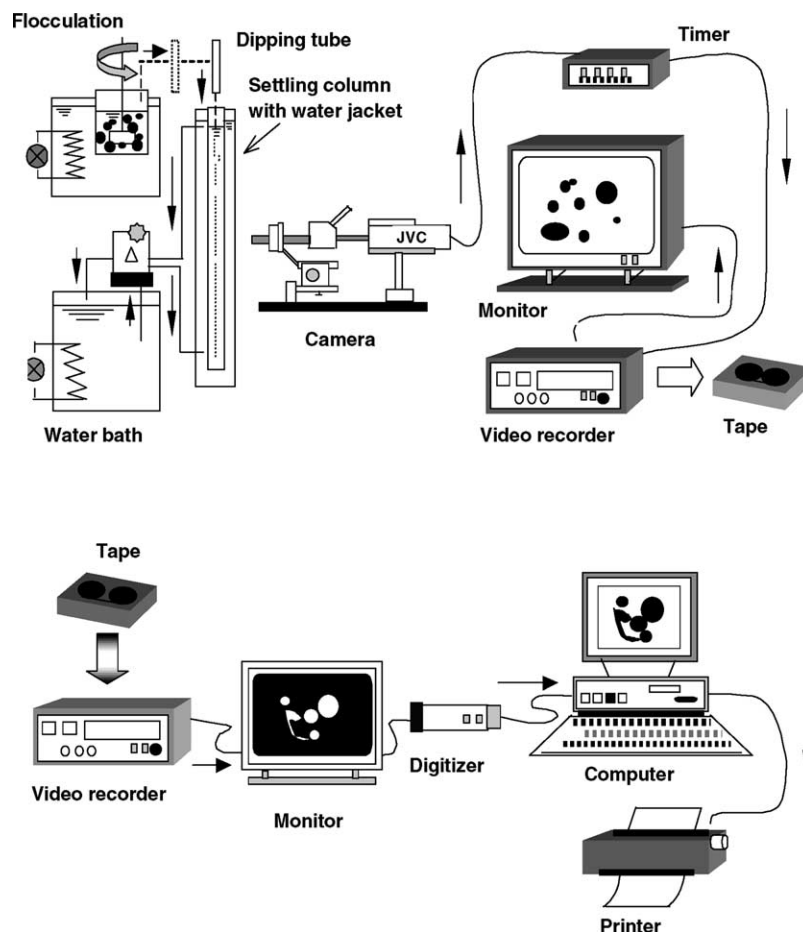


Fig. 1. Schematic description of methodology for images analysis system: recording of floc images (above) and floc images digitised and analysed (bottom).

of the column at 18 °C, 2 °C below the temperature of the water bath which held the sludge floc sample in Jar test equipment. This ensured that when flocs were transferred into the column, the sampled water containing sludge flocs was less dense than the water within the column and effectively floats. Flocs then settle through this layer. After slow mixing for 10 min, small samples of flocs were transferred using a 0.7 cm diameter dipping tube and carefully released into the sedimentation column. Movements of individual flocs in the settling column were recorded in a tape by video camera equipped with a microscope. Thereafter, the recorded flocs were analysed using the image analysis program via the replaying of the video tape, shown in Fig. 1. Each data set contained details of over 100 flocs.

The image analysis software makes use of Stokes' equation to calculate the density as described in Bache and Hossain [8] and Bache et al. [18]. Here, the floc effective diameter is defined as the geometric mean $d = (d_{\max} \times d_{\min})^{1/2}$ in which d_{\max} and d_{\min} are the maximum and minimum dimensions across the floc image, respectively. The image analysis program provides information on floc perimeter, area, maximum projection, minimum projection and degree of circularity and translates the observed terminal settling velocity into the effective density.

2.3. Dewatering tests

An air pressure plate apparatus was employed for the dewatering tests, as described in Zhao and Bache [19]. The air pressure plate apparatus is a porous ceramic plate located in a pressure chamber. Samples are placed on the porous ceramic plate and a positive air pressure is supplied via a compressor. Moisture is driven from the samples through the ceramic plate. Conditioned alum sludge samples were poured into standard plastic rings (1 cm in height and 5 cm in diameter), which were placed on the ceramic plate of the air pressure plate. The air pressure was maintained at 5 bar (1 bar = 100 kPa). Moisture contents (MC) of sludge cakes were measured hourly as an indicator of the dewatering extent corresponding to the dewatering time for the apparatus.

3. Results

Fig. 2 illustrates the response of modified SRF as a function of polymer dose. The optimum dose which brings about the lowest modified SRF in Fig. 2 is 10 mg/l.

Fig. 3 shows a typical plot of data (derived from the image system) between floc diameter and effective density at

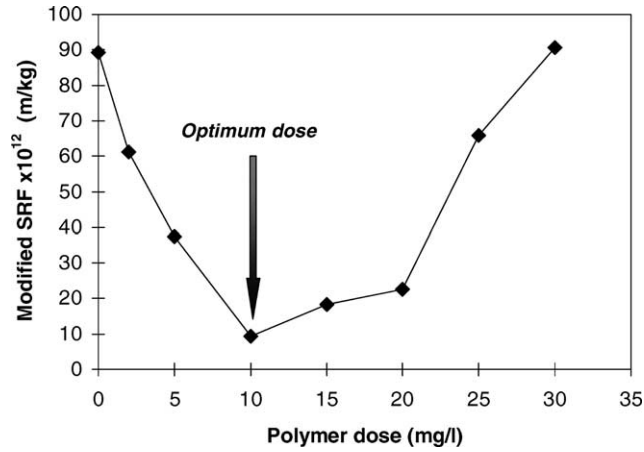


Fig. 2. Modified SRF as a function of polymer dose.

fixed polymer dose. It indicates clearly that floc effective density increases with decreasing floc diameter. According to the floc effective density data and floc dry density value of 1.76 g/cm³ (determined by a pycnometer in this study), floc porosity (ϵ) can be calculated using the equation derived by Tambo and Watanabe [4]. Assuming that the sludge floc consists of two parts, a solid part and a part filled with supernatant, the porosity within floc can be expressed as follows:

$$\epsilon = 1 - \frac{\rho_f - \rho_w}{\rho_s - \rho_w} = 1 - \frac{\rho_e}{\rho_s - \rho_w} \quad (7)$$

The result of calculated ϵ is also shown in Fig. 3. It can be seen that the increase of floc effective density is due to the decrease of floc porosity, indicating the tight compactness of floc.

Additionally, Fig. 4 provides the plots of floc size and effective density with varied polymer dose in the range from 0 to 20.0 mg/l. Comparison of the plots in Fig. 4 shows at the high dose, there is considerable reduction in the scatter. The trend lines in each set were calculated using a least squares analysis. Inspection of Fig. 4 shows that the effective density increases with increasing amount of polymer added. By using the size–density function, as shown in Eq. (1), and further relation to fractal dimension, D_F , shown in Eq. (6), computed values of D_F are in the range 1.06–1.77 corresponding to the polymer dose in the range 0–20 mg/l. This leads to the illustration shown in Fig. 5. As the D_F is the indicator of floc structure, the plot in Fig. 5 leads to a reasonable belief that the degree of sludge floc compactness increases after polymer conditioning. However, it is noted that

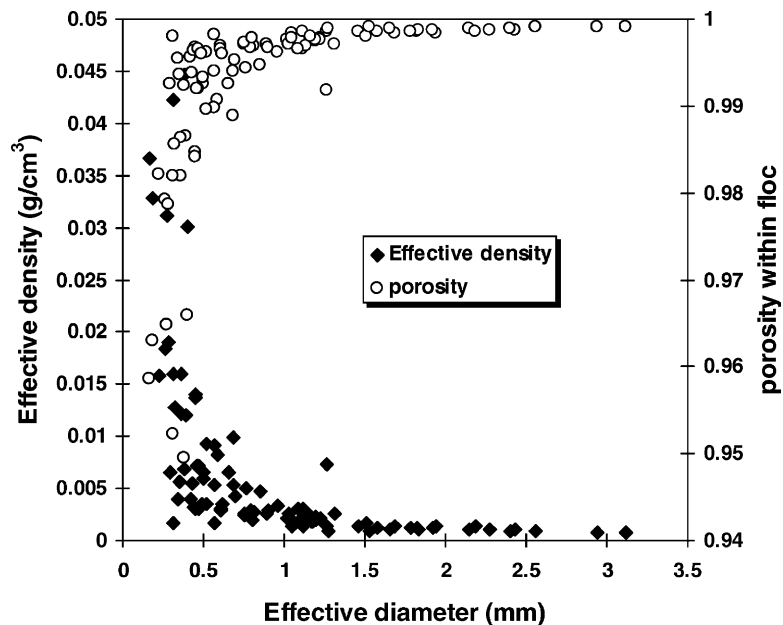


Fig. 3. Plotting of floc effective density and porosity versus effective diameter at polymer dose of 10 mg/l.

D_F is not a critical parameter in determining the optimum dosage which occurs at 10.0 mg/l.

The trends shown in Fig. 6 illustrate the sensitivity of the particle size distribution to the polymer dose. The vertical

axis of Fig. 6 represents a mass fraction of the total mass which is derived from the CCTV caught flocs. It is seen from Fig. 6 that the whole particle size distribution shifts progressively to larger sizes with increasing polymer dosage, when

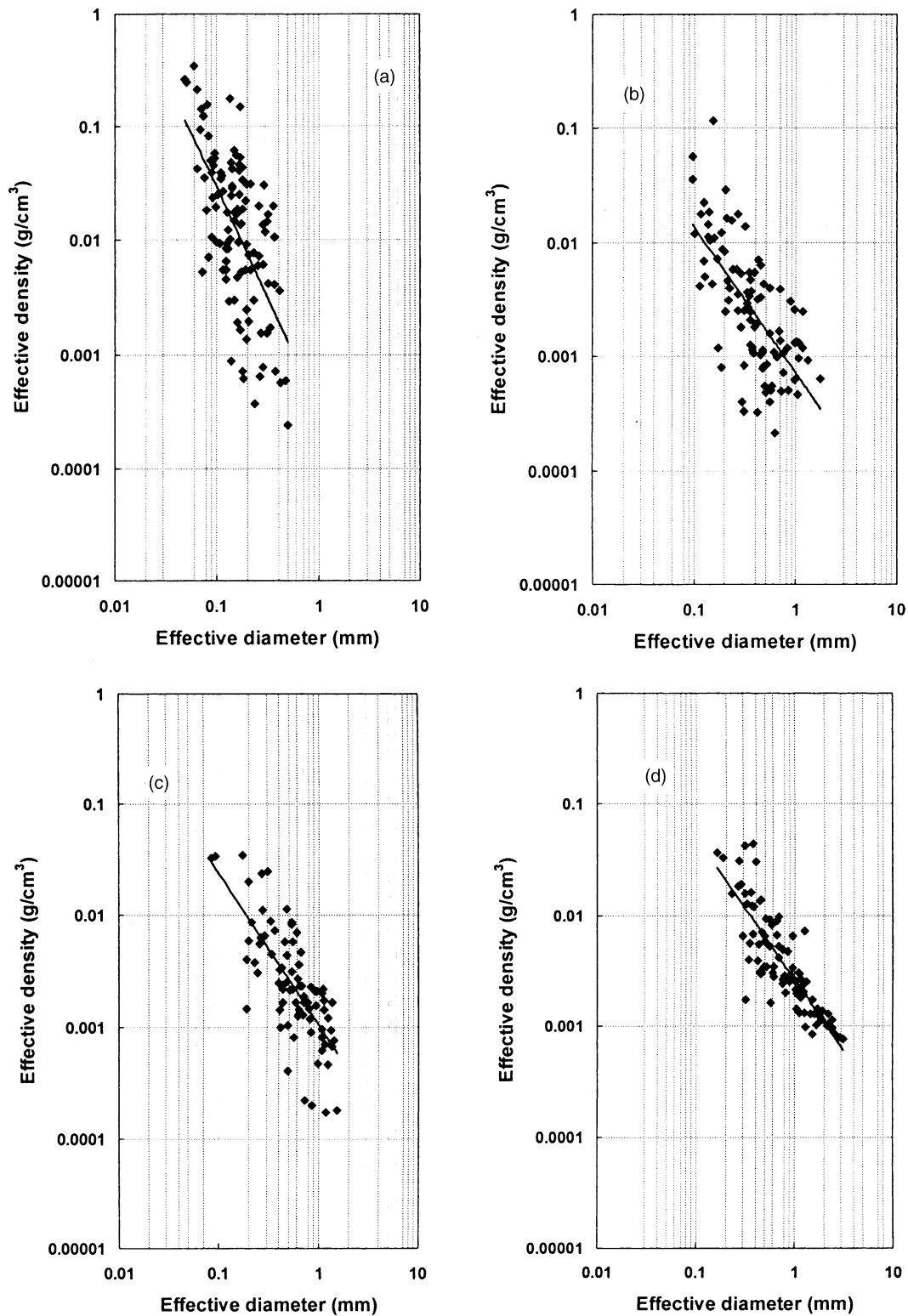


Fig. 4. Plots of floc size against the effective density for varied polymer doses: (a) raw alum sludge, (b) at dose of 2 mg/l, (c) 5 mg/l, (d) 10 mg/l, (e) 15 mg/l, (f) 20 mg/l (sludge SS = 4.595 mg/l).

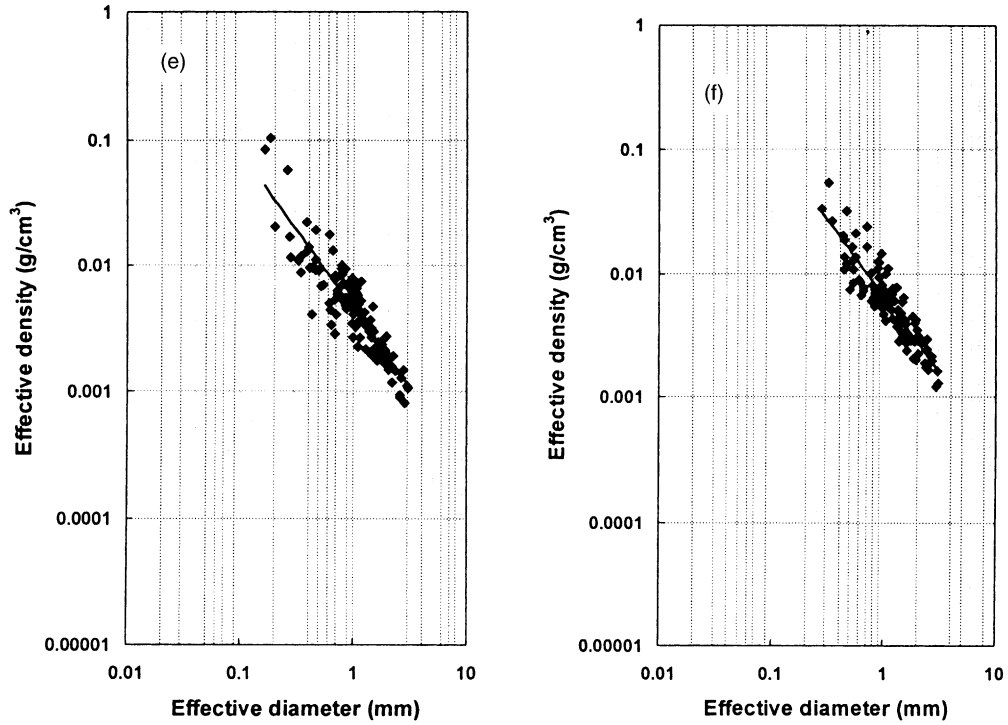


Fig. 4. (Continued).

dose ≤ 10 mg/l, which is the optimum dose determined by modified SRF, as shown in Fig. 2. Beyond 10 mg/l the particle size distribution becomes insensitive to further increases in polymer dose.

The results of dewatering test using an air pressure plate apparatus are shown in Fig. 7. Under the condition of applied pressure of 5.0 bar, the dewatering extent (in terms of cake moisture content) associated with the dewatering

time follows a pattern showing decrease in MC with increased dewatering time. It is noted that the silent feature in Fig. 7 is the insensitivity of MC with polymer dose, particularly after 2 h dewatering. Again, comparing with the dewatering behaviour for the doses of 2.0–20.0 mg/l, there is no significant change in dewatering extent at the polymer dose of 10 mg/l, which is the optimum dose evaluated by modified SRF.

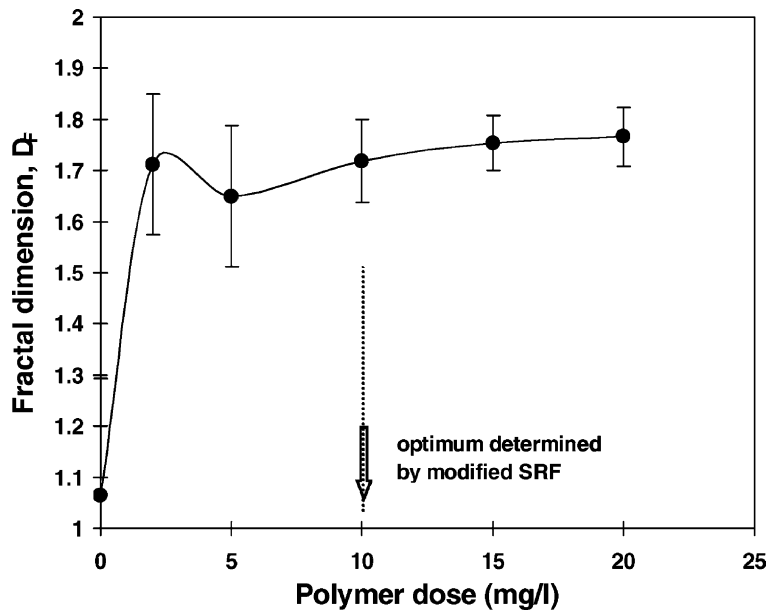


Fig. 5. Fractal dimension (D_F) as a function of polymer dose (calculation of D_F being derived from the data illustrated in Fig. 4).

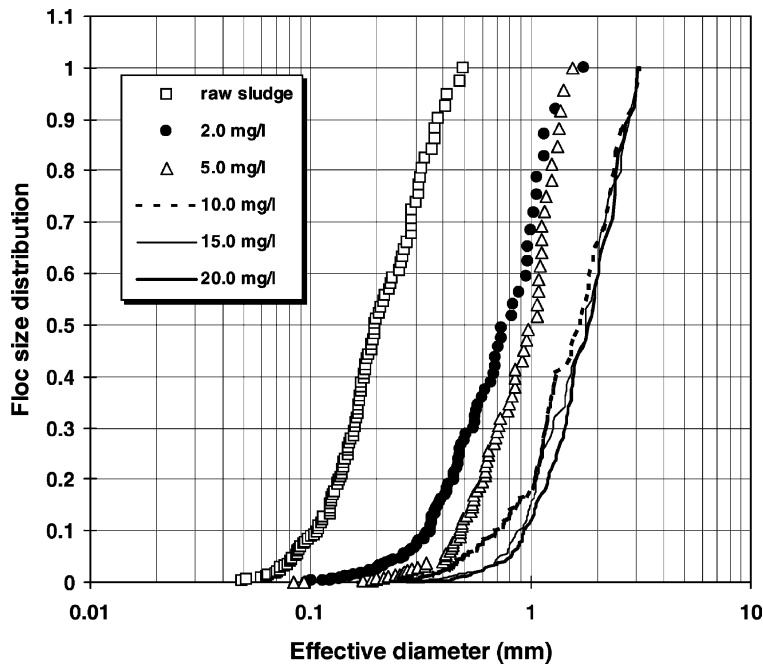


Fig. 6. Trend lines of mass based particle size distributions of polymer dosed alum sludge.

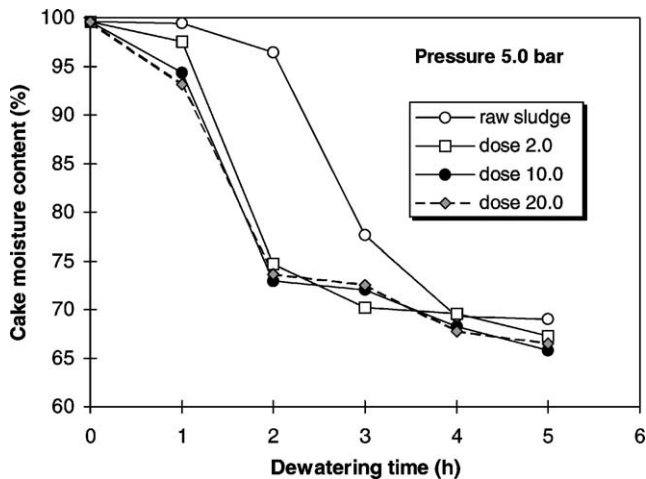


Fig. 7. Cake moisture content as a function of polymer dose during dewatering using an air pressure plate apparatus.

4. Discussion

The aim of this study lies in the investigation of the correlations between floc physical properties, such as floc size, effective density, structure and an alum sludge dewaterability in terms of polymer optimum dosage during the conditioning and dewatering. To achieve this, optimum dosage was firstly determined by modified SRF in which its utility has been demonstrated in early work [16]. Thereafter, floc physical properties of an alum sludge were investigated in greater detail by making use of the image analysis system. At first sight, the relationship between floc size and effective density

at fixed polymer dose as shown in Fig. 3 appears to be remote from the aim of this paper. Yet, it reinforces a complex physicochemical process of floc formation since the flocs are of different sizes, of different degree of compactness and are interconnected to form large aggregate structures.

Emphasis stemmed from the image system data was the information of the response of floc physical properties to polymer addition, as shown in Figs. 4–6. Although previous studies from the literature revealed certain discrepancies on the changes of alum sludge characteristics under the polymer addition [20], the results from this study indicate that polymer dosing can result in a shift towards large size aggregates of flocs, this shift ultimately tending to a plateau irrespective of the increasing polymer dose (see Fig. 6). Moreover, evidence demonstrates higher floc effective densities being associated with higher polymer dose (see Fig. 4). To illustrate the change of particle size quantitatively, the median particle diameter (d_{50}) derived from each particle size distribution curve in Fig. 6 is plotted as a function of polymer dose in Fig. 8. This provides a useful indicator of the response of trends to increasing polymer dose. More importantly, the change of floc size in Fig. 8 at dose of 10 mg/l marks some type of optimum which links that as gauged by modified SRF in this study (Fig. 2). However, the inspection of Fig. 4 shows that, for a given floc size (say 1 mm), the effective density follows the pattern which is also illustrated in Fig. 8. Of interest is that there is no significant change in behaviour in terms of effective density at 10.0 mg/l. It suggests that optimum is not directly attributable to the behaviour of the floc density.

D_F is a quantitative measurement of floc structure and a description of how the original particles are organised with

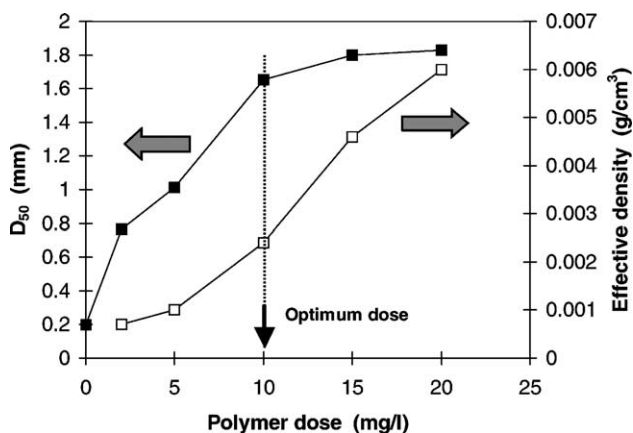


Fig. 8. Dependence of the floc size (D_{50}) and effective density (for floc diameter of 1 mm) in the polymer dosage, based on data shown in Figs. 4 and 6.

the floc interior. This study shows there is significant difference of the fractal dimension (D_F) between raw and polymer dosed sludge samples (see Fig. 5). Once the dose exceeds about 2.0 mg/l, the D_F value, though showing a marginal increase with dose, is more or less constant at the average value of 1.72 ± 0.09 , indicating that the degree of sludge floc compactness is insensitive with polymer dosage. More importantly, it is noted that the D_F appears not to influence the position of the optimum because D_F is hardly changing with dose above 2.0 mg/l. Of interest is that it appears that the similarity in the patterns in Figs. 5 and 7 beyond polymer dose of 2.0 mg/l reflects some type of correlation, but it needs the further investigation.

Although it is widely accepted that the floc physical properties have a significant effect on sludge dewaterability, this study reveals that there appears no direct correlation between either floc size, density or structure and sludge dewaterability (evaluated by the modified SRF) in spite of the weak correlation of floc size and optimum dose, as shown in Fig. 8. This view is reinforced by the results of dewatering tests using a lab-scale air pressure plate apparatus in which the obviously improved dewatering extent (started from the dose of 2.0 mg/l, see Fig. 7) does not show the link with optimum dosage (at dose of 10.0 mg/l, see Fig. 2). Here, it should be pointed out that, although the MC is the measurement of dewatering extent, MC is not standardised for evaluating dewaterability [21]. Actually, it is strongly influenced by the type of dewatering mechanism, the procedure of dewatering process and the scale of the dewatering apparatus, etc. [19], thus causing a broad range of values. Nevertheless, the dewatering test in this study shown in Fig. 7 provides the useful profile of dewatering behaviour with varied polymer dosage.

Although it is questionable to compare current work with the results obtained from other type of sludges due to the lack of alum sludge data in the literature, the finding from this study agreed with that reported by Wen et al. [11] and

recently by Lee and Liu [22]. Both studies have reported the failure of the attempt to seek the direct link between floc size and optimum dosage determined on the basis of sludge dewatering. This appears to contradict the role of floc physical properties in polymer conditioning. However, it is believed that the floc properties (size, density, structure, strength and even viscosity of the bulk solution, etc.) are the reflects of the interaction between polymer and the sludge particles. Any single floc property index may not correlate well with the true sludge dewaterability. The best dewatering ability after polymer addition may be tied in the integrated effects of above mentioned floc properties.

Overall, concerning with the relations between optimum dose and floc size, density and fractal dimension, etc. under polymer conditioning, one should keep in mind that the integrated effects should be considered. However, further research is required in order to reveal the mechanism behind the optimum is highly desirable.

5. Conclusions

Despite the possible limitations in the laboratory tests, the following conclusions can be drawn from the present study.

- It appears that the polymer dosing leads to a shift of the particle size towards groupings of larger diameter with a plateau to be reached in higher dosages. Higher floc effective densities are observed which associated with the increased polymer doses. Polymer dose can result in an obvious change of floc structure in terms of fractal dimension, particularly in small dose (say 2.0 mg/l), meaning the increased compactness of floc structure. However, further increase of polymer dose will lead to the quite similar floc structure to be formed as the fractal dimension is insensitive to further doses.
- The weak correlation in floc size and optimum polymer dosage evaluated by modified SRF is observed in this study. But it is noted that there is an indication that the optimal dewatering behaviour does not occur in the case of flocs with the highest density and most compact structure.
- Sludge best dewaterability may be the results of the integrated effects of floc properties on dewatering behaviour. Any single floc property index, such as floc size, density and fractal dimension, etc. may not correlate well with the true sludge dewaterability.

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