American Scientific Research Journal for Engineering, Technology, and Sciences (ASRJETS)

ISSN (Print) 2313-4410, ISSN (Online) 2313-4402

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http://asrjetsjournal.org/

Removal of Suspended Clay Particles in Water by Weathered Volcanic Ash-Based Material

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Abstract

The present study aims to investigate removal capacity of suspended clay particles in water by a flocculant prepared from weathered volcanic ash rich in allophane and imogolite. The optimum flocculant dosage and pH values of suspensions required to achieve maximum removal of clay particles were determined. Flocculation experiments of clay suspensions were conducted with jar test device in the laboratory. The results indicate that the flocculant performs well in removing clay particles. The highest efficiency was kaolinite removal approx. 98%), and lower capacity was with montmorilonite (approx. 93%). The optimum solid ratios of 0.2:1 and 1:1 are determined for flocculant to remove kaolinite (Kao) and montmorilonite (Mon). Solution pH affects the clay particle removal. The acidic condition of suspensions enhances flocculation and removal efficiency. Sedimentation time of 20 min is necessary for completed flocculation process of clay particles with flocculant. The results of flocculation tests clay particles also suggest that volcanic ash-based flocculants removed kaolinite particles more effectively than for montmorillonite.

Keywords: Water treatment; Flocculation; Kaolinite; Montmorillonite; Surface charge neutralization.

1. Introduction

Suspended clay particles in water cause turbidity which not only has negative impact on water environment but also increases treatment costs. Kaolinite and montmorillonite are most abundant clay minerals in tropical soils and widely used for industrial aspects.

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Recently, exploring clay minerals have been expanded in many regions to meet increasing demand for manufacturing. The occurrence of clay particle in waters as result of discharging from clay processing industry is a big problem faced by many countries. To deal with this problem, a lot of previous researches have been conducted aiming to remove turbidity in water. Faust and Ally (1983) [1] studied purification of kaolinite turbidity of raw surface water by coagulation and flocculation with Jar test in the laboratory. Tripathy and De Ranjan (2006) [2] suggested adding flocculating agents to remove suspended materials via electrostatic attraction of charged ions. Inorganic coagulants such as alum in combination with lime have been conventionally used for the removal of clay particles in the effluents from clay processing industry as well as from raw water. Some synthetic agents, such as poly diallyldimethylammonium chloride (PDADMA or Cat-Floc), used either alone or in combination with alum, have been reported to be effective in flocculation of negatively charged suspended particles in water [1,2]. Long chain synthetic polymers are also popular flocculating agents applied to removing suspended materials under bridging and electrostatic patch mechanism [3]. The use of these flocculating agents is effective for removing suspended particles. However, the aluminum salts and synthetic polymers cause possible physiological effects on organisms as well as aluminum accumulation in the environment and its connection with Alzheimer disease [4]. Some natural substances such as chitosan and carboxymethyl cellulose are nontoxic to environment, available from renewable resources and very effective in kaolinite removal [5] but they are not stable against microbial attack during storage [2]. Using with high dosage may increase the biological oxygen demand of processed water. Thus, development of natural materials to remove turbidity in water is very necessary. Products from soil were found to be effective and low cost adsorbents in removing pollutants form water [6]. Weathered volcanic soils are abundant in volcanic areas. Volcanic ash soil based treatment agents easily adsorb contaminants due to the presence of allophane and imogolite. Kuchibune (2006) [7] reported that the flocculants prepared from allophanic weathered volcanic ash were as effective as PAC for flocculating suspended clay particles in some natural reservoirs. The research of Nga, N.T.H (2012) [6] indicated effects of mineralogy and colloidal characteristics of clay suspension on flocculation performance of volcanic ash soil flocculant. However, studies on the optimization flocculation conditions for turbidity treatment due to clay suspensions have not been conducted. The present study aims to investigate clay particle removal by using treatment material based on weathered volcanic ash soil rich in allophane and imogilite in tropical areas.

2. Materials and methods

2.1 Materials

The study is conducted in laboratory with a commercial flocculant supplied from Astec.Co. and clay suspensions separated from soil samples. Flocculant was made from subsurface layer of weathered volcanic soil rich in allophane and imogolite collected in Himeji province, Japan. The original dried soil was treated by mechanical dispersion using ultra sonic equipment for 2 hours. Then pH adjustment at 4-5 by HCl acid was followed. The original product was thick slurry with solid content of 132 g/L. It was diluted three times with distilled water just before using in the flocculation experiments. Clay suspensions were prepared from four clays samples including refined powder collected in Iriki, Kagoshima, Japan (K1), soil collected in Nakhon Ratchasima, Thai (K2), refine montmorillonite powder supplied by Kunimine Co., Tokyo, Japan (M1) and a soil of Ap horizon of Fluvaquents in Fukuoka, Japan (M2). The clay fraction having equivalent spherical diameter of < 2 µm was separated following the procedure of Nga and his colleagues (2012) [6]. The separated stock clay suspensions from several sedimentation cylinders were mixed and kept in a polypropylene bottle with fitted stopper and diluted with deionized water to a concentration of 500mg/L.

2.2 Methods

Determination of characterization of clay suspensions and flocculants

Exchangeable cation composition was determined by 1 mol $L^{-1}NH_4OAc$ extraction. Particle size distribution of the suspended clay minerals was determined by photon correlation spectroscopy (ELSZ, Photal Co, Japan). The spectrometer was calibrated with spherical colloidal latex having a diameter of 100 nm. Zeta (ζ) potential of the suspended clay particles was determined by a ζ potential analyzer (Zetasizer 2000, Malvern Instruments, UK). Mineralogical analysis of the clay suspensions by X-ray diffraction was followed the procedure described by Wada and Umegaki (2001) [8] with a Cu K_α radiation at 40 kV and 20 mA. The approximate contents of layer silicate clay minerals, gibbsite, quartz and feldspars were estimated from the XRD peak intensities following the procedure described by Moslehuddin (1998) [9]. Mineralogical analysis of flocculant was carried out by Nga, N.T.H (2012) [6] based on electron microscopy on the < 2 µm fraction.

Flocculation experiments

The flocculation experiments were performed by the Jar-test device at room temperature 20-24 ^oC. Flocculating agent was added in to suspensions, and then suspension was stirred at a speed of 300 rpm for 3 min and at 50 rpm for 5 min. After settling time for 30 minute, a 10 mL portion of the supernatant then was collected from 2cm below the water surface and absorbance was measured at a wave length of 660nm by a spectrophotometer (U1900, Hitachi, Japan). All of tests were carried out in triplicate. The mean absorbance value of treatments was recorded.

3. Results and discussion

3.1 Mineralogy of flocculant and soil clay samples

X-ray diffraction patterns of the Mg-saturated and glycerol-solvated clay samples are shown in Fig.1. The flocculant gave faint diffraction peaks only at about 1.4, 0.7 and 0.334nm after Mg-saturation and glycerol-solvation but the former two peaks disappeared after heating at 550 ºC (not shown). This suggests that these peaks arose mostly from imogolite but not from layer silicate minerals. The 0.334 nm peak persisted after heating, indicating that the flocculant contained small amount of quartz. Fig. 2 shows an electron micrograph of the < 2 µm fraction of the flocculant. The aggregates of very fine granules and threads indicate the dominance of allophane and imogolite.

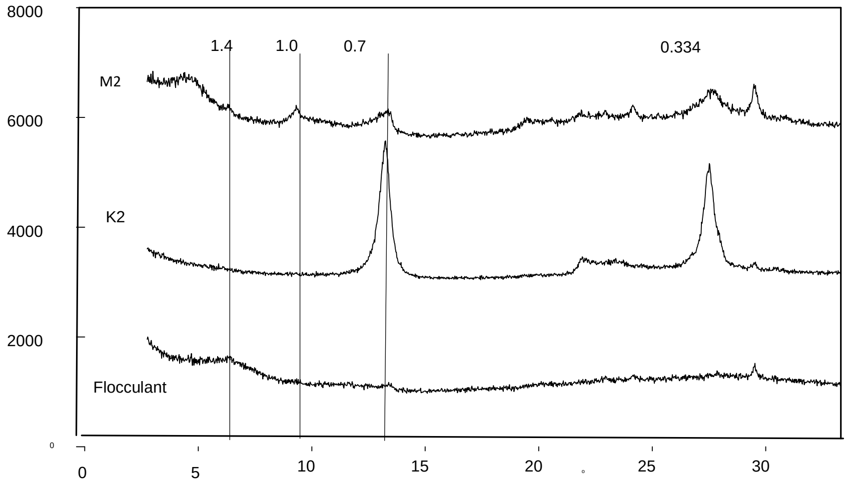

Figure 1: X-ray diffraction patterns of the clay suspensions and flocculant

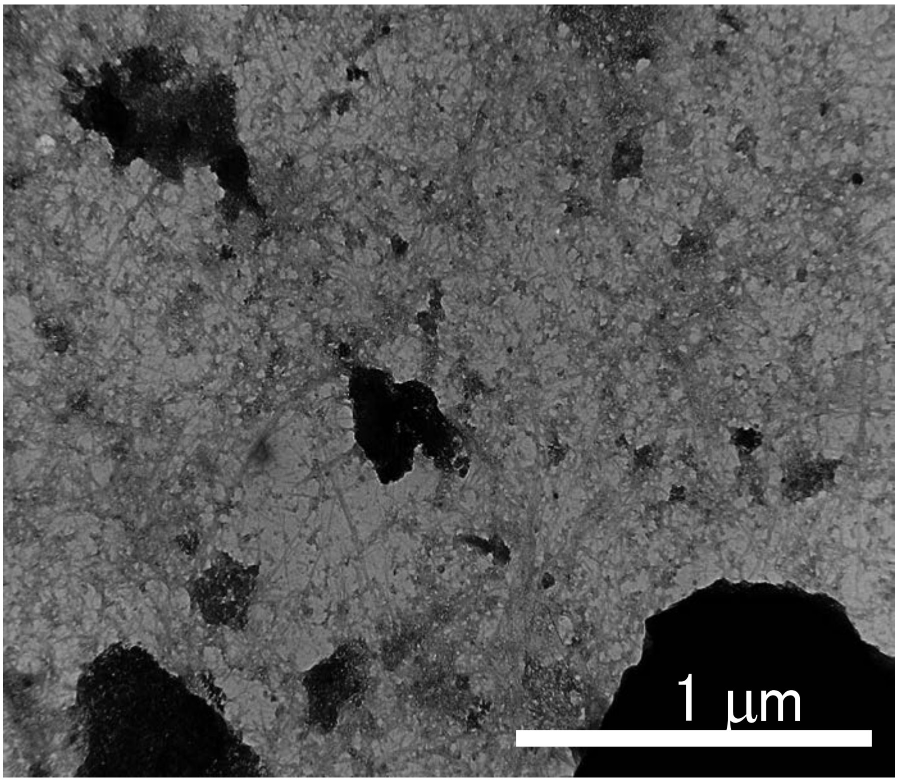

Figure 2: Electron micrograph of < 2 µm fraction of flocculant

The soil clay sample (K2) contained almost kaolinite and oxides and hydroxides of iron. M2 sample contained significant amount of smectite as indicated by the broad diffraction peak at 1.7-1.9 nm (Fig. 1). The approximate relative contents of layer silicate minerals, quartz, feldspars and gibbsite were estimated following the procedure described by Mosslehuddin (1998) [9] and combined with the free iron oxide content determined by selective dissolution to calculate the approximate mineralogical composition of the clay samples used. Thus estimated mineralogical composition of the clay samples are listed in Table 1.

Table 1: Mineral contents of clay samples

Sample	Approximate clay mineral percentage									
	Mc	Ch	Vt	VtCh	Sm	Kt	Gb	Qz	Fd	Fe
K1	0	0	0	0	0	100	0	0	0	0
K2	0	0	0	0	0	96	0	0	0	4
M1	0	0	0	0	100	0	0	0	0	0
M2	18	1	17	3	11	18	4	14	11	3

Mc= Mica, ChVt = Vermiculite-Chloriteintergade, Sm= Smectite, Kt= Kaolinite, Qz=Quartz,

Fd = Feldspar, Gb = Gibbsite, Fe = Oxides and hydroxides of iron

3.2 Colloidal properties of clay suspensions and flocculant.

The pH and electric conductivity of the suspension, exchangeable cation composition, average particle size and the average ζ-potential of the suspended particles are tabulated in Table 2. The suspension pH was in a narrow range from 6.8 to 6.86. The electric conductivity was also not much different among samples. The effective cation exchange capacity (ECEC), i.e., the sum of the exchangeable cations, was 3.67, 6.14, 99.05 and 29.8 $\text{cmol}_c\ \text{kg}^{-1}$ for the K1, K2, M1 and M2, respectively.

Table 2: Colloidal properties of clay samples.

Sample	pH	EC /dS m^{-1}	ECEC /cmol_c kg^{-1}	Particle size/ nm	Zeta potential / mV
K1	6.86	0.04	3.67	384	-45.1
K2	6.82	0.02	5.79	86	16.7
M1	6.80	0.04	99.05	224	-55.7
M2	6.81	0.03	29.76	187	-36.6
Flocculant	6.22	0.08	122.2	150	-18.2

The particle size distribution showed that the flocculant comprised of 28% of coarse sand (200-2000 µm), 12% of fine sand (20-200 µm), 13% of silt (2-20 µm) and 47% of clay (< 2 µm) by weight. The allophane plus imogolite content determined by the selective dissolution using ammonium oxalate-oxalic acid was 19% on the oven-dry basis [10]. This value combined with the solid content of the flocculant (132 g L^{-1}) gives the allophane plus imogolite concentration in the flocculant to be 25 g L^{-1}. The average Si/Al molar ratio of the allophane and imogolite in the flocculant calculated from the selective dissolution data was 0.82.The oxalate-oxalic acid soluble iron mineral content was 20 g kg^{-1} as Fe_2O_3. This is equivalent to the concentration of 2.6 g L^{-1} in the flocculant.

3.3 The removal of clay suspensions at the original pH

The original pH experimented for clay suspensions after being diluted to concentration of 500mg/L from the stock suspensions were 6.43 - 6.67. The flocculation experiments used various flocculant dosages to investigate clay removal. The results are presented in Fig 3, where percentage of residual particles against flocculant dosage was plotted. The percentage of residual particles was calculated from the ratio of absorbance of a treated suspension to that of the initial suspension.

The plots show that as the flocculent dose increased the absorbance and percentage of residual particles gradually decreased, and then increased again after passing the lowest value at the addition of optimum dose. The re-increase is probably due to the presence of the excess flocculants and/or re-dispersed clay particles [6]. The minimum amount of flocculants added to remove the most clay particles (optimum flocculant dose) were 1-5 ml for Kaolinite particles (K1, K2) and 10-15 ml for montmorillonite particles (M1, M2). The addition of optimum flocculant did removed 96.7-99% of clay particles in water.

The lowest absorbance at the optimum dose indicates that most of clay interacted with the added flocculants to form large flocks based on charge neutralization.

Negative charge on clay particle at the original pH neutralized positive charges on the face of allophane and imogolite in weathered volcanic ash flocculant. It was proven by Follett (1965) [11] that electrostatic attraction force is more acceptable than chemisorption in retention of amorphous and colloidal ferric hydroxides by clay particles, have no bonding rearrangement occurred upon sorption of ferric colloids onto clay particles. Weiss and Russow (1963) [12] also indicated a similar absorption behavior of positively charged AgI particles by clay particles.

The study concluded that the retention of cobalt on vermiculite in the presence of excess calcium is due to attraction force alone and not to the formation of chemical bond.

Flocculant removed soil clay removal (K2, M2) less effectively than on refine clay particles (K1, M1). In addition, K1 and K2 having main mineralogy compositions of kaolinite were removed better than M1 and M2 having main mineralogy compositions of montmorillonite.

The reasons to explain are based on negative charges of clay minerals [6]. M1 and M2 had more negative charges indicted by higher ECEC (Table 1), they needed much more flocculants to neutralize. Besides, smaller particle size and stable behavior of K2, M1, M2 also affected the flocculation performance.

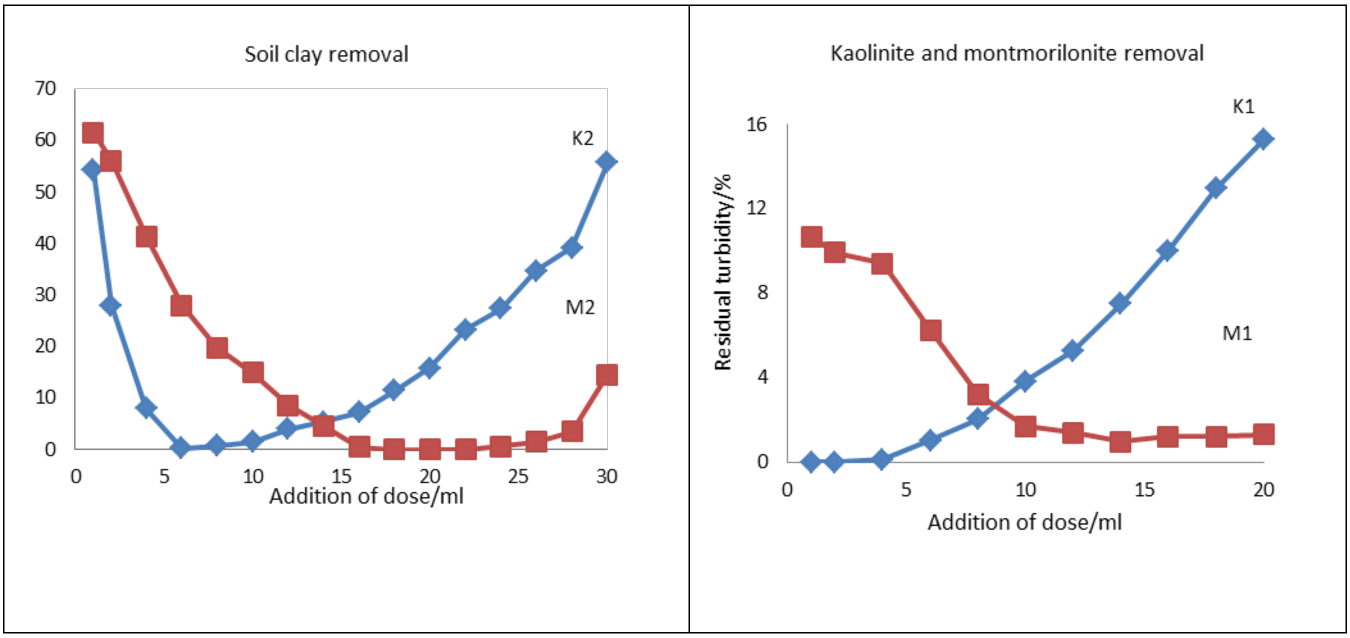

Figure 3: Effects of flocculant doses on clay particle removal at the original pH

3.4 Effect of pH on the removal of clay particles

Solution pH value that the most clay particles can be removed at is determined aiming to archive high effectiveness in application of water turbidity treatment. This study conducted flocculation experiments with flocculants at varying pH values (i.e., 4, 5, 6.5, 7, 8 and 9). This pH range was selected because the pHs of natural waters usually lie in a range from 6 to 8.5 but lower pHs are expected for some wastewater. The doses of 1, 5, 10, 15 ml of flocculant were tested for K1, K2, M1 and M2, respectively.

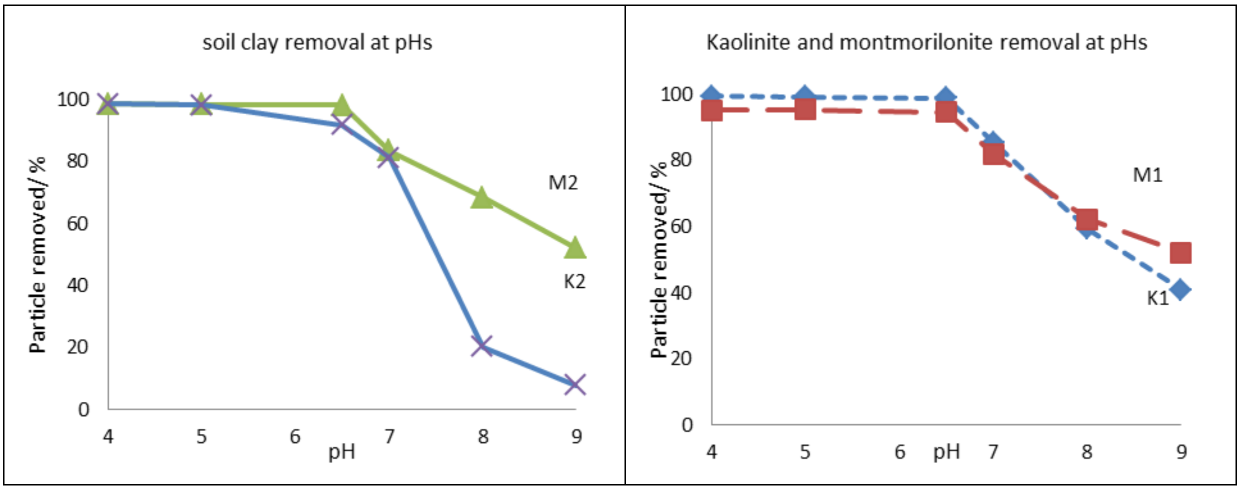

Figure 4: The clay particle removal as pH change

Fig. 4 shows the effect of pHs on the removal of clay particles in water with the addition of flocculants. It was noticed that at strong acidic pH values (i,e., pH 4-6), the flocculant removed effectively clay particles and the decreased efficiency was at pH 6.5-7. The poor removal was indicated at the alkaline pH values. The removal performance was very satisfying at the pH 4-7, indicated by the removal rates of 91-99% for clay particles. The removal efficiency much decreased to 30% at pH 8-9.

This is probably because, in acidic conditions, the edge of clay particles carries positive charges promoting an electrostatic attraction between edges and faces in addition to the Van der Waals attraction and consequently clay particles flocculated better. However, their edges become neutral or negative at alkaline pH causing breakdown of flocs and results in re-increase in turbidity. Nasser and James (2009) [13] with the study on sedimentation characteristics of kaolinite in a 0.001M NaCl solution indicated that the kaolinite particles settled in flocculated form at the acidic pH, while deflocculated settling form was found at pH 9. Furthermore, the clay suspension itself is extremely stable at the alkaline condition, flocculation efficiency decreased at these pHs [13]. The similar results in kaolinite flocculation using chitosan were also investigated by the study of Divakaran and Pillai (2001) [5].

4. Conclusion

Volcanic ash soil is a potential material resource for clay particle removal in water. Performance of this material is based on charge neutralization mechanism between negative charges (clay particles) and positive charges (imogolite and allophane). Flocculation experiments of clay suspensions were conducted with jar test device in the laboratory. The highest efficiency was found for kaolinite removal (approx. 98%), and lower capacity for montmorilonite (approx. 93%). The optimum solid ratios of 0.2:1 and 1:1 are determined for flocculant to remove refined kaolinite (Kao) and montmorilonite (Mon). Solution pH affects the clay particle removal. The acidic condition of suspensions enhances flocculation and improves removal efficiency. Sedimentation time of 20 min is necessary for completed flocculation process of clay particles with used flocculant. The study also suggests that volcanic ash-based flocculants removes kaolinite particles more effectively than montmorillonite.

5. Recommendations

The article mentioned on removal of clay particles from water that was conducted at laboratory scale. So, in order to apply for practical applications, effects of temperature, microbiology, lights, etc., on removal capacity of clay particles using weathered volcanic ash-based material are recommended to extra-experiments.

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