Asian Journal of Chemistry; Vol. 25, No. 10 (2013), 5851-5855

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2013.OH109

Evaluation of the Modified Clays in the Treatment of Car-washing Wastewater†

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AJC-13352

The modification and use of clays as a new type of agents for the treatment of car washing effluent were investigated. The raw clays were montmorillonites K10 and KSF and were modified by either polymeric Al or Fe species, or an Al/Fe mixing polymeric species, or the cationic polymer species. The performance of modified clays was compared with aluminium sulphate, ferric sulphate and polyaluminium chloride in terms of the removal of turbidity, suspended solids, total COD and the oil contents (extracted with *n*-Hexane). The results demonstrated that after being modified with polymeric Al/Fe species, two montmorillonite clays possess greater properties to remove the particles (as suspended solids), organic pollutants (as COD) and oils from car-washing wastewater.

Key Words: Clay, Coagulation, Polymeric Al/Fe species, Car-washing wastewater treatment.

INTRODUCTION

In Korea, car-washing effluent is generated in the various car-washing sites at an approximate amount of 0.5-1 m^3 per car par day. Such effluents contain a lot of synthetic detergent, waste anti-freezing agent, waste oils and heavy metals and cause a range of problems if they are not treated properly. For example, when the untreated car-washing wastewater is discharged into surface water, suspended materials will be accumulated on the surface of water, which interrupts the oxygen transfer and reduces the dissolved oxygen concentration in surface water and therefore deteriorates the surface water qualities. And also, the car-washing wastewater will block the discharge pipes and prevent oxygen transfer and thus interfere the activated sludge process if it is discharged into the sewers and wastewater treatment plant directly.

The general processes for the treatment of car-washing wastewater in Korea include sand screen and oil/water separator, which can remove 35-50 % oils (as *n*-hexane extracted compounds) and coagulation/sedimentation, which can remove 65 % COD and suspended solids. In some cases, filtration is used which can only remove 20 % oils, 10 % COD and 12 % suspended solids. Obviously, the treatment efficiency of car-wash wastewater is not very high and in most cases, the oil and suspended solids concentrations in the treated effluent can exceed the waste discharge standards. An alternative process or new treatment chemical is required to be investigated in order to improve the general treatment performance of the car-washing wastewater.

The natural mineral clays have attracted a lot of research interest. The potential use of natural or modified clays as adsorbents for treating heavy metals and organic pollutants, or as coagulant aids for improving the settling performance in coagulating low particle content water have been investigated. By replacing the natural inorganic exchange cations with alkylammonium ions, clay surfaces are converted from being primarily hydrophilic to hydrophobic, which enable them to interact strongly with organic vapours and organic compounds dissolved in water[1]. Also, the combination of the natural mineral clays with polymeric Al/Fe species[2] can produce somewhat the optimal properties and offer the comparatively great affinities for the organic compounds (*e.g.*, phenol[3], humic acids[4] and heavy metals[5].

In addition to being used as adsorbent, natural mineral clays has been used as coagulant aids to improve the settling performance when using metal-based coagulants to treat the low particle content water[6]. Preliminary study on the modification of clay for the production of new kind coagulant has been tried[7] by inserting the Mn^{2+} ion into the clay layers. However, Mn^{2+} may not be the optimum cationic ion to be introduced into the clay layers. As stated previously, the polymeric Al/Fe species represented the best coagulating species. This study thus aims to evaluate the treatment performance of car washing

†Presented to the 6th China-Korea International Conference on Multi-functional Materials and Application, 22-24 November 2012, Daejeon, Korea

wastewater with various modified and raw clays (montmorillonites KSF and K10) in comparison with conventional metal based coagulants (*e.g.*, ferric sulphate and aluminium sulphate).

Principles of clay modifications for the coagulation: At the geometric mid-plane of each clay layer resides an atom octahedrally coordinated to those oxygens comprising the tetrahedron tips. In trioctahedral 2:1 clays such as vermiculite, all octahedral sites are filled, primarily with Mg^{2+}. The approximate chemical formula for the vermiculites is $[Mg_3(Si_3Al)O_{10}(OH)_2)(Mg_{0.5}(H_2O)_y]$; where the first set of brackets denotes the host layer, the second set denotes the guest layer and the hydration state is variable. The host layers in clays can adopt a number of interesting stacking arrangements to form ordered, partially ordered, or disordered three-dimensional structures. The proposed modification mechanisms could include the chemisorption, physisorption, ion-exchange, hydrogen-bonding, charge transfer and complex formation. In general, this can be summarized as three basic categories according to the predominant reaction features: 1) Adsorption, modifier molecules are adsorbed on the external surface of the clay by chemisorption and physisorption mechanism; 2) Ion exchange, modifiers are bonded by ion exchange (mostly by cation exchange) reaction, while the structure of the host (such as interlayer spacing) is not changed; 3) Intercalation, modifier molecules are inserted into gallery (interlayer) of the host, with maintaining the layered structural feature of the host.

EXPERIMENTAL

Modification and characterization of clays: The modification, characterization and preparation of various clays were conducted at Environmental Engineering Laboratory of University of Surrey, UK. The raw clays used in this study, *i.e.* montmorillonites K10 and KSF and the other chemicals were supplied by Sigma-Aldrich Chemicals Corporation UK. The polymeric Al/Fe modifiers were prepared following an established procedure[2]. The modification involved with the mixing of the given amount of clays with the polymeric metal species for 4 h at 55 ºC and then the mixtures were separated by filtration to obtain the solid phase of the modified clays. The chemical composition of the modified clays were analysed using X-ray fluorescence and the X-ray fluorescence data was collected on a Philips PW1480 X-ray fluorescence spectrometer.

Procedures of coagulation experiments and the effluent quality measurement: Car-washing wastewater samples were taken from the Garages of Yusoung, Taejeon City and the coagulation jar test experiments were conducted at Department of Environmental Engineering Laboratory, Hanbat University of Korea. All coagulants used in this study were listed in Table-1. Except for the modified clay coagulants, other coagulants were ferric sulphate, aluminium sulphate and polyaluminium chloride. The dosages of clays were 200, 400, 600, 800, 1000 and 1200 mg/L, respectively and the dosage of aluminium sulphate, ferric sulphate and polyaluminium chloride was in the range of 2-12 mg/L as Al, or as Fe, respectively. A standard jar test apparatus (Model PB-900, Phipps & Bird Co, USA) and a procedure were used in the study, including a fast mixing at 250 rotations per minute for 1 min, a slow mixing for 0.5 h at 45 rpm and a settling time of 1 h the supernatant was taken for the quality measurement.

TABLE-1
LABEL OF THE COAGULANTS USED

Coagulant	Label
Raw montmorillonite K10	K10
Polymeric Fe modified montmorillonite K10	Fe-K10
Polymeric Al modified montmorillonite K10	Al-K10
Polymeric Al/Fe modified montmorillonite K10	Al/Fe-K10
Organic polymer modified montmorillonite K10	P7-K10
Raw montmorillonite KSF	KSF
Polymeric Fe modified montmorillonite KSF	Fe-KSF
Polymeric Al modified montmorillonite KSF	Al-KSF
Polymeric Al/Fe modified montmorillonite KSF	Al/Fe-KSF
Organic polymer modified montmorillonite KSF	P7-KSF
Aluminium sulphate	AS
Polyaluminium chloride	PACl
Ferric sulphate	FS

Water quality analysis: The measurement of turbidity, suspended solids, total chemical oxygen demand (CODCr) and the oil contents followed the Korean Standard Methods (Korea EPA, 2000)[8].

RESULTS AND DISCUSSION

The X-ray fluorescence analysis results demonstrated that the mass ratio of the polymeric Al, Fe and Al/Fe mixtures which have been fixed onto the clays to that which were used in the modification process was about 15 % and thus, the effective polymeric species in the modified clays was approximate 0.3 mmol per gram of clay although the nominal polymeric species used in the modification was 2 mmol per gram of clay.

The quality characteristics of raw car-washing effluent can be seen in Table-2. The variation of quality characteristics of car-washing wastewater was due to the variations of the type of vehicles, personal preference in washing a car (*e.g.*, the selection of the detergents) and the climate (*e.g.*, raining) in the experimental period.

TABLE-2
QUALITY CHARACTERISTICS OF RAW CAR-WASHING EFFLUENT

Parameter	Range	Mean value
pH	6.9-7.1	7.0
Alkalinity (mg L^{-1} as $CaCO_3$)	110-160	135
Turbidity (NTU)	81-160	120
Total suspended solids (mg L^{-1})	44-116	80
COD_{Cr} (mg L^{-1})	49-121	85
Oil contents (mg L^{-1} as hexane extractant)	76-150	113

The coagulation results are presented as the percentage removal of suspended solids, CODCr and Oil content. The percentage removal was calculated against the quality parameters of controlled samples, which were undergone the full coagulation procedures but without the addition of any coagulants.

Turbidity and suspended solid removal: Fig. 1(a-c) shows the percentage removal of suspended solids with modified clay and metal/polymer coagulants. For the KSF based clays, > 90 % suspended solids removal was achieved with the polymer and mixing Al/Fe modified clay coagulants at a dose of 800 mg/L. The raw KSF clay also achieved good suspended solids removal. For the K10 based clays, polymeric iron modified clay achieved the best performance, 90 % suspended solids

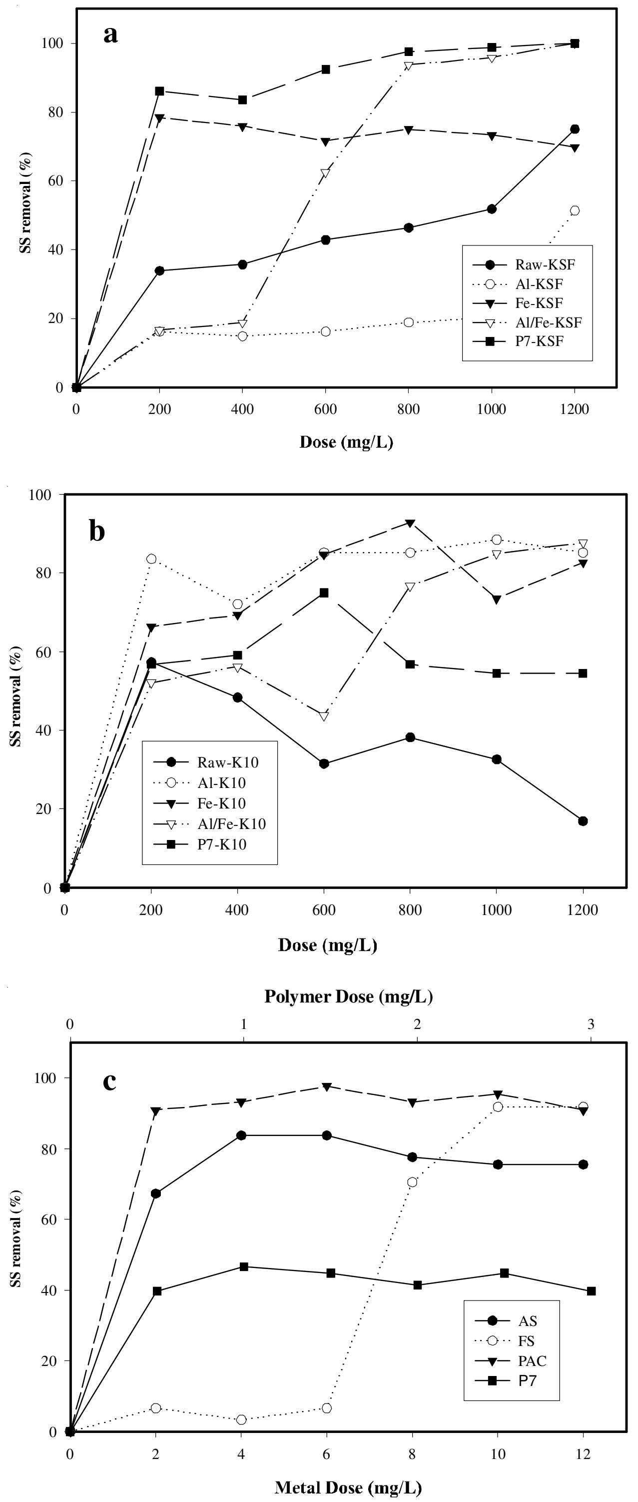


Fig. 1. Suspended solids removal with (a) montmorillonite KSF based coagulants, (b) montmorillonite K10 based coagulants and (c) metal and polymer coagulants

can be removed at a dose of 800 mg/L. Polymeric Al/Fe modified K10 also achieved adequate good performance. Among metal and polymer based coagulants, polyaluminium chloride can remove 90 % suspended solids at a low dose, 2 mg/L as Al.

CODCr removal: Fig. 2(a-c) shows the percentage removal of COD with modified clay and metal/polymer coagulants. For the KSF based clays, 80 and 90 % COD removal were achieved with the polymer modified clay coagulant at the dose of 600 and 800 mg/L, respectively. The raw KSF can achieve about 67 % COD removal at a low dose (400 mg/L), but can't achieve > 80 % when the dose was greater than 1000 mg/L. polymeric Fe and Al/Fe modified KSF performed similar to the raw KSF. Polymer modified KSF didn't perform as well as other clays.

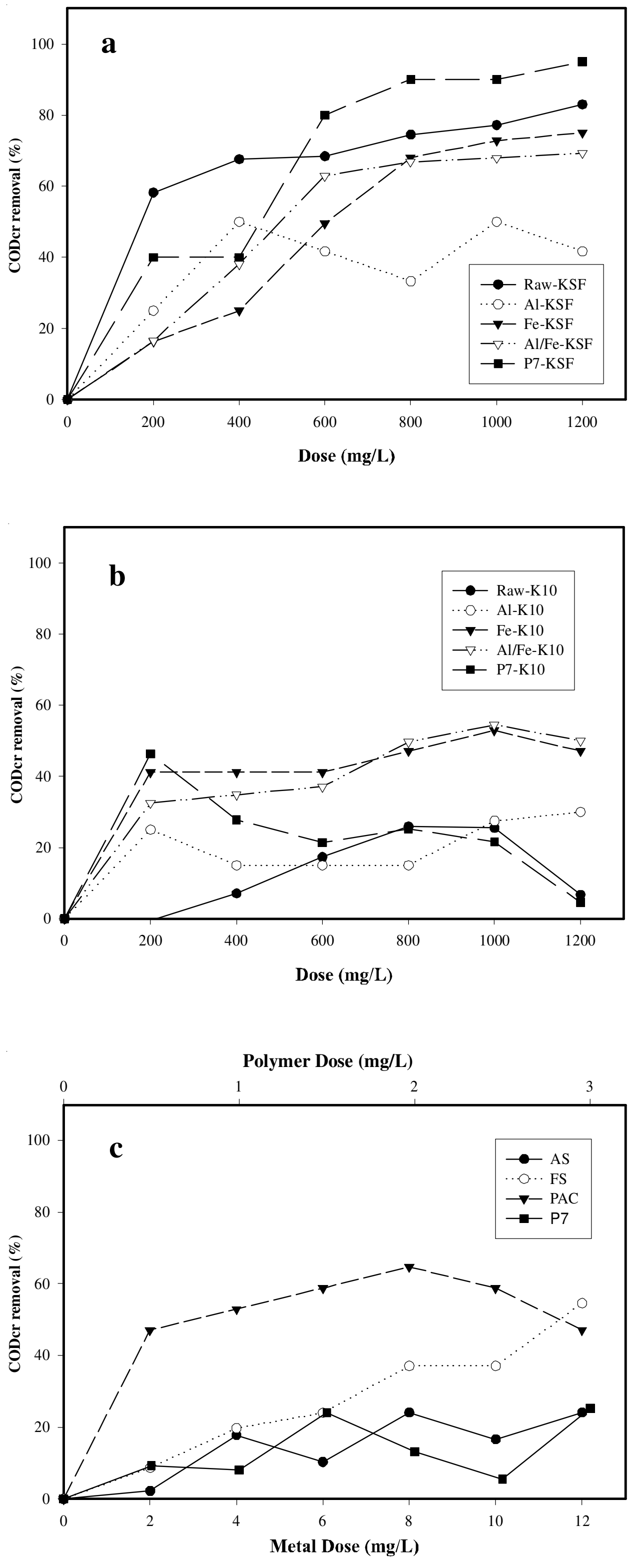


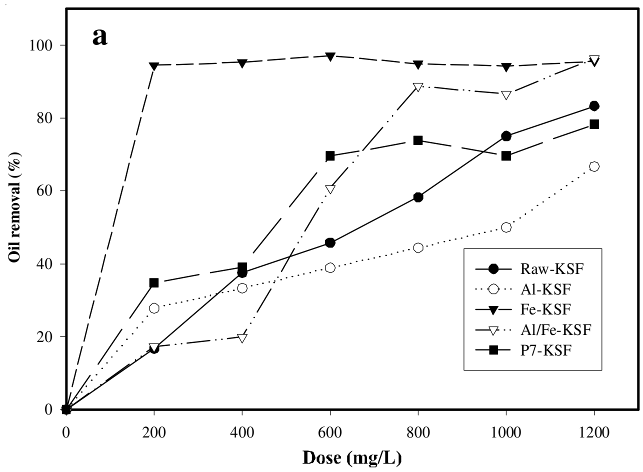
Fig. 2. Chemical oxygen demand (COD) removal with (a) montmorillonite KSF based coagulants, (b) montmorillonite K10 based coagulants and (c) metal and polymer coagulants

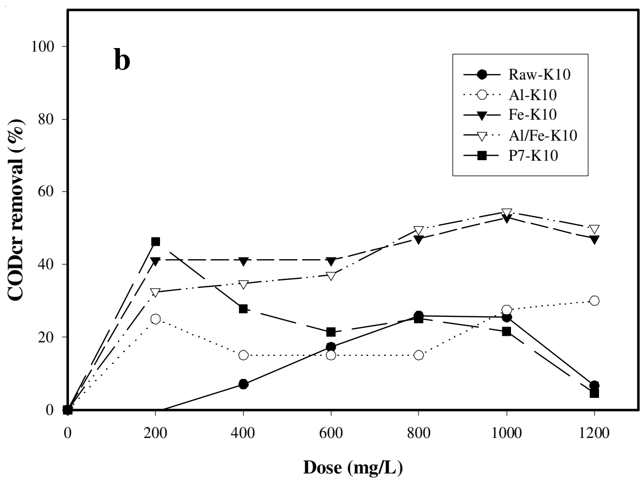
For the K10 based clays, both polymeric iron and mixing Al/Fe modified clays achieved the best performance, 50 % COD can be removed at a dose of 800 mg/L. Other three K10 based coagulants didn't perform as well as Fe-K10 and Al/Fe-K10. Among metal and polymer based coagulants, polyaluminium chloride can remove 60 % COD at a dose of 8 mg/L as Al, all other three coagulants can't achieve such a high removal.

Oil contents removal: Fig. 3(a-c) presents the percentage removal of oil from the car-washing effluent with modified clay and metal/polymer coagulants. For the KSF based clays, polymeric iron modified KSF can achieve > 90 % oil removal at a very low dose (200 mg/L) and polymereic Al/Fe modified KSF can achieve the similar removal performance at a high dose (1200 mg/L). However, all other therree KSFs can't achieve such a removal even at highest dose studied (1200 mg/L).

For the K10 based clays, both polymeric iron and aluminium modified K10 clays achieved the best performance, >90 % oil can be removed at a low dose of 200 mg/L. Other three K10 based coagulants didn't perform as well as Fe-K10 and Al-K10. Among metal and polymer based coagulants, polyaluminium chloride can remove 80 % COD at a dose of 2 mg/L as Al, all other three coagulants can't achieve such a high removal.

This study demonstrated that polymeric iron modified KSF and polymeric iron or aluminium modified K10 possessed very high efficiency to remove the oil; 200 mg/L dose of which can remove more than 90 % oil. Comparing to this, polyaluminium chloride can achieve the maximum 80 % oil removal at a low dose of 2 mg/L as Al, but never could achieve > 90 % oil removal. Since 200 mg/L modified clay is equivalent to 1.62 mg/L as Al or 3.36 mg/L as Fe, the modified clay coagulants can remove more oil than polyaluminium chloride at low doses.





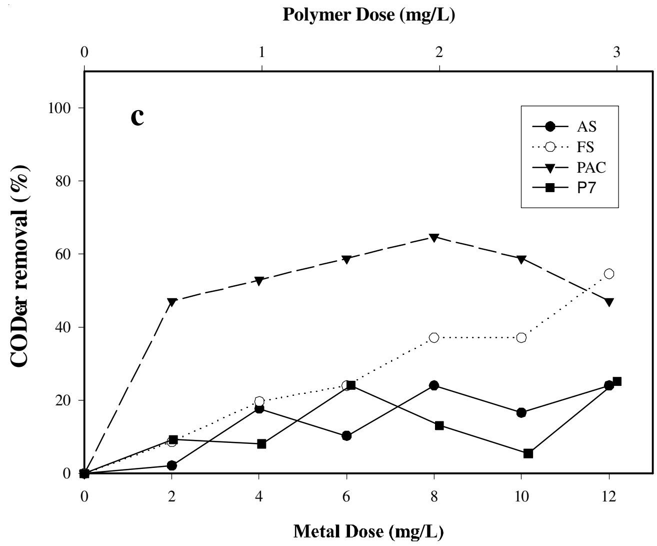


Fig. 3. Oil removal with (a) montmorillonite KSF based coagulants, (b) montmorillonite K10 based coagulants and (c) metal and polymer coagulants

Comparing the effectiveness in the removal of CODCr, polymer (P7) modified KSF coagulant performed better than all other coagulants, at a dose of 600 mg/L, P7-KSF can remove 80 % COD. It is interesting to note that with P7 alone, it can only remove the maximum COD about 22 %. The other good clay-based coagulants in terms of better COD removal were Al/Fe-KSF, raw KSF, Fe-K10, Al/Fe-K10 and polyaluminium chloride. For the clay based coagulants, a dose of 200 mg/L (equivalent to 1.62 mg/L as Al) can remove 40-50 % COD whilst for polyaluminium chloride, a dose of 2 mg/L can achieve 50 % COD. Therefore, lower dose required with clay based coagulants than the polyaluminium chloride in order to achieve the similar COD removal performance.

For the suspended solids or turbidity removal, polymer (P7) or polymeric Fe or Al/Fe modified clays and polyaluminium chloride can remove more suspended solids at low doses. It is interesting to note that the raw KSF clay can remove more suspended solids and COD than raw K10 clay and some other coagulants. This could be attributed to the KSF clay's acidity nature. The KSF is an acid-pretreated montmorillonite and it will cause the pH drop down to 1-3 units when it was added into water (Fig. 4). In contrast, all other modified KSF and K10 clays and metal coagulants can only cause pH go down 0.5-1 units. Lower pH might favour to the suspended solids and COD removal, but is not the case for the oil removal. The advantage of using modified KSF and K10 coagulants is that the modified clays will not cause pH go down too low but still can achieve the best overall treatment.

As raw clays possess somewhat adsorption capacities, they could adsorb organic/inorganic molecules; this could be one of the mechanisms of the clay modification. The adsorbed

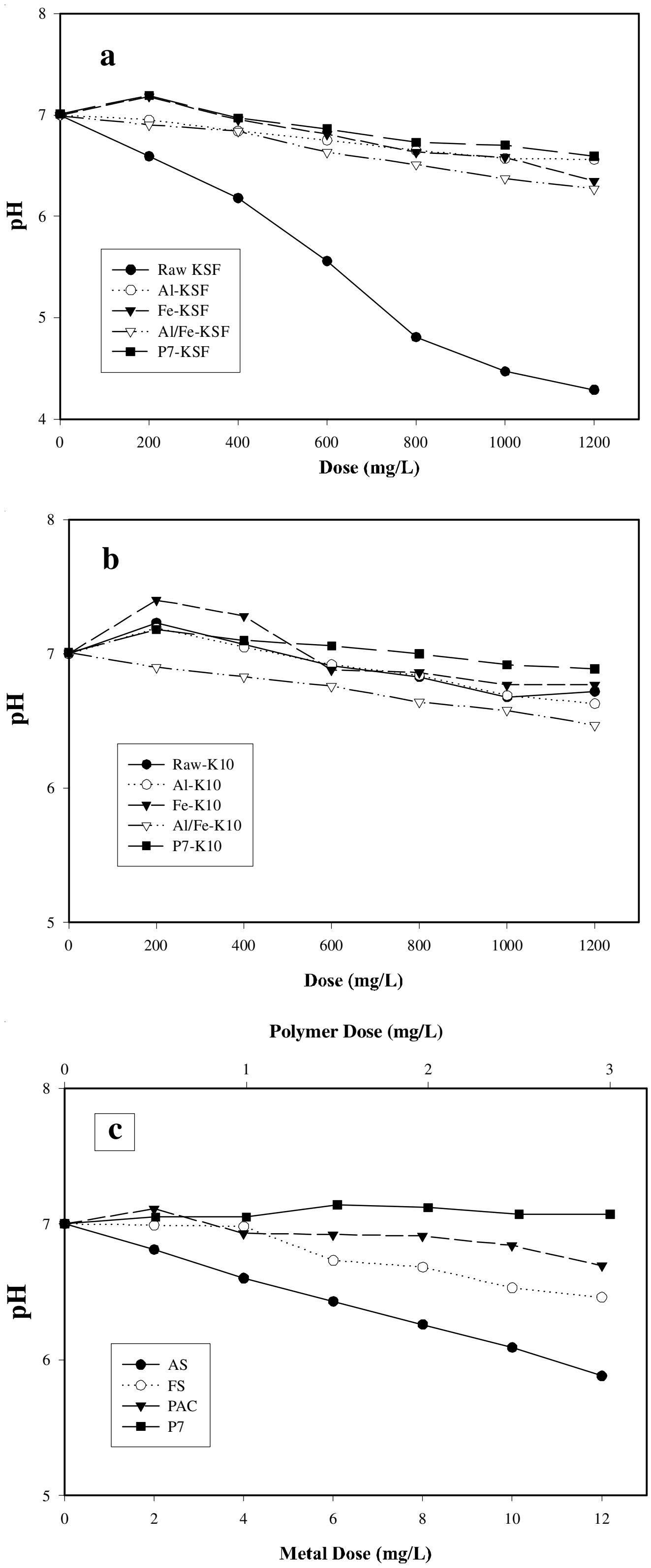


Fig. 4. pH variation after sedimentation; (a) montmorillonite KSF based coagulants, (b) montmorillonite K10 based coagulants and (c) metal and polymer coagulants

modifiers sometimes act as a stock for ion exchange of toxic ions in solution[9], or will be effective reinforcement for capturing ions or organic matters in water[10]. In this study, the superior performance of modified clays in removing COD and oil suggests that there could be strong interactions between the pollutants and the modifiers and the resulting "modifier-pollutant complexes" will be retained by the modified clays to enhance the coagulation performance. This assumption can be supported by a research where the modified clay behaved as a real coagulant[11].

Chemical coagulants are used widely internationally in the treatment of surface water for the supply of potable water and in sewage and industrial effluent treatment. They play an important role in the removal of particulate and dissolved pollutants. Such coagulants are predominantly inorganic salts of iron and aluminium. This study has demonstrated that a new, highly efficient and potential cost-effective, clay-based coagulant has been developed. Subsequently, this will make it to be competitive in the market of water treatment chemicals. However, in the use of modified-clay coagulant in the full-scale water and wastewater treatment, further work is needed to assess its performance technically and economically by conducting various studies using different type of water and wastewaters.

Conclusion

Polymeric Fe-KSF, Fe- or Al-K10 and the polyaluminium chloride can achieve the highest oil removal efficiency. For a low dose of clay, 200 mg/L (equivalent to a metal dose of 0.06 mM as metal), the polymeric Fe-KSF and Fe- or Al-K10 can remove 95 % oil but polyaluminium chloride can only achieve about 80 % oil removal at a dose of 1.62 mg/L as Al (equivalent to a metal dose of 0.06 mM as Al). Polymer (P7) modified KSF coagulant can achieve the greatest removals of suspended solids and COD in comparison with the polyaluminium chloride and other clay-based coagulants. It can be concluded from this study that montmorillonites K10 and KSF can be modified by the mixing polymeric Al/Fe species or a cationic polymer with a procedure developed. The resulting modified clay coagulants possess the specific properties to react with particles, organic constitutes and oils and can be used as coagulants for car-washing wastewater treatment. The treatment performance of modified clay coagulants was greater than that of conventional processes, *i.e.*, sand screen with oil/water separation and coagulation/sedimentation. The modified clay coagulants are thus representing a new type of coagulants having high potentials in the treatment of various wastewaters.

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