Removal of an anionic dye by adsorption/precipitation processes using alkaline white mud

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Abstract

Alkaline white mud (AWM) has been investigated as a low-cost material for removal of an anionic dye, acid blue 80. The effects of contact time, initial pH of dye solution, AWM dosage, and the presence of inorganic anion sulphate or phosphate ion on removal of the dye were evaluated. The results show that AWM could be used as an effective material for removal of acid blue 80 in a pre or main process, particularly at high dye concentration ($>300\,\mathrm{mg\,L^{-1}}$), reaching maximum removal efficiency of 95%. At low dye concentration, surface adsorption is mainly responsible for the dye removal, while chemical precipitation of the dye anions with soluble Ca^{2+} and Mg^{2+} may play a dominant role for the dye removal at high concentration, producing much less sludge than conventional adsorption method. Solution pH has only a limited effect on the dye removal due to high alkalinity and large pH buffer capacity of AWM suspension and thereby pH is not a limiting factor in pursuing high dye removal. The presence of SO_4^{2-} could reduce the dye removal by AWM only when SO_4^{2-} concentration is beyond $0.7\,\mathrm{mmol\,L^{-1}}$. The dye removal may be significantly suppressed by the presence of phosphate with increasing concentration, and the reduction in the dye removal is much larger at high dye concentrations than at low ones.
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Keywords: Alkaline white mud; Anionic dye; Adsorption; Chemical precipitation; Wastewater treatment

1. Introduction

The wide use of synthetic dyes in dyeing, paper and pulp, textile, and other industrial applications has caused large-scale development of dye industries, and consequently has produced large volume of dye wastewaters [1]. Dye wastewater is characteristically high in organic content, high salt content and low in biodegradation [2]. Direct discharge of dye effluents from these industries may cause serious problems to the environment because they contribute organic load and toxicity to the environment and are the source of aesthetic pollution related to colour [2,3]. In addition, coloration of water by the dyes may impede light penetration, thus affecting aquatic ecosystems [4]. Hence, colour elimination from dye effluents is one of several major environmental concerns. Traditionally, biological, physical and chemical methods have been tested for dye removal [5–8]. Biological process is probably the most inexpensive one but many

dyes are poorly biodegradable due to their complex structure and xenobiotic properties [9]. Moreover, many dyes are toxic to microorganisms, causing direct destruction or inhibition of their catalytic capabilities [10]. Reverse osmosis and electrochemical coagulation are complex and generally not feasible on a large-scale due to economic consideration. Advanced oxidation processes (H_2O_2/UV, O_3) have the potential to eliminate organic carbon of dye wastewater; however, they are too expensive and complex apart from being effective only for very low dye concentrations [11,12]. Chemical coagulation for dye removal needs loading of chemical coagulant, and optimal operation conditions such as pH and coagulant dosage should be rigidly remained in order to achieve a maximum dye removal [2,3,13]. Adsorption removal is an effective and simple method for dye treatment but usually produces large amount of sludge especially for wastewaters with high dye concentration. Adsorption of dyes on various adsorbents have been extensively investigated and activated carbon has proved the most effective because of its high specific surface area, high adsorption capacity and low selectivity for both ionic and nonionic dyes [5,14–16]. Unfortunately, activated carbon adsorption is an expensive method due

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to its high price and the difficulties involved in its regeneration for reuse. In recent years, many synthetic adsorbent such as hydrotalcite, low-cost and easily obtainable natural materials such as montmorillonite, zeolite and pyrophyllite, biomaterials produced from agricultural by-products, and industrial solid wastes such as fly ash, as adsorbents have been tested for pollutant removal [17–22]. Those studies indicated that the sorption capacity of most low-cost materials is much less effective than that of activated carbon. Therefore, large amount of loading of those materials is usually needed for colour removal particularly in the case of high dye concentration, consequently producing large volume of sludge. To our knowledge, no individual treatment technique alone is efficient enough to completely remove dye from wastewaters because of varying physicochemical conditions of dye effluents. Effort has been tried to combine two or more treatment techniques such as activated carbon adsorption/chemical coagulation to overcome the disadvantages of individual unit operation and enhance the overall treatment performance [2,3]. Effort is still going on to seek alternative materials for dye removal with high efficiency and low cost, yet producing low volume of sludge.

Alkaline white mud (AWM) is fine-sized solid waste in alkali manufacturing, characterized of high water content, high alkalinity and high concentrations of soluble Ca^{2+}, Mg^{2+} and Cl^- ions. In this study, AWM is tested as a low-cost material for removal of acid blue 80, a commonly used anionic dye in the textile industry, from synthetic dye wastewaters.

2. Materials and methods

2.1. Alkaline white mud sample

Alkaline white mud collected from the Qingdao chemical factory was dried at 110 °C overnight and ground to pass through a 100 mesh sieve for use. Main constituents of the AWM are given in Table 1. Densities of wet AWM (containing water 50–60% by weight) and those after dried are 1160–1200 kg m^{-3} and 2710 kg m^{-3}, respectively. Surface area and average pore diameter of the AWM are 68 m^2 g^{-1} and 5.4 nm, respectively, as determined using the BET method. Grain size distribution of the AWM is shown in Table 2. As can be seen, more than 80% of the fine particles is less than 3.4 μm in diameter. pH of AWM suspension (1.0 g dried AWM in 250 mL deionized water) is 10.8 and the concentrations of Ca^{2+} and Mg^{2+} in supernatant separated from the suspension above are 4.46 mmol L^{-1}

Table 1
Chemical constituents of alkaline white mud (AWM)

Constituent	Percentage by weight (%)
CaCO$_3$	45.38
CaSO$_4$	12.10
Mg(OH)$_2$	9.04
Fe$_2$O$_3$	1.08
AL$_2$O$_3$	3.2
SiO$_2$	9.09
CaO	4.09
CaC1$_2$	10.23
NaC1	2.36

Table 2
Grain size distribution of alkaline white mud (AWM)

Grain size (μm)	Percentage (%)
<1.6	49.8
1.6–3.4	32.9
>3.4	17.3

natant separated from the suspension above are 4.46 mmol L^{-1} and 0.447 mmol L^{-1}, respectively, as determined using the standard complexometric titration method [23]. Acid blue 80 (purity > 99%) was provided by the Qingdao Shuangtao dyestuff factory and used without further purification. The chemical structure of the dye is shown in Fig. 1. Dye solution was prepared by dissolving acid blue 80 in deionized water and adjusted using dilute HCl or NaOH solutions to obtain desired pH values of the dye solutions.

2.2. Dye removal

Experiments of the dye removal were conducted using a batch method by adding dried AWM into 100 mL conical beakers containing 25 mL dye solutions of varying concentrations (typically ranging from 50 to 500 mg L^{-1}). 0.1 g AWM was used in the experiments, unless otherwise stated. After capping and vigorously shaking by hand, the conical beakers were placed in a water bath at 27 °C and gently shaken for specific periods of time from 30 min to 18 h. The suspensions were then centrifuged and filtered (0.45 μm) and pH values of the filtrates were measured immediately after filtration. Dye concentrations were determined using a Hewlett-Packard 8453 UV–VIS spectrophotometer at $\lambda_{max} = 627$ nm. Amounts of the dye removal were determined by difference. Effects of contact time, initial pH (2.8–11.5) of the dye solutions, dye concentration (50–500 mg L^{-1}) and AWM dosage (2–40 g L^{-1}) used on the dye removal were investigated. Efficiency $\eta(\%)$ for the dye removal is defined as:

$$\eta(\%) = \frac{C_0 - C_t}{C_0} \times 100\%$$

where C_0 (mg L^{-1}) is initial concentration of acid blue 80 and C_t (mg L^{-1}) concentration of the dye at time t.
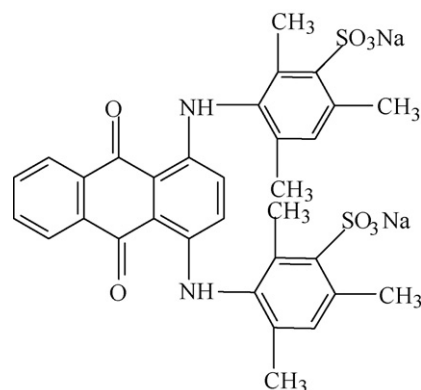

Fig. 1. Chemical structure of acid blue 80.

In order to evaluate the contribution of soluble components in AWM suspension to colour elimination, removal of the dye was determined in mixing systems of dye and AWM supernatants. The supernatants were separated from AWM suspension (1.0 g AWM in 125 mL deionized water) by centrifugation and filtration (0.45 μm) after equilibrium for 3 h. After the mixing of 10 mL of the supernatants and 10 mL of dye solutions (50–500 mg L^{-1}), the mixing solutions were allowed to stand for 6 h in a water bath at 27 °C and then centrifuged and filtered. The concentrations of dye in filtrates were determined using the same method described above.

In order to glean information about the mechanism of chemical precipitation for removal of the dye, effects of Ca^{2+} and Mg^{2+} on removal of the dye were investigated by addition of $CaCl_2$ and $MgCl_2$ solutions of varying concentrations to the dye–AWM systems. Inorganic anions such as SO_4^{2-}, PO_4^{3-} and Cl^- ions are often found in dye effluents. In this study, sulphate and phosphate anions were chosen to evaluate their effects on removal of the dye. Sodium sulphate (Na_2SO_4) and sodium dihydrogenphosphate (NaH_2PO_4) were used as the sources of sulphate and phosphate anions, respectively. Aliquots of 0.1 g dried AWM were weighted into 100 mL conical beakers containing 25 mL dye solutions of constant concentrations (three concentration levels: 50, 100 and 400 mg L^{-1}) but varying Ca^{2+}(0–8 mmol L^{-1}), Mg^{2+}(0–8 mmol L^{-1}), SO_4^{2-} (0.35–3.5 mmol L^{-1}) or PO_4^{3-} (1.6–16 mmol L^{-1}) concentrations for each level of dye concentration. After shaking in a water bath at 27 °C for 6 h, the suspensions were then centrifuged and filtered. The concentrations of dye in filtrates were determined.

All the experiments were run in duplicate and all the data presented were the mean of duplicate analysis.

3. Results and discussion

3.1. Effect of contact time on dye removal

The effect of contact time on removal of the dye is shown in Fig. 2. The removal increased quickly within the initial 3 h and remained almost unchanged after 6 h, indicating reaching an apparent equilibrium. Initial dye concentration had no signif-
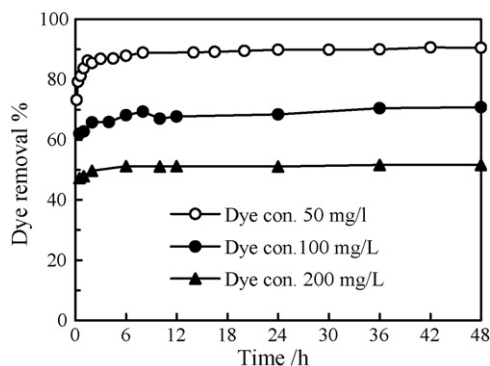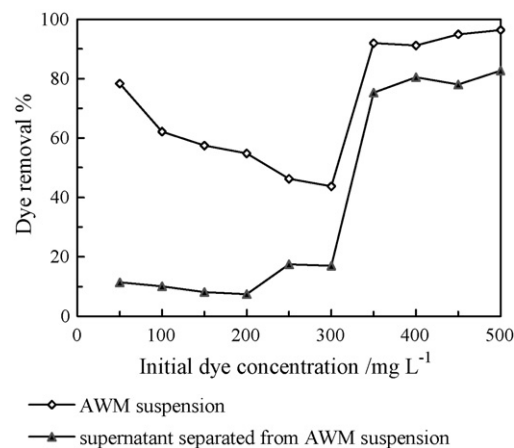
Fig. 3. Comparison of removal of acid blue 80 by alkaline whit mud (AWM) suspension and that by supernatant separated from AWM.

icant effect on the equilibrium time. Thus, 6 h contact time was chosen in subsequent batch equilibrium experiments.

3.2. Effect of dye concentration

The effects of initial dye concentration on removal of the dye by AWM suspensions and supernatants separated from the suspensions are shown in Fig. 3. For the suspension system, the dye removal decreased down to a minimum when the initial concentration of dye was increased up to about 300 mg L^{-1}, after which an abrupt increase in the dye removal was followed from 40 to 92%, but further increase in the dye removal was not observed when initial dye concentration was continuously increased. At a low initial dye concentration (<300 mg L^{-1}), the dye removal could be attributed mainly to surface adsorption mechanism. Therefore, the dye removal decreases with increasing concentration of the dye because the total number of sorption sites available is constant. The isotherm data for the dye removal at low concentration range (20–250 mg L^{-1}) could be well described using the Freundlich isotherm (Fig. 4), indicating chemical heterogeneity of the sorption sites [24]. The Freundlich equation can be described as:

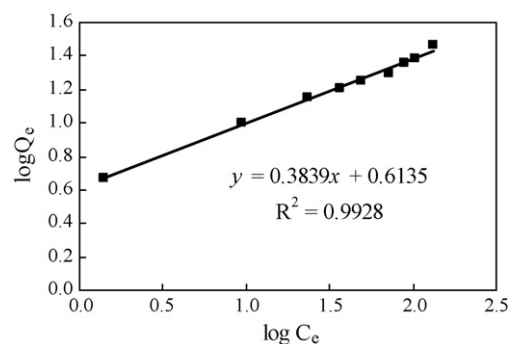$$Q_e = KC_e^n \quad \text{or} \quad \log Q_e = \log K + n \log C_e$$

Fig. 2. Effect of contact time on removal of acid blue 80 by alkaline white mud (AWM).

Fig. 4. Freundlich isotherm for adsorption of acid blue 80 at low initial concentrations (20–250 mg L^{-1}), equilibrium pH 10.8 ± 0.02.

where Q_e (mg g^{-1}) is the amount of acid blue 80 adsorbed at equilibrium, C_e (mg L^{-1}) is equilibrium concentration of the dye in solution, and K, n are empirical constants. The calculated K and n were 4.107 and 0.3839, respectively, from the adsorption isotherm data. At a high initial dye concentration (>300 mg L^{-1}), on the other hand, an abrupt increase in the dye removal is probably due mainly to chemical precipitation process, which was confirmed by a similar pattern of the dye removal in supernatants separated from AWM suspensions. As shown in Fig. 3, when initial dye concentration was low (<300 mg L^{-1}), the removal of dye from the supernatants was below 20%, much less than that from the suspension. An abrupt increase in the dye removal in the supernatants was also observed when the concentrations of dye were up to about 300 mg L^{-1}. The abrupt increase is expected to be the result of chemical precipitation. As a matter of fact, precipitat was observed at the bottom of conical beakers in the dye–supernatant systems. A further increase in the dye removal was slight when dye concentration was continuously enhanced above 350 mg L^{-1}. By comparing the dye removal by AWM suspensions with that by the corresponding supernatants, it is clear that, at high initial concentration of dye (>300 mg L^{-1}), the dye removal from the supernatants could account for most portion of the total removal from the suspension system. The above facts suggest that surface sorption is the main mechanism for the dye removal at low dye concentrations, while chemical precipitation is the dominant mechanism at high dye concentrations (>300 mg L^{-1}) with minor contribution from surface sorption. At a high dye concentration, precipitation of the dye anions with soluble Ca^{2+} and Mg^{2+} in AWM suspensions is expected to occur, which then built conglomerates and floccules. In this process, precipitate may have scavenged a fraction of the dye molecules, which could improve the dye removal to some extent. At a low dye concentration, chemical precipitation, if any, played only a minor role in the dye removal due probably to low supersaturation and/or relatively slow kinetic rate of precipitate formation. It deserves noting that a limited increase in the dye removal with increasing dye concentration from 350 to 500 mg L^{-1} implies that soluble Ca^{2+} and Mg^{2+} concentrations are high enough for dye precipitation in the experimental system, because, if the case is the opposite, a consumption of soluble Ca^{2+} and Mg^{2+} through chemical precipitation would have obviously suppressed the dye removal with an increase in initial dye concentrations. We may conclude that AWM could be used to treat anionic dye wastewater of high concentration in a pre or main step, producing much less sludge through adsorption/precipitation mechanism than using conventional adsorption technique.

3.3. Effect of AWM dosage

The effect of AWM dosage on removal of the dye is shown in Fig. 5. The removal increased with increased amount of AWM up to a maximum efficiency (95%), after which an increase in AWM dosage does not further improve the dye removal, implying that a complete dye removal could not be achieved even though using large amount of the AWM. Prior to reaching the maximum efficiency of 95%, the dye removal is increasingly
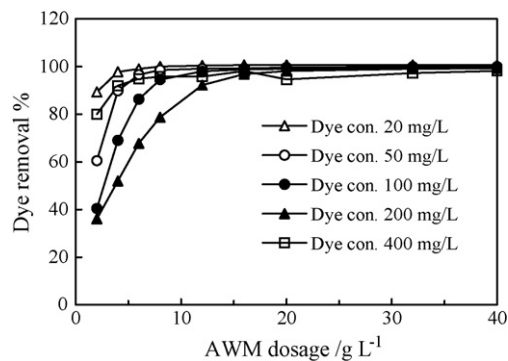

Fig. 5. Effect of alkaline white mud (AWM) dosage loaded on removal of acid blue 80 by alkaline white mud (AWM).

dependent on AWM dose used with an increase in dye concentration in the range of 20–200 mg L^{-1}; for dye concentration of 400 mg L^{-1}, however, the dye removal is much less dependent on AWM dosage. The results reconfirmed the different mechanisms for the dye removal at low and high dye concentrations discussed in Section 3.2. For surface sorption mechanism at a low dye concentration (<300 mg L^{-1}), sorption sites available for sorption increase with an increase in AWM dose used, resulting in an increase in the dye removal. For chemical precipitation mechanism at a high dye concentration (>300 mg L^{-1}), however, soluble Ca^{2+} and Mg^{2+} played a critical role in the dye removal, which is believed to result in a weak dependency of the dye removal on AWM dosage. It implies that AWM is much more efficient for the dye removal at high dye concentration than at low one based on per gram of dry AWM used, and thereby producing less sludge based on per gram of the dye removal. It is estimated that, to treat 1 t wastewater of high dye concentrations (e.g. 400–450 mg L^{-1}) with an efficiency above 90%, ca 6 kg dry AWM is needed. For wastewater treatment with low dye concentration (<300 mg L^{-1}), however, a similar amount of the AWM (6 kg) is only capable of treating dye wastewater with concentrations less than 50 mg L^{-1}, and a much larger volume of sludge will be produced for treatment of the dye with concentrations between 50 and 300 mg L^{-1}.

It is expected that both surface sorption sites and concentrations of soluble Ca^{2+} and Mg^{2+} in suspensions increase with an increase in AWM dose used. However, the increase in concentration of Ca^{2+} and Mg^{2+} when AWM dose was increased (>15 g L^{-1}) seemingly did not improve the dye removal significantly (Fig. 5), which was verified by another test. An addition of CaCl$_2$ or MgCl$_2$ salts of different concentrations to the dye–AWM suspensions did not significantly enhance the dye removal (Fig. 6a and b). This implies that the concentration of soluble Ca^{2+} and Mg^{2+} in AWM suspensions is high enough for dye anion precipitation when AWM amount used is beyond a certain value, and thereby an extra increase in Ca^{2+} and Mg^{2+} cannot improve the dye removal.

As far as removal of high-concentration anionic dye is concerned, although a complete removal by the AWM could not be achieved, a much high efficiency could be obtained. It is economically of importance for application of AWM in wastewater treatment, because, although a similar high dye removal could
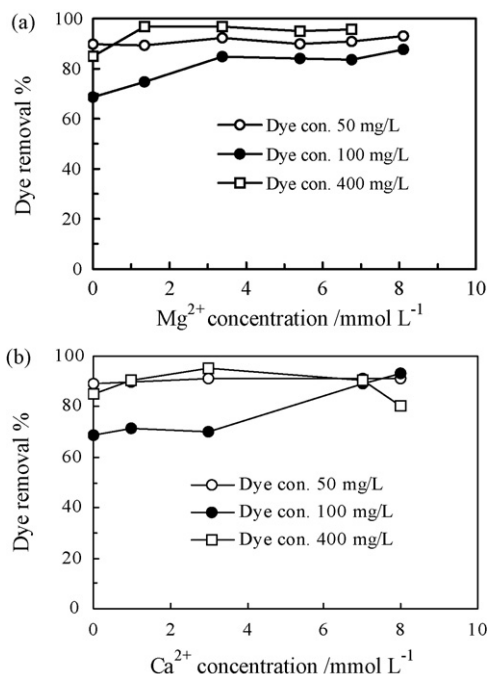
Fig. 6. Effect of Mg^{2+} (a) and Ca^{2+} (b) concentrations added on removal of acid blue 80 by alkaline white mud (AWM).

be achieved using activated carbon adsorption or chemical coagulation, high loadings are needed of activated carbon or specific chemical coagulants, consequently greatly enhancing treatment cost [15,16]. For other low-cost but less efficient adsorbents such as modified clay or agricultural by-products, high loading of the adsorbents is needed and thus a much greater volume of sludge would be produced [18,19]. Thus, AWM is superior to other low-cost adsorbents for removal of high concentration anionic dyes. The use of AWM is also superior to conventional coagulation/flocculation methods because the former is exempted from loading of chemical coagulants.

3.4. Effect of initial pH of dye solutions

The effect of initial pH of dye solution on removal of the dye is shown in Fig. 7. At pH ranging from 2.8 to 11.5, the effect of initial pH on the dye removal was slight, and the final pH values
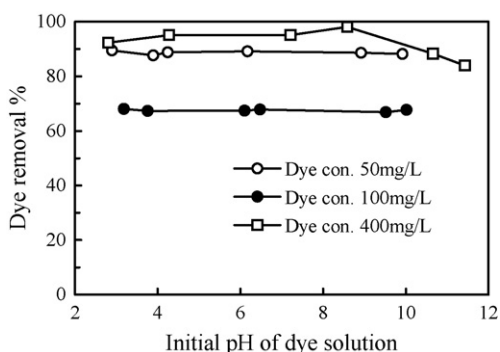
were all stabilized around 10.5. The slight effect of pH on the dye removal as well as high and stable final pH of the suspensions is mainly determined by the nature of high alkalinity and large pH buffer capacity of AWM suspension. Therefore, pH is not a critical limiting factor in pursuing a high efficiency of the dye removal using AWM and no rigid pH control is needed. That is an important advantage for AWM application because dye removal using conventional adsorbents or chemical coagulants is strongly pH dependent and thereby an optimal pH condition should be remained to achieve a satisfactory result.

3.5. Effect of inorganic anions SO_4^{2-} and PO_4^{3-}

The effect of two inorganic anions SO_4^{2-} and PO_4^{3-} on removal of the dye by AWM suspension is shown in Fig. 8(a and b). The dye removal remained almost unchanged with an increase in SO_4^{2-} concentration when initial dye concentrations were 50 and 100 mg L^{-1} (Fig. 8a). That implies that competition of SO_4^{2-} with the dye anions for sorption sites is weak, given that surface sorption is the main mechanism at low dye concentration (<300 mg L^{-1}). At 400 mg L^{-1} of dye concentration, the dye removal was also kept almost unchanged when SO_4^{2-} concentration increased up to 0.7 mol L^{-1}. However, the dye removal decreased rapidly with a further increase in SO_4^{2-} concentration (>0.7 mol L^{-1}). The rapid decrease is expected to be the result of competition between SO_4^{2-} and the dye anions for Ca^{2+} and Mg^{2+} to precipitate when SO_4^{2-} concentration is sufficiently high, given that chemical precipitation is the dominant mechanism for the dye removal at high dye concentration (>300 mg L^{-1}). In this process, although precipitation of $CaSO_4$
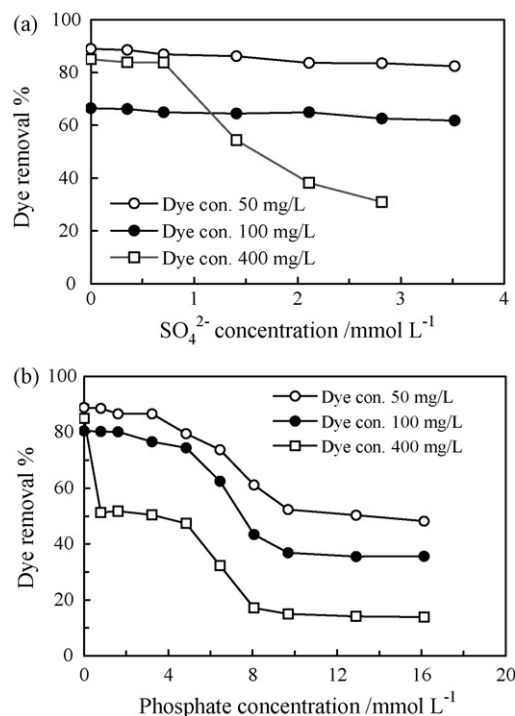

Fig. 7. Effect of initial pH on removal of acid blue 80 by alkaline white mud (AWM).

Fig. 8. Effect of sulphate ion (a) and phosphate ion (b) on removal of acid blue 80 by alkaline white mud (AWM).

and $MgSO_4$ may have scavenged a fraction of the dye anions, beneficial to overall removal of the dye to some extent, direct precipitation of the dye molecule, however, is largely suppressed due to depletion of Ca^{2+} and Mg^{2+}, leading to a substantial decrease in overall removal of the dye from 85% to 31%.

The dye removal decreased with an increase in phosphate concentration up to $10\,mmol\,L^{-1}$ at all dye concentrations (Fig. 8b), and then leveled off with further increase in phosphate concentration ($>10\,mmol\,L^{-1}$). At high initial dye concentration ($400\,mg\,L^{-1}$), the effect of phosphate on the dye removal is markedly higher than at low dye concentration (50 and $300\,mg\,L^{-1}$), particularly when phosphate concentration is low. The above difference could also be attributed to different mechanisms for the dye removal at low and high dye concentrations. Besides formation of $Ca_3(PO_4)_2$, $Mg_3(PO_4)_2$ and, perhaps other Ca–P phases such as $Ca_{10}(PO_4)_6(OH)_2$ and $CaHPO_4 \cdot 2H_2O)$ depending on solution pH and Ca/P ratio [25,26], the presence of PO_4^{3-} species (approximately 8–10% at pH 10.5 [23]) may efficiently compete sorption sites with dye anions due to high negative charge of PO_4^{3-} species, leading to a progressive decrease in the dye removal with increasing phosphate concentration. For chemical precipitation mechanism at high dye concentration ($>300\,mg\,L^{-1}$), formation of (Ca, Mg)–P precipitates may consume large amounts of Ca^{2+} and Mg^{2+} with increasing phosphate concentration, greatly suppressing direct precipitation of the dye anions with Ca^{2+} and Mg^{2+} and thus resulting in a substantial decrease in the dye removal. At a sufficiently high concentration of phosphate ($>10\,mmol\,L^{-1}$), soluble Ca^{2+} and Mg^{2+} probably have been almost completely consumed through precipitation with phosphate. Therefore, a continuous increase in phosphate will not further reduce the dye removal in an appreciable way as shown in Fig. 8b.

4. Conclusion

Alkaline white mud could be used as an effective yet low-cost material for removal of anionic dye acid blue 80 in a pre or main process, particularly at high dye concentration ($>300\,mg\,L^{-1}$), reaching maximum efficiency of 95%. However, a finishing and polishing step is necessary due to an incomplete dye removal even though large amount of AWM is used. Two mechanisms contribute to the dye removal by AWM, with surface adsorption the dominant at low dye concentration ($<300\,mg\,L^{-1}$) and chemical precipitation with soluble Ca^{2+} and Mg^{2+} the dominant at high dye concentration ($>300\,mg\,L^{-1}$), respectively. Solution pH has only a limited effect on the dye removal due to high alkalinity and large pH buffer capacity of AWM suspension and thereby pH is not a limiting factor in pursuing high dye removal. The presence of sulphate ions can reduce the dye removal by AWM only when their concentration is beyond $0.7\,mmol\,L^{-1}$. The dye removal could be significantly suppressed by the presence of phosphate with increasing concentration, and the reduction of the dye removal is much larger at high dye concentrations than at low ones. In practical application of AWM for removal of acid blue 80 with an efficiency above 90%, the optimal reaction time is 6 h, the optimal amount of AWM used is $6\,g\,L^{-1}$ and $6–12\,g\,L^{-1}$ for treatment of high

($400\,mg\,L^{-1}$) and low ($50–300\,mg\,L^{-1}$) dye concentrations, respectively. Unlike many other adsorbents or chemical coagulants, no rigorous pH control is needed using AWM to treat anionic dye wastewaters.

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