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Original Article

The settling behavior of quartz using chitosan as flocculant

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ABSTRACT

The settling behavior of quartz using chitosan as flocculant has been studied and the mechanism has been discussed. The sedimentation results show that pH has an influence on the settling behavior of quartz particles and the sedimentation velocity is more quickly at acidic pH range. Chitosan is a useful flocculant for the settling of quartz but its flocculation effect is influenced greatly by pH. The sedimentation velocity of quartz is quickly and the volume of sediment is large when chitosan was added at pH 9. The reason is that chitosan is only sparingly soluble in water at pH 9, thus the adsorption amount is large and produce strongly flocculation effect. However, when the pH was changed from 9 to 3, the adsorbed chitosan desorption from quartz surface and the flocculation effect disappeared. The flocs were disorganized to the particles and the sediment can be consolidated to significantly higher densities.

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1. Introduction

Because of the very slow settling of fine solids in the tailing ponds, it is necessary to flocculate fine particles to produce more rapid settling and easy removal of the solids by gravity in the tailings treatment process [1]. Over the last several years, many attempts have been made to realize the fast solid liquid separation. This includes the addition of excess electrolyte (coagulation), the addition of a high molecular weight polymer (bridging flocculation) and change of pH [2–5]. Bridging flocculation is extremely important in mineral tailings disposal. However, polymeric flocculants, which are widely used in the flocculation of tailings have the drawback that the flocs contain large amounts of water which cannot be easily removed. To solve this problem, stimuli-responsive polymers were used in the solid liquid separation process [6–10].

In recent years, much interest has been focused on polymer systems that show a phase transition in response to external stimuli such as temperature, pH, ionic strength, and electric potential because of their scientific or technological importance [11–14]. A temperature-sensitive polymer, poly(N-isopropylacrylamide) has been widely used in settlement process and improved dewatering efficiency by producing

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both fast sedimentation of fine particles (by aggregation) and dense (low moisture) sediment beds and filter cakes [15–17]. However, it is necessary to heat the slurry above the critical solution temperature to achieve fast sedimentation of fine particles, which will waste a lot of energy [18].

The settling behavior of quartz using chitosan as flocculant has been studied and the mechanism has been discussed in this paper. The aim of this paper is to provide a novel solid/liquid separation reagent, which is sensitive to the change of pH.

2. Materials and methods

2.1. *Pure minerals and reagents*

Pure quartz was sourced from Jiangxi, China. X-ray powder diffraction data confirmed that the quartz was 99% pure (Fig. 1). The sample was dry ground and screened. The $-20\,\mu m$ fraction was used in the settling tests and adsorption tests. Samples further ground to $-2\,\mu m$ in an agate mortar were used for zeta potential measurements.

The sample of chitosan (molecular weight is 250,000 mol/l and degree of deacetylation ≥95%) used in this study was obtained from Shanghai Civi Chemical Technology Co., Ltd. Hydrochloric acid (HCL) and sodium hydroxide (NaOH) were used as pH regulators. Deionized water was used for all tests.

2.2. *Sedimentation tests*

For the sedimentation tests, 1 g of sample was taken and made up to 100 ml after addition of distilled water in a beaker. Then desired amount of chitosan was added to the suspensions and agitated for half an hour using a magnetic stirrer at different pH, and then transferred to 100 ml graduated cylinders. As soon as the cylinder was placed on a flat solid surface, the settling test began and no further disturbances were allowed. The descent of the solids/liquid interface (mud line) was carefully observed and recorded as a function of settling time. Photographs were also taken of the settling suspensions periodically, initially every few min, then every few hours.

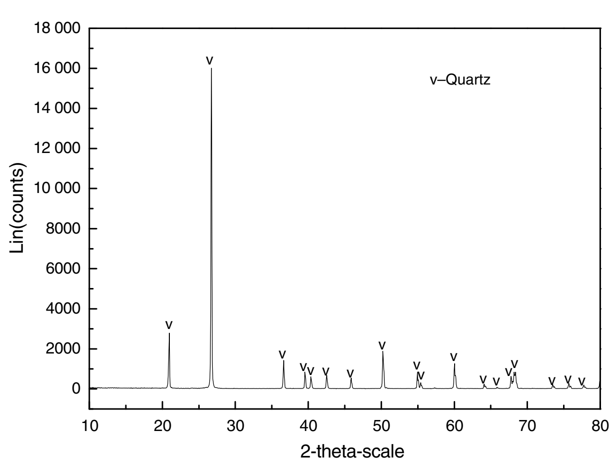

Fig. 1 – XRD diagram of quartz.

2.3. *Adsorption tests*

For the adsorption tests, 1 g of mineral powder was taken and made up to 50 ml after addition of desired concentration of chitosan solution in 250 ml Erlenmeyer flasks. The suspensions were mixed and placed on a rotator for 1 h, ensuring that the adsorption process had reached equilibrium. Each sample was then centrifuged and the concentration of chitosan remaining in the supernatant is measured by determining the total organic carbon (TOC) in the supernatant and comparing the value to a known calibration standard.

2.4. *Zeta potential measurements*

For these measurements, a mineral suspension was prepared by adding 1 g mineral to 50 ml of 10^{-3} M potassium nitrate solution and magnetically stirred for 10 min and the pH adjusted using HCl or NaOH. The zeta potential of samples was then measured using a zeta potential meter.

3. Results and discussion

3.1. *The settling behavior of quartz at different pH*

The effect of pH on the settling behavior of quartz was studied and the results are shown in Fig. 2. It is evident from Fig. 2 that pH has influence on the sedimentation velocity of quartz and the quartz particles settling more quickly at pH 3. The reason is that the surface charge of quartz increased with the increase of pH, and so is the electrostatic repulsion force between quartz particles.

Fig. 3 shows the effect of chitosan amount on the settling behavior of quartz at pH 3. It is evident from Fig. 3 that the addition of chitosan increased the sedimentation velocity of quartz, but the sedimentation velocity is still slow. A large number of fine particles are still suspended when the settling time is 30 min. The results also show that when the chitosan amount increased from 300 mg/L to 600 mg/L, the sedimentation velocity of quartz decreased. This is due to the fact that adsorption of chitosan makes the quartz particles have more

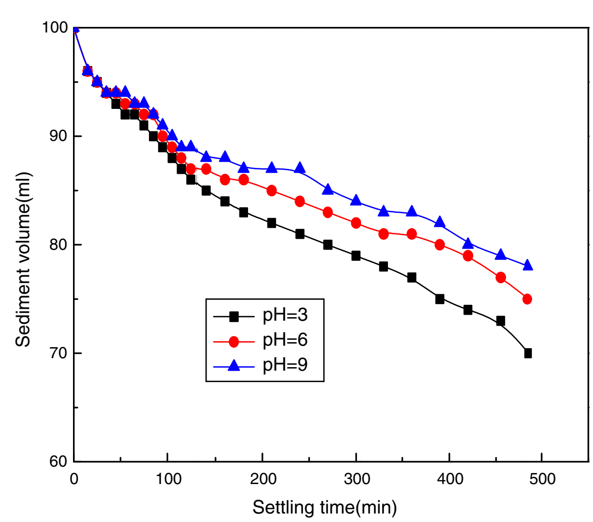

Fig. 2 – Effect of pH on the settling behavior of quartz.

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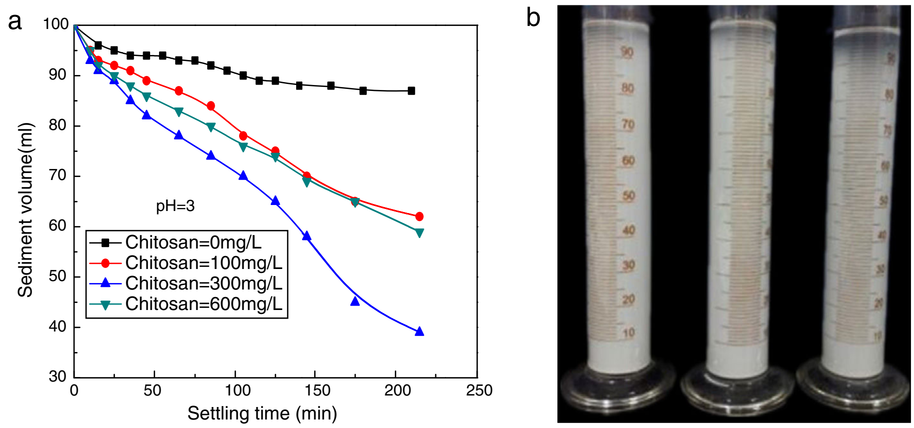

Fig. 3 – (a) Effect of chitosan amount on the settling behavior of quartz at pH 3. (b) Photograph at the settling time of 30 min. The dosage of chitosan from left to right is 100 mg/L, 300 mg/L, 600 mg/L, respectively.

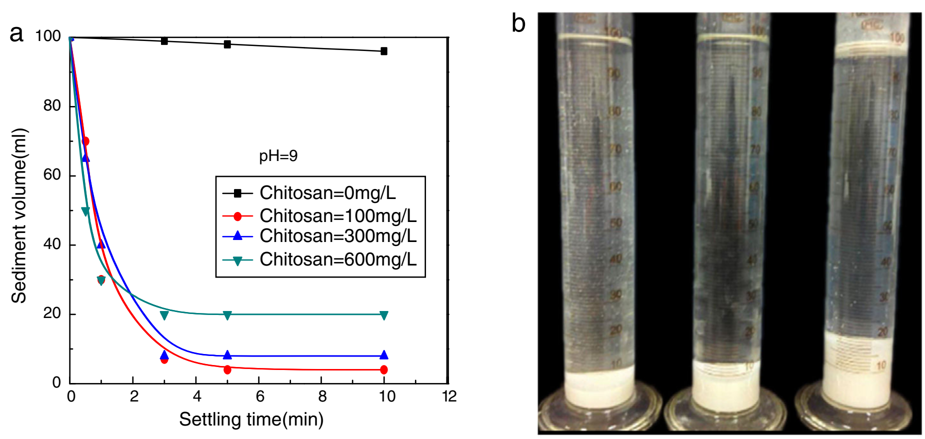

Fig. 4 – (a) Effect of chitosan amount on the settling behavior of quartz at pH 9. (b) Photograph at the settling time of 3 min. The dosage of chitosan from left to right is 100 mg/L, 300 mg/L, 600 mg/L.

positive charge, resulting in a strong electrostatic repulsive force between particles, which hinders the flocculation and settling of quartz particles. The results in Fig. 3 illustrate that chitosan has flocculating effect on quartz particles at pH 3, but the chitosan amount should be appropriate.

Fig. 4 shows the effect of chitosan amount on the settling behavior of quartz at pH 9. It is evident from Fig. 4(a) that the sedimentation velocity of quartz is very quickly with the addition of chitosan at pH 9. The upper parts of all the three cylinders in Fig. 4(b) become very clear when the settling time is only 3 min. The more the chitosan dosage is, the larger the sediment volume is.

Fig. 5 shows the settling behavior of quartz at pH 3 and 9 when 300 mg/L chitosan is added. The result illustrates that the quartz particles is settling more quickly at pH 9. It can be seen that no sediment is formed and the suspension occupied nearly 100% of the cylinder volume at pH 3 when the settling time is 5 min. When the pH is 9, the upper part of the cylinder is clear and the sediment occupied less than 10% of the cylinder volume.

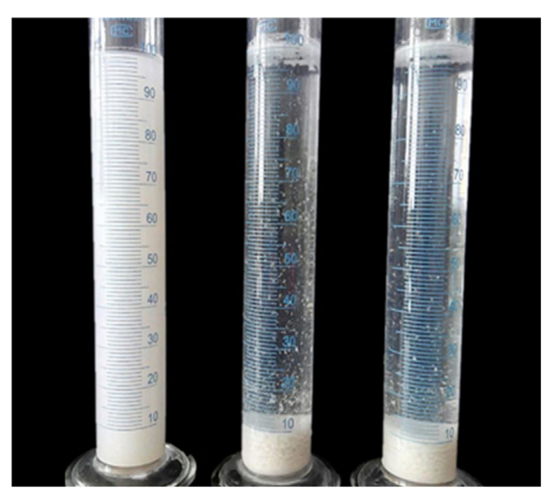

Fig. 5 – Effect of chitosan on the settling behavior of quartz at different pH (settling time = 5 min; left: pH = 3, middle and right: pH = 9).

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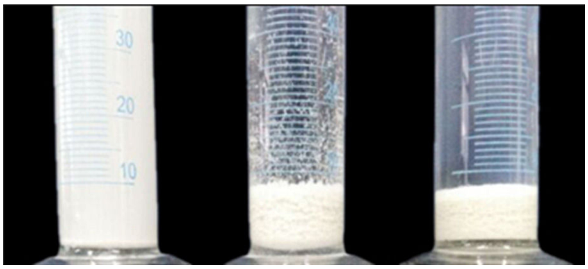

Fig. 6 – Effect of the change of pH on the settling behavior of quartz (settling time = 60 min; left: pH 3, middle: pH 9, right: pH 9-3).

After 1 h of settling process of quartz, we changed the pH of the suspension in the right cylinder from 9 to 3 and continue to observe the settling behavior of the three cylinders. The results are showing in Fig. 6. As shown in Fig. 6, the sediment in the right cylinder is consolidated to significantly higher densities after the pH was changed from 9 to 3.

3.2. *The adsorption mechanism of chitosan to quartz at different pH*

Chitosan is positively charged at low pH, but loses its charge as pH is increased above neutral. When it loses its charge it becomes hydrophobic and is only sparingly soluble in water [19,20]. The dissolution behavior of chitosan at different pH was studied and the results were shown in Fig. 7. It can be seen that the chitosan solution is clear at pH 3. The chitosan became insoluble and the solution became turbidity when the pH value is increased to 9. However, when the pH is further decreased to 3.4, the solution becomes clear again.

Fig. 8 shows the adsorption behavior of chitosan onto quartz surfaces at different pH. The results show that the adsorption amount of chitosan at pH 9 is significantly higher than the amount that is adsorbed at pH 3. The reason is that in addition to the electrostatic interactions, which drive adsorption at pH 3, the chitosan which is poorly soluble in water at pH 9 deposits onto the surface [21].

The effect of chitosan amount on the zeta potential of quartz at different pH was studied and the results are given in Fig. 9. It is clear from Fig. 9 that the zeta potential values of quartz are −19.47 mv and −45.3 mv, respectively, at pH 3 and 9. With the addition of chitosan, the surface potential of quartz changed from negative to positive at pH 3. However, the addition of chitosan at pH 9 makes the surface potential of quartz close to zero. The result in Fig. 9 illustrates that the chitosan is positively charged at pH 3 and adsorbs on quartz surface by electrostatic interaction between the reagent and surface. When the pH increased to 9, chitosan loses its charge

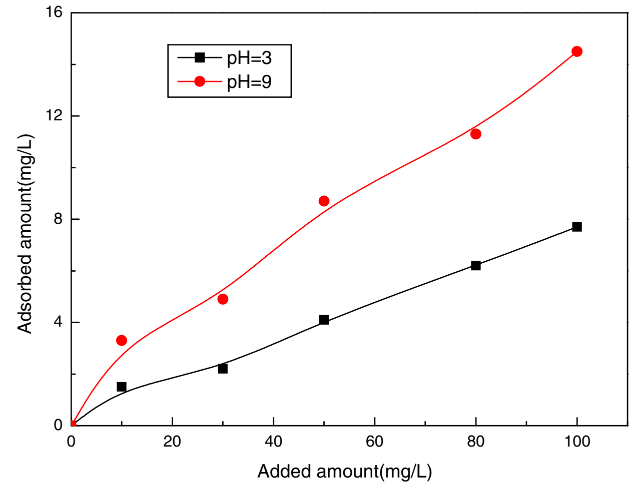

Fig. 8 – Effect of pH on the adsorption behavior of chitosan onto quartz.

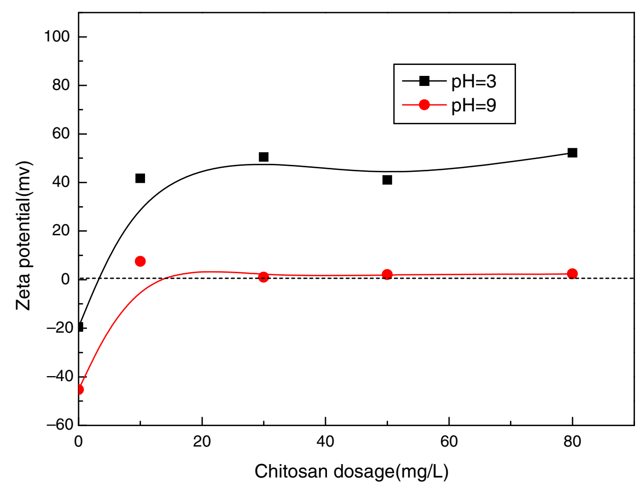

Fig. 9 – Effect of chitosan dosage on the zeta potential of quartz at different pH.

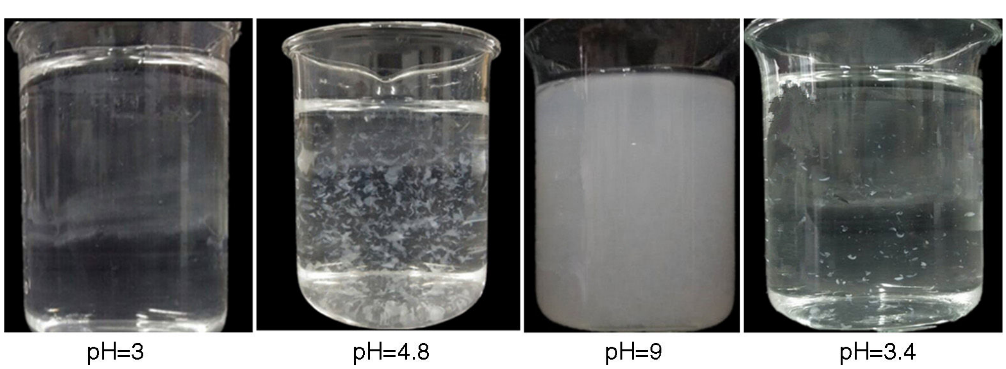

Fig. 7 – Effect of pH on the dissolution behavior of chitosan.

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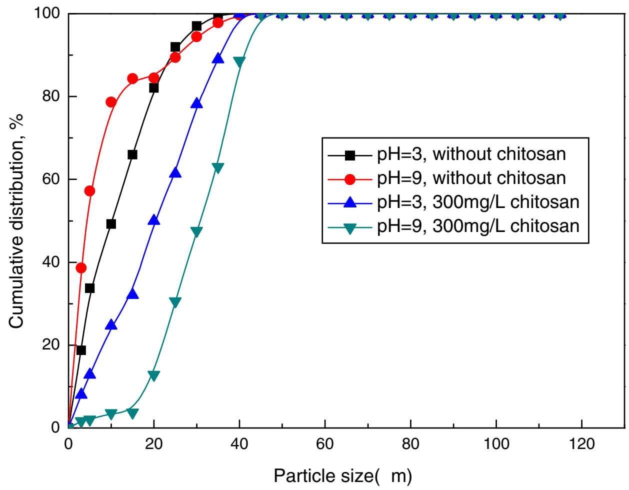

Fig. 10 – Effect of pH on the particle size distribution of quartz in the absence and presence of chitosan.

and the adsorption of the non-charged chitosan moved the slip surface of electric double layer.

The effect of pH on the particle size distribution of quartz in the absence and presence of chitosan were studied and the results are shown in Fig. 10. It is clear from Fig. 10 that pH has influence on the particle size distribution of quartz and the size increased when the pH decreased from 9 to 3 as the electrostatic repulsive force between particles at pH 9 is larger than the value at pH 3. With the addition of chitosan, the particle size of quartz increased at both pH 3 and 9, however, the increase of particle size at pH 9 is more obvious. The results in Fig. 10 illustrate that chitosan produce flocculation effect on quartz particle.

4. Conclusions

Chitosan is a useful flocculant for the settling of quartz but its flocculation effect is influenced greatly by pH. At pH 3, the addition of chitosan increased the sedimentation velocity of quartz, but the sedimentation velocity is still slow. The sedimentation velocity of quartz is quickly and the volume of sediment is large when chitosan was added at pH 9. The reason is that the chitosan is positively charged at pH 3 and adsorbs on quartz surface by electrostatic interaction between the reagent and surface, thus the adsorption amount is small. When the pH is increased to 9, chitosan is only slightly soluble in water and the adsorption amount is large, thus produced strongly flocculation effect. When the pH of sediment was changed from 9 to 3, the adsorbed chitosan desorption from quartz surface and the flocculation effect disappeared. The flocks were disorganized to the particles and the sediment can be consolidated to significantly higher densities.

Conflicts of interest

The authors declare no conflicts of interest.

Acknowledgements

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