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Flocculation study of aqueous iron ore suspension using Shellac

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Abstract

The flocculation of iron oxide can be achieved using Shellac in suitable concentration ranges. Alkaline Shellac solution was used in ppm concentration as the flocculating agent. Experiments were carried out on tap water containing dispersed iron ore (5%) that simulates typical industrial waste water scenario by varying the operating parameters, such as shellac dosage, pH in order to study their effect in flocculation process by using shellac. The optimum results were achieved for this study was at 15 ppm concentration of 0.1% (W/V) shellac in 0.5 M NaOH solution.

Keywords:

Flocculation;
Iron Oxide;
Zeta Potential;
Turbidity;
Hydrodynamic Volume.

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1. Introduction

Waste waters emanated from different industries contain different smaller size suspended particles [1-2]. Difficulties have been faced over the years to remove these solid particles because of their smaller size and they carry surface charges in most of the cases [3-7]. Attempts have been made to separate these suspended solids (that may be even toxic in nature in some cases) for purification and possible reusage of water by means of synthetic, semi synthetic or natural polymeric materials coined as flocculant. Evidences are there in literature for synthetic polymeric materials such as Polyacrylamide (PAM) [1, 4, 6, 8], poly (ethylene oxide) (PEO) [9], poly(acrylic acid) [10] and its derivatives, poly(styrene sulfonic acid) (PSSA) [11] to be used as flocculant. Two serious drawback of synthetic polymer are the non biodegradability and the toxicity and this helps in opening the account of natural polymeric material to be used as flocculant [12-14].

Shellac secreted by the parasitic insect Kerria lacca (order Hemiptera, family Kerridae also known as *Laccifer lacca*) [15] is not a polymeric material in true sense as it is devoid of any sort of repeating unit that is necessary to have in its structural back bone for a material to be printed as polymer. We will not go into confusion about the inclusion of shellac into the polymer category after simplifying shellac as a natural oligomeric (MW~100 D) resinous material. Shellac has been widely used for varnish in India [16] as well as all over the world. It also used as coating for edible things may be from early 19th century. Recently, industries of pharmaceuticals and that of foods and vegetables are using shellac as edible coatings [17]. In our present study we helped Shellac to add another feather on its crown after investigating its flocculation efficiency when used for settling suspended iron ore particles from aqueous iron ore suspension.

Iron oxide is a waste product coming of industries such as steel industry. Iron oxide represents typical hydrophilic mineral oxides that form both a large part of both valuable and waste mineral dispersions that

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must be routinely dewatered during hydrometallurgical mineral processing operations. Due to its hydrophilic nature colloidal stable iron oxide dispersion has proven to be significantly difficult to dewater to a high solid loading. Iron oxide contains high positive charges in its surfaces. Ionic interaction between these surface charges provides the means of suspension stabilization. Synthetic or natural polymeric material known as polyelectrolyte capable of producing charges in its surfaces, by means of charge neutralization and bridging the destabilized colloidal particles provides the means of suspension destabilization and therefore leading to separation from the liquid medium [18]. Polyelectrolyte carrying negative surface charges is quite capable of producing floc form iron ore suspension depending on the pH of the medium and amount of flocculant added. Extensive studies on the composition Shellac show that it is a complex mixture of resin, wax and dye. Various hydroxy acids have been isolated by the chemical degradation of the hard resin portion [15]. For the sake of simplicity it is considered that shellac as an acidic material that shows polyelectrolytic behavior when dissolved in aqueous caustic soda solution. We used alkaline shellac solution as the flocculant in our study.
The zeta potential of the colloidal particle and the flocculant is an important parameter in selecting the flocculant as well as in deciding flocculation condition [19-20]. Zeta potential is the potential difference between the shear plane of the colloidal particle and that of the bulk of the solution. Zeta potential actually gives an indirect insight of the charged colloidal particles. When these particles are in presence of enough counter ions then they become electrically neutral and this point is called the isoelectric point (IEP) of the colloidal particles. The zeta potential of the colloidal particle is zero at the isoelectric point. Therefore utilizing the concept of the isoelectric point of the colloidal particle suitable flocculant can be selected for a particular colloidal system.

2. Experimental

2.1. Materials:

The iron ore sample of which settling rate was studied in the present work was supplied by Tata Steel, Jamshedpur, India. The iron ore sample was dried thoroughly in the oven at around ~ 100^0C to remove any sort of moisture that it may contain within it before conducting the experiments. The natural biodegradable polymeric flocculant that was used for this settling experiment was shellac which was collected from the general laboratory, department of polymer science of technology, University of Calcutta.

2.2. Preparation of Shellac solution

0.1% (W/V) Shellac solution was prepared by dissolving it into 0.1 M and 0.5 M aqueous Sodium Hydroxide solution after grinding the shellac into fine powder by mortar and pestle.

2.3. FTIR spectroscopy

The Fourier Transform Infrared Spectroscopy (FTIR) of the shellac was carried out on a System 2000 FTIR of Perkin Elmer, Norwalk, USA with a scan range of 400 - 4000 cm^{-1} at a resolution of 4 cm^{-1}. The FTIR spectrum of the resin was taken from compressed potassium bromide (KBr) pellet.

2.4. Reduced Viscosity measurement

Viscosity measurements of the alkaline Shellac solutions were carried out by using an Ubbelohde viscometer (as per ASTM-D-445) at 25^0C. The flow time was measured for solutions at four different concentrations in order to verify the polyelectrolyte character of the Shellac. Relative viscosity of the flocculant solutions (($\eta_{rel} = t/t_0$) were calculated utilizing the data points.

2.5. Flocculation characteristics

A suspension of model waste water prepared by 5 g iron ore in 100 c.c. of tap water was used for flocculation study. The suspension was taken in a 100cc graduated settling cylinder. 10, 15 and 20 ml 0.01% shellac solution were added to the solution to make concentration of flocculant solution in the suspension as 10 ppm, 15 ppm and 20 ppm. Immediately after the addition of flocculant, the cylinder was turned upside down 10 times for thorough mixing and homogenization. After 1 min equilibration the cylinder was set upright, and the height of interface between water and settling solid bed was measured over time. The change of interfacial height versus time data was collected until 30 cm from the initial height was diminished.

2.6. Measurement of hydrodynamic size and zeta potentials

Zeta potentials of the Shellac in different concentration of NaOH were measured in a Dynamic Light Scattering instrument, Zetasizer nano-ZS90, purchased from Malvern, United Kingdom. The measurements were carried out with the filtrate after the filtration of Shellac solutions.

2.7. Turbidity Studies

The turbidity of the supernatant liquid after experimentation was measured by Systronics Digital Nephelo-Turbidity Meter, Model 132 in comparison to a standard formazin suspension. A sample of 2 ml from the suspended liquid was withdrawn from the depth of 12 cm and its turbidity was measured. Initially the data was recorded for five hours with 1 hour interval and finally after 24 hr to observe the change of turbidity for different flocculants over a day to optimize the flocculant nature for a wide period of time.

2.8. Determination of floc size

The SEM micrographs of the flocs were taken in a Scanning Electron Microscope (SEM, Carl Zeiss 5800) operated at 15 KV. The flocs were dried to remove the entrapped water. The SEM images were taken with dried flocs.

2.9. Water Entrapment Calculation

A weighed mass of the slurry after 24 hr of the experiment was taken and dried in a hot air oven until a constant weight at 110^0C. The weight difference obtained was expressed as the percentage water entrapped during each experiment.

3. Results and Discussion

3.1. Characterization of shellac

The FTIR spectrum of the shellac is shown in Figure 1. It shows a transmission peak at 3450 cm^{-1} which attributes the stretching of –O-H bond [21-22]. The transmission peak at 1717 cm^{-1} indicates the presence of –C=O unit of ester group in the shellac molecular structure. The peaks at 2851 & 2822 cm^{-1} are results of the aliphatic –C-H stretchings. This is showing the complex nature of the shellac resin. Shellac is considered to be a complex ester of polyhydroxy polybasic acids. Various hydroxy acids such as aleuritic acid, shellolic acid, kerrolic acid, butolic acid, and jalaric acid have been isolated by chemical degradation of the hard resin portion of shellac.

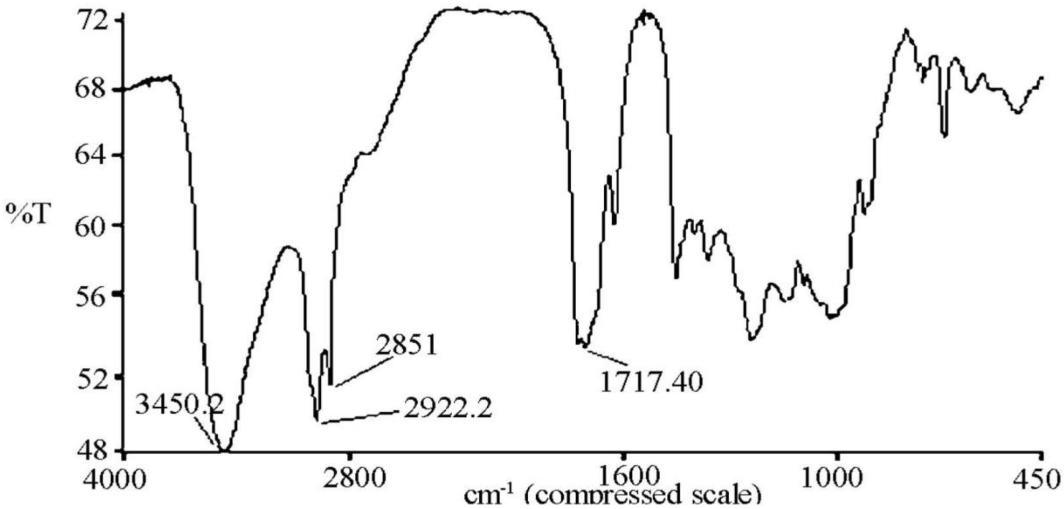

Figure 1. FTIR of Shellac

3.2. Relative Viscosity

Figure 2 displays the reduced viscosity measurements of shellac in different concentrations of NaOH. Iit has been found that the viscosity of Shellac solution in 0.5 M NaOH is higher than that in 0.05 M NaOH or in 0.1 M NaOH; this is because the solubility of shellac is higher in 0.5 M NaOH.

3.3. Flocculation characteristics

Flocculation performances of different doses of shellac in three different concentrations of alkaline solution (0.05M, 0.1M and 0.5M) were compared in Figure 3a-c. Sedimentation of iron ore suspensions by alkaline shellac solution is found to be almost linear. The linearity can be presented in the following form.

$$h = h_0 - kt \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

Where h denotes displacement of the sedimenting layer at any settling time t, k is the settling constant and h_0 is the initial height. Settling constants are 0.1257 cm/s, 0.1397 cm/s and 0.1333 cm/s for 10 ppm, 15 ppm and 20 ppm shellac in 0.05 M NaOH solution respectively; 0.1411 cm/s, 0.1575 cm/s and 0.1481 cm/s for 10 ppm, 15 ppm and 20 ppm shellac in 0.1 M NaOH solution and whereas these values are 0.1710 cm/s, 0.1873 cm/s and 0.1612 cm/s for 10 ppm, 15 ppm and 20 ppm shellac in 0.5 M NaOH solution.

It has been quite clearly observed that the flocculation performance of shellac is better at 15 ppm concentration compared to other concentration. With the increase in shellac concentration from 10 ppm to 15 ppm the flocculation activity increases as expected. On going from 15 ppm to 20 ppm, the sedimentation rate decreases. This may be due to flocculant overdosing. Because of this overdosing, some amount of the flocculant remains unadsorbed. Therefore it inhibits the upward rate of flow of fluid which ultimately decreases the sedimentation rate. Shellac in 0.5 M NaOH solution shows better flocculation efficacy than that in 0.1 M NaOH or in 0.05 M NaOH. It is attributed to the greater relative viscosity of shellac in 0.5 M NaOH than in 0.05 M and in 0.1 M NaOH solution. The higher value of reduced viscosity of shellac in 0.5 M NaOH solution indicates higher hydrodynamic volume as well as larger surface area, which improves the extent of adsorption of shellac onto iron ore particles.

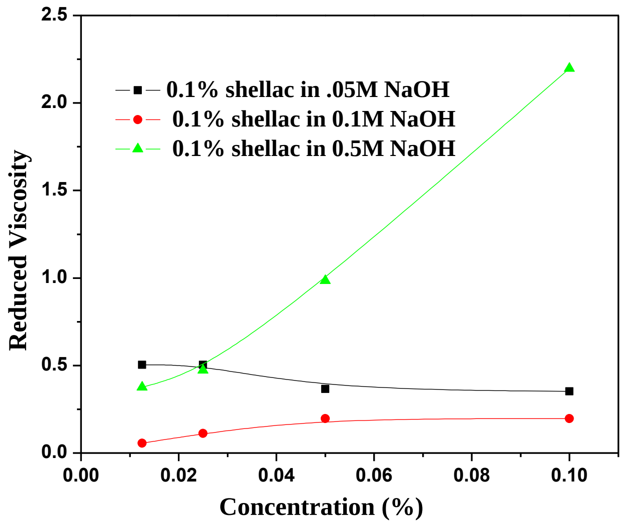

Figure 2. Intrinsic viscosity study of 0.1% shellac solution at different pH.

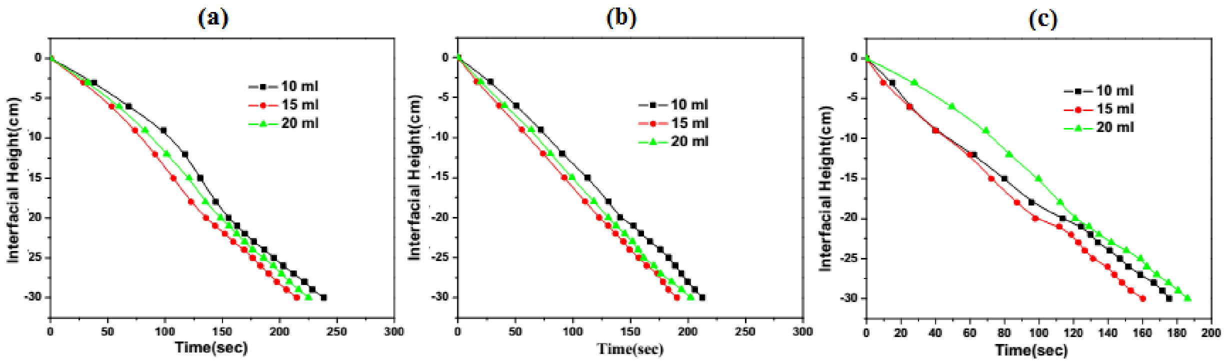

Figure 3. Settling study of 5% iron ore suspension using 0.01% Shellac in (a) 0.05 M NaOH, (b) 0.1 M NaOH and (c) 0.5 M NaOH.

Therefore, settling of iron ore particles becomes faster when shellac is used as flocculant in 0.5 M NaOH solution. But, if the high value of hydrodynamic volume is the only factor controlling the flocculation rate, then shellac would show better flocculation efficacy when it is in 0.05 M NaOH solution rather than in 0.1 M NaOH

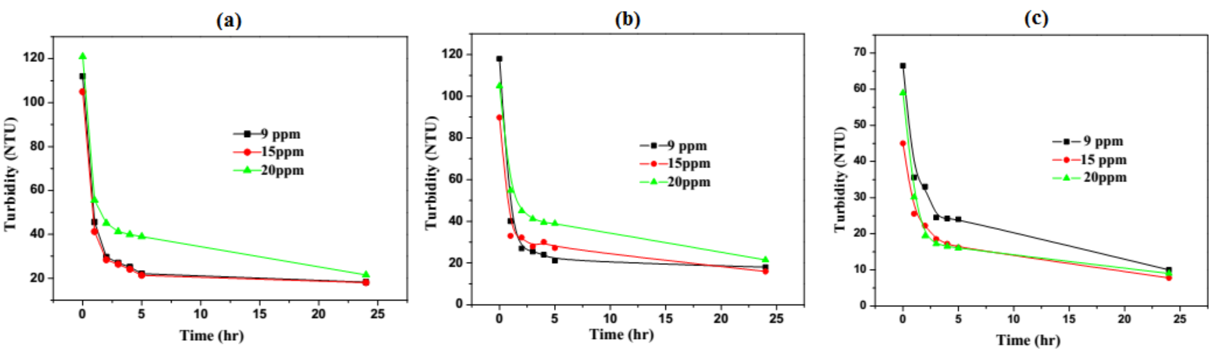

Figure 4. Turbidity study of 5% iron ore suspension using different ppm of 0.01% Shellac solution in (a) 0.05 M NaOH, (b 0.1 M NaOH and (c) 0.5 M NaOH.

solution as it is mentioned earlier that reduced viscosity of shellac is higher in 0.05 M NaOH solution than that in 0.1 M NaOH solution. But, on contrary to our expectation, shellac in 0.1 M NaOH solution produces the better results than that in 0.05 M NaOH solution. Another very important factor which is playing a pivotal role in the flocculation mechanism is zeta potential. Zeta potential of shellac in 0.5 M, 0.1 M and 0.05 M NaOH solution are -22.5 mV, -14.3 mV and -10.8 mV respectively. Earlier, it is mentioned that shellac is a complex ester of polyhydroxy polybasic acid. Therefore, the high negative zeta potential values of shellac in NaOH solution are due to the conversion of carboxylic acid and ester groups to carboxylate ions. At first, the negatively charged carboxylate ions present in the alkaline shellac solution neutralizes the positively charged iron ore particles and destabilize the iron ore suspension and in the second step, the destabilized iron ore particles get adsorbed onto shellac structure and form larger flocs and ultimately settle down. Hence, the high negative value of zeta potential as well as high reduced viscosity value enhances the flocculation efficacy of shellac in 0.5 M NaOH solution for the separation of iron ore from its aqueous suspension. Shellac in 0.1 M NaOH solution has lower reduced viscosity value and higher negative value of zeta potential than that in 0.05 m NaOH solution. So, shellac in 0.1 M NaOH solution shows the better settling results due the favourable zeta potential factor over that in 0.05 M NaOH solution.

Figure 4a-c show long term turbidity analysis of the iron ore suspension after flocculation experiments. From these it can be concluded that most of turbidity removal takes palce in very fist hour and after that it slows

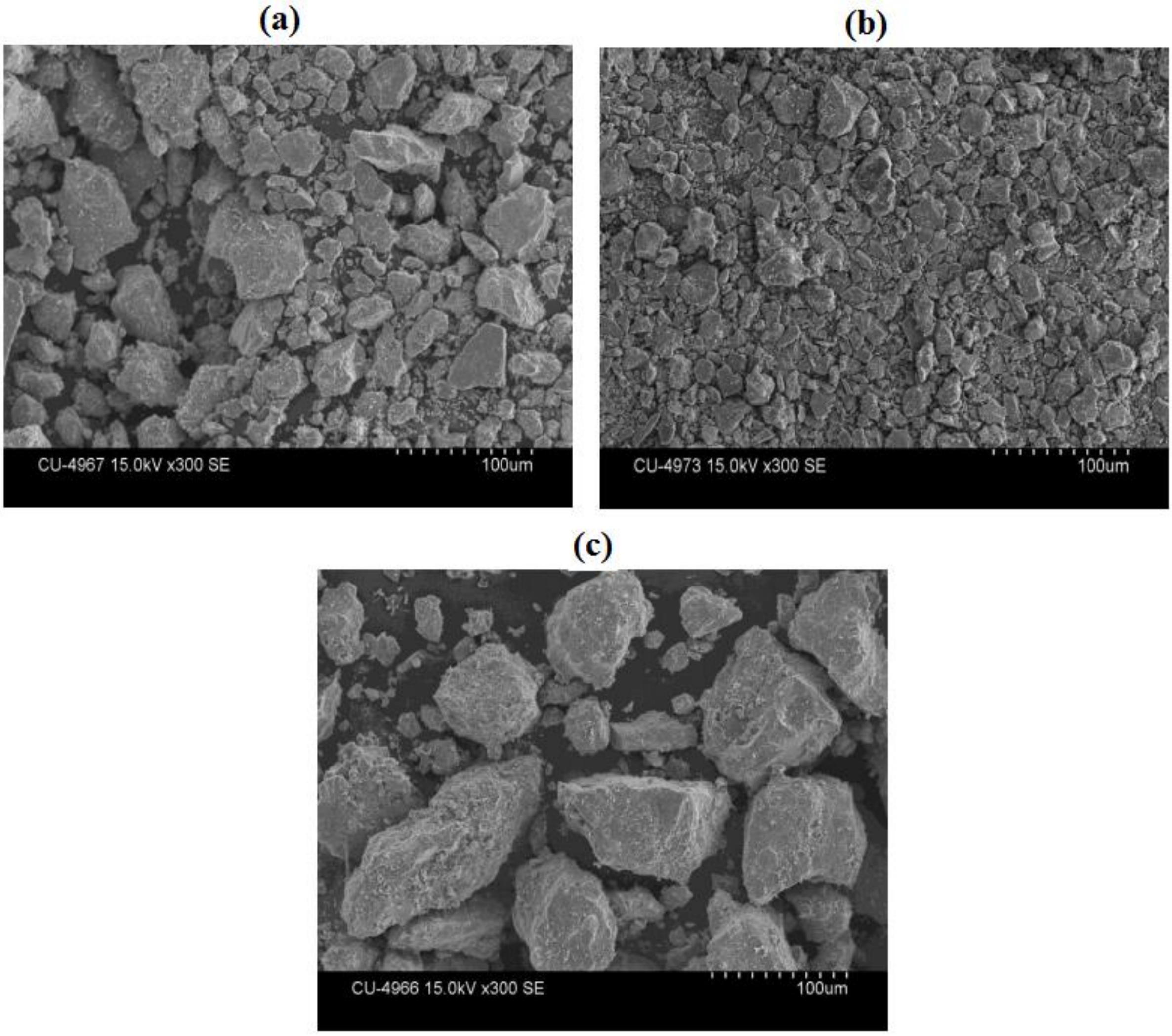

Figure 5. SEM images of the flocs produced by 0.01% Shellac solution in (a) 0.05 M NaOH, (b) 0.1 M NaOH and (c) 0.5 NaOH.

down drastically. Shellac in 0.5 M NaOH solution produces the lowest residual turbidity value, whereas that in 0.05 M NaOH solution shows the highest residual turbidity value. Because of the higher adsorbate area and favorable negative zeta potential, shellac in 0.5 M NaOH removes most of the iron ore form the suspension leading to the lowest residual turbidity value.

SEM micrographs of the flocs obtained from different shellac solution are displayed in Figure 5a-c. Shellac in 0.1 M NaOH solution produces flocs of smaller size compared to that obtained from shellac in 0.05 M and 0.5 M NaOH solutions. Large floc size has nothing to do with the flocculation efficiency of the flocculants, whereas it directly depends upon the high hydrodynamic volume of shellac. Hence, shellac in 0.5 M NaOH produces larger sized flocs followed by shellac in 0.05 M and 0.1 M NaOH solution respectively as high hydrodynamic volume enables it to aggregate with greater number iron ore particles to yield larger sized flocs, while shellac in 0.1 M NaOH due to its comparatively low hydrodynamic volume produces smallest flocs.

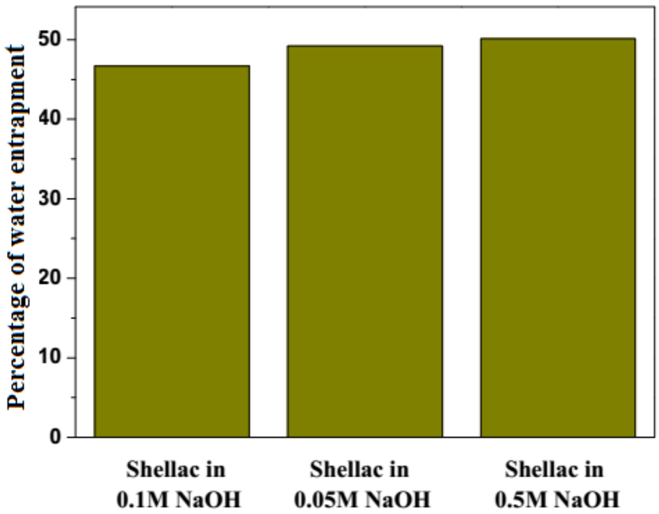

Figure 6. Percentage of water entrapment in the flocs produced by Shellac in different concentrations of NaOH.

Figure 6 shows the percentages of water entrapment value in the flocs produced by shellac. The percentage of water entrapped values are 46.7%, 49.2% and 50.1% using shellac in 0.1 M, 0.05 M and 0.5 M NaOH solutions respectively. Larger the size of the flocs greater will be the available space among the flocs, which results in the higher value of water entrapment. Therefore, shellac in 0.1 M NaOH solution entraps lowest amount of water in the flocs and shellac in 0.5 M NaOH solution entraps maximum water.

4. Conclusion

Shellac in 0.5 M NaOH solution is found to be the optimum one for the flocculation of iron ore from its aqueous suspension and 15 ppm of the flocculant is the optimum dose. Reduced viscosity and zeta potential both play important roles for controlling the settling rate and residual turbidity of iron ore suspension. This also proves the fact that the flocculation is not governed by any particular mechanism. If it depends upon solely on hydrodynamic volume parameter, then process would follow bridging mechanism and the process should move through the charge neutralization pathways if it depends only on the zeta potential factor. Therefore, the process is governed by the electrostatic patch mechanism where both hydrodynamic volume and zeta potential come into play.

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