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Application of guar gum for the removal of dissolved lead from wastewater

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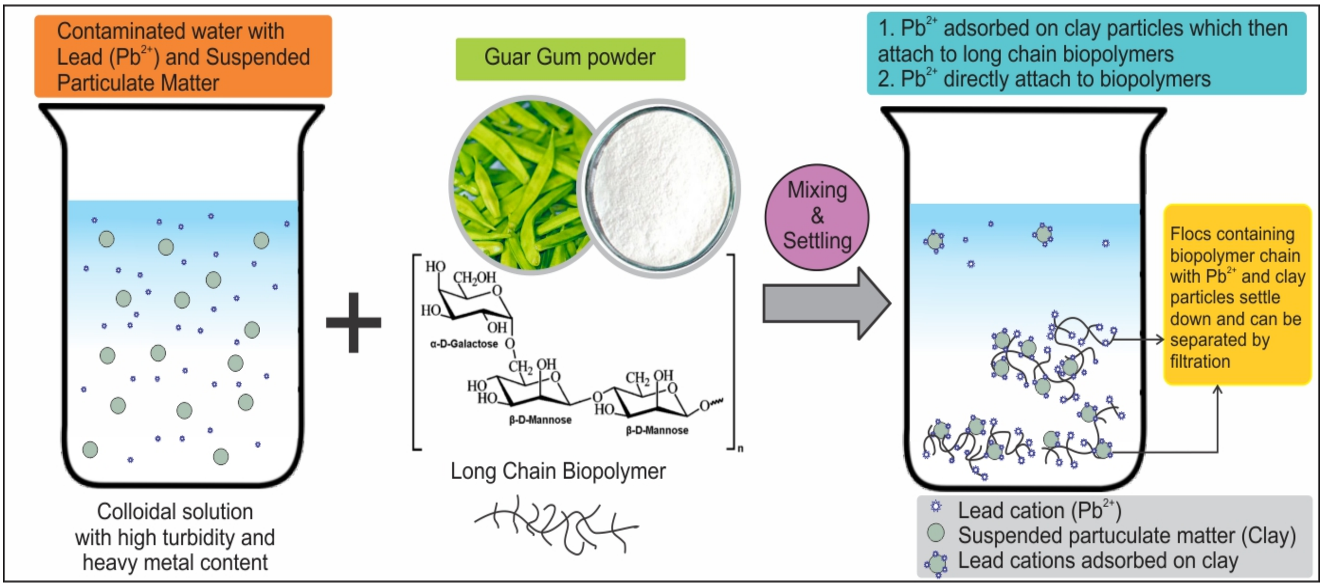

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ABSTRACT

Lead (Pb) is a toxic heavy metal with highly recalcitrant property. It easily accumulates in the food chain by interacting with calcium and iron components of the biomolecules found in living organisms. In this study, guar gum, a long chain polysaccharide was used for the first time to remove Pb from wastewater. Alum, an inorganic coagulant was also studied in order to compare its Pb removal efficiency with the biopolymer. About 83% removal of Pb was observed at an initial Pb concentration of 15 mgL^{-1}. Optimization study was performed using Box-Behnken design to determine the optimal process parameters. FTIR and zeta potential of guar gum-Pb aggregates were studied to define the removal mechanism. Absorption peaks at 3618.79cm^{-1} in the flocs indicate hydrogen bond between Pb and guar gum. SEM micrographs of the guar gum flocs indicate that the flocs formed by guar gum are very compact and since guar gum is biodegradable and non-toxic, the use of guar gum as a flocculating agent for treatment of heavy metal containing wastewater is highly recommended. Requirement of ultra-low amount of biopolymer in the range of 1.25 mgL^{-1} to treat relatively high volume of water provides an additional economic advantage.

Keywords: heavy metal, lead, biopolymer, guar gum, zeta potential, flocs

1 INTRODUCTION

Lead is a post-transition metal with high toxicity, affecting the central nervous system, liver, kidney and basic cellular processes and brain function in human beings (Fu and Wang, 2011). Elemental lead has been used for thousands of years by human beings. The use of lead in manufacturing processes is being phased out from the beginning of the 20th century; however, lead acid battery industry remains one of the largest users of lead in its end product. A recent survey of three storage battery producers showed that the pH of wastewater at the source ranged between 1.6 and 2.9, while the concentration of soluble lead in the wastewater was in the range of 5–15 mg/L (Bahadir et al., 2007). The recycling of lead acid batteries also generates large quantities of heavy metal containing wastewater. Pb also comes into water through the combustion of fossil fuels and the smelting of sulphide ore, and into lakes and streams by acid mine drainage (Gupta et al., 2001). Lead is highly reactive and easily finds its way into the living systems by interacting with calcium, iron and zinc (Goyer, 1997). Therefore, removal of Pb from wastewater is essential.

Removal of heavy metals from wastewaters can be achieved by various chemical, biological and physico-chemical processes (Wan Ngah and Hanafiah, 2008; Fu and Wang, 2011; Fu et al., 2012; Tang et al., 2014). ‘Coagulation and flocculation’ is one such physico-chemical process that has been used in the treatment of different types of wastewaters since it is highly effective, efficient and a cost effective process for removal of fine particulate matters and other pollutants (Bratby, 2006; Lee et al., 2012). Common chemical coagulants such as inorganic salts of iron and aluminium tend to produce high sludge volume and residual metal ions in the treated water resulting in secondary pollution, increasing handling and disposal costs (Bratby, 2006; Lee et al., 2014). In recent years, biopolymers such as chitosan, tannin, gums and cellulose have been studied for the removal of contaminants from wastewater

(Mishra and Bajpai, 2005; Beltrán Heredia and Sánchez Martín, 2009; Renault et al., 2009; Das et al., 2012; Mukherjee et al., 2014). Biopolymers tend to produce compact flocs and do not cause any secondary pollution in the treated water. Also, they are inexpensive and easily available (Bratby, 2006; Mukherjee et al., 2014).

Guar gum is a biopolymer of plant origin and is widely grown in the Indian subcontinent, USA, Australia and Africa. It is a polysaccharide composed of mannose backbone and galactose side branch on every alternate mannose units (Altrafine Gums, 2014). Recent studies have shown that it can be applied for the treatment of drinking water, industrial effluent and removal of persistent organic pollutants (Sen Gupta and Ako, 2005; Mukherjee et al., 2013; Kee et al., 2015).

The objective of this work is to evaluate the feasibility of using guar gum biopolymer to remove a toxic heavy metal Pb from wastewater for the very first time. The efficiency of guar gum in the removal of Pb has been compared to a conventional inorganic coagulant alum and attempt has been made to understand the mechanism of Pb removal through FTIR and zeta potential studies. The settling characteristics of the flocs produced by the two coagulants were also studied.

2 MATERIAL AND METHODS

2.1 Simulated wastewater and chemicals

Synthetic wastewater was prepared by combining lead nitrate (Pb $(NO_3)_2$) solution and kaolinite suspension. Kaolinite was used in preparation of wastewater in order to obtain a colloidal suspension to aid the flocculation process. A 250 mg L^{-1} stock solution of lead nitrate was prepared by dissolving 0.399 gm of the salt into 1L distilled water. The kaolinite suspension was prepared by mixing 0.1 gm kaolinite into 1L distilled water. The kaolinite solution was thoroughly mixed and the solution was allowed to stand for 30 minutes. The supernatant liquid containing the suspended colloidal clay particles was decanted and used for the experiments. The turbidity of the resulting solution was 64 FAU. 250 mL of the kaolinite suspension was used for each experiment. The pH of the suspension was adjusted to below 5 prior to the addition of Pb $(NO_3)_2$, to prevent the precipitation of Pb.

Guar gum is a plant origin food grade gum obtained by grounding the endosperm of guar beans. Figure 1 shows the chemical structure of guar gum. A solution of 1000 mgL^{-1} concentration was obtained by dissolving 0.1 g of guar gum in 100 mL distilled water. New batch of guar gum solution was prepared every twelve hours to prevent the growth of moulds. Alum (aluminium potassium sulphate dodecahydrate; $KAl(SO_4)_2$) was added directly to the water sample.

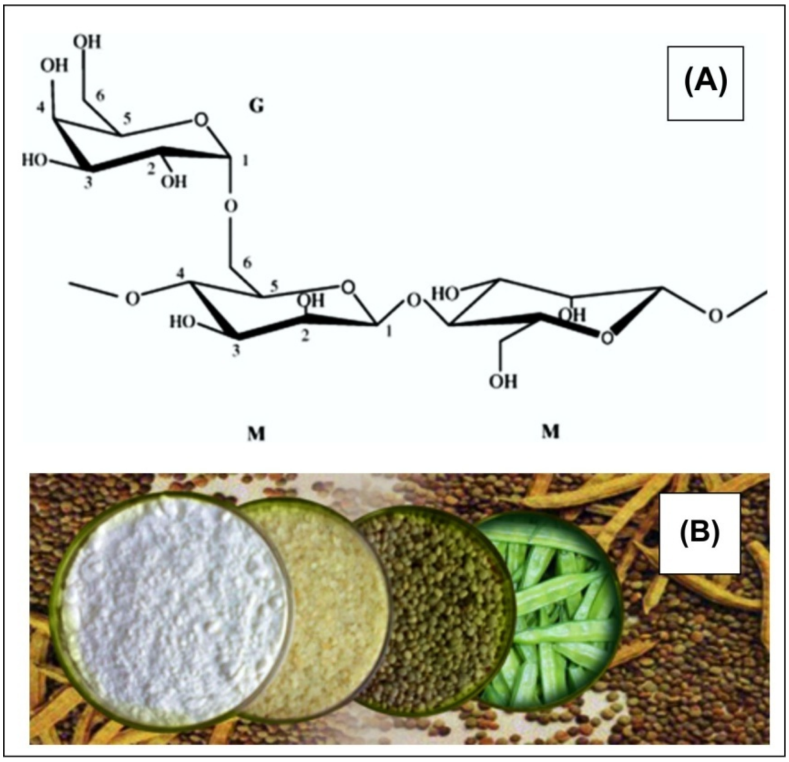

Figure 1. (A) Chemical structure of guar gum showing the position of Galactose (G) and Mannose (M) in the guar gum polymer chain (Ding et al., 2008); Fig 2.1. (B) Guar gum seed and powder

2.2 Analytical methods

Wastewater samples were analysed for a range of physicochemical parameters namely pH, turbidity, zeta potential and heavy metal concentrations. The turbidity was measured using HACH DR/890 portable spectrophotometer. This spectrometer was calibrated using formazin turbidity standards and the readings are in terms of Formazin Attenuation Units (FAU). Zetasizer Nano ZS was used to measure the zeta potential of the surface water samples in presence of different coagulants. The heavy metal content was analysed using ICP-OES (Perkin-Elmer Optima 7000DV) using Perkin-Elmer multi-metal standard solutions. The pH measurement was done using Metler Toledo Delta 320 pH meter. The images from Scanning Electron Microscope (SEM) of the flocs, produced after the wastewater clarification, were obtained using the SEM microscope operating with SE2 detector of ZEISS Auriga Scanning electron microscope. The FTIR of the flocs and wastewater was studied in Bruker Vertex (United States) 70/70V spectrophotometer.

2.3 Settling velocity distribution curves

A method described by Hudson (1981), was used to examine the settling characteristics of the flocculent suspensions produced. For experimental runs, the pH of the three jars was adjusted to pH 5 prior to the experiments since Pb tends to precipitate at higher pH. After attaining the required pH, the samples were homogenised. The mixing was done at two stages: first flash mixing at 250 rpm for 10 minutes followed by slow mixing at 60 rpm for 15 minutes. Dosing of guar gum and alum was done two minutes after the beginning of flash mixing. After 25 minutes of mixing, samples were drawn from a fixed depth of 2 cm below the liquid surface of the flocculent suspension at time intervals of 1,2, 4, 8, 16, 32 and 64 minutes following flocculation tests of Sen Gupta and Ako (2005), and analyzed for turbidity removal. According to Bartby (1981), there are several benefits of collecting samples according to this method. Traditional sampling method involving transferring of the flocs formed from one container to another for floc size, permeability and compressibility study can be completely avoided by doing away with handling operations.

2.4 Flocculation and removal of heavy metals

Clarification of the wastewater was performed using a jar test apparatus (Phipps and Bird 7790-402 Jar Tester). The optimum concentration of guar gum and alum with respect to turbidity and Pb removal were determined through jar test studies. The treatment of wastewater was carried out in 500 ml glass beakers at various dosages of the biopolymer and alum and the supernatant solution was analysed for Pb removal. The pH of the kaolinite suspension in each beaker was first adjusted by 0.1N HCl or NaOH. After obtaining the desired pH levels, the Pb solution was added, thus constituting the wastewater. The flocculation study was carried out as mentioned in Section 2.4. After 25 minutes of mixing, the flocs were allowed to settle for 30 minutes and samples were collected for analysis. To prevent Pb from precipitating, the samples were preserved by the addition of 1% HNO_3 acid.

2.5 EXPERIMENTAL DESIGN AND DATA ANALYSIS

The experimental design, mathematical modelling and optimization studies were completed using Design Expert 7 software. Design Expert software facilitates the design and interpretation of multifactor experiments. A class of five level central composite design for the estimation of parameters in a second order model was developed by Box–Hunter (Montgomery, 2001). Several factors influence the removal Pb by guar gum such as dose of biopolymer solution, pH of the wastewater and initial heavy metal concentration. Hence, these critical variables were selected and designed as A, B and C. The low, middle, and high levels of each variable are designated as –α, 0 and +α, respectively, the corresponding actual values for each variable is listed in Table 1. The range of the variables was fixed based on preliminary experiments.

Table 1. Experimental Design Summary

Variables	Actual values for the coded values				
	-α	-1	0	+1	+α
Dose of flocculants, mgL-1 (**A**)	0.41	0.75	1.25	1.75	2.09
pH (**B**)	2.32	3	4	5	5.68
Initial Pb concentration, mgL^{-1}, (**C**)	1.59	5	10	15	18.41

The interaction among process variables and response was determined by graphically analysing the data by ANOVA. The behaviour of the system is explained by the following second-degree polynomial equation (Eq1):

$$y = \beta_0 + \sum_{i=1}^{k} \beta_i x_i + \sum_{i=1}^{k} \beta_{ii} x_i^2 + \sum_{i \supseteq j}^{k} \sum_{i=1}^{k} \beta_{ij} x_i x_j \qquad (1)$$

where, y = predicted response, β_0 = offset term, β_i = linear effect, β_{ii} = squared effect, β_{ij} = interaction effect.

The same programme determined the quality of fit of the polynomial model, expressed by the coefficient of determination, R^2, and its statistical significance was checked by the Fisher *F*-test (Fisher variation ratio). Model terms were selected or rejected based on the *P* value (probability) with a 95% confidence level. The experimental design, as provided by the software, is given in Table 2.

Table 2. Actual design of the experiment

Run	**Dose (mgL^{-1})**	**pH**	**Initial Concentration of Pb (mgL^{-1})**
1	1.25	4	18.4
2	0.41	4	10
3	0.75	3	15
4	1.25	4	10
5	1.75	5	15
6	0.75	5	5
7	1.25	4	10
8	1.75	3	15
9	0.75	3	5
10	2.1	4	10
11	1.25	5.6	10
12	1.25	2.3	10
13	1.25	4	10
14	1.25	4	1.6
15	1.25	4	10
16	1.25	4	10
17	1.75	3	5
18	0.75	5	15
19	1.75	5	5
20	1.25	4	10

3 RESULTS AND DISCUSSION

3.1 PERFORMANCE OF GUAR GUM AND ALUM FOR THE REMOVAL OF LEAD

Preliminary studies were conducted in order to determine the performance of alum and guar gum for removal of Pb from wastewater. It was found that alum was not as effective as guar gum in the removal of Pb. The percent removal was found to be only 29% from an initial Pb concentration of 15 mgL^{-1} at pH 5 and an alum dose of 0.1 gmL^{-1}. However, turbidity removal by alum is high (54%). As observed by (Omar and Al-Itawi, 2007), Pb has an affinity for kaolinite and has been used as an adsorbent for the removal of Pb from wastewater (Jiang et al., 2010; Salem and Akbari Sene, 2011). In our case the removal of Pb through attachment with suspended kaolinite particles was prohibited by the presence of positively charged Al^{3+} ions, the hydrolysed product of alum. This is because Al^{3+} and the Pb^{2+} are both positively charged causing repulsion between the two species and a competition for the active sites on kaolinite particles.

Guar gum on the other hand is successful in the removal of Pb. Figure 2 shows a Box-Whisker plot of guar gum’s performance at different pH and dose. Removal of Pb by guar gum was influenced both by pH of the wastewater and dose of guar gum. The removal is highest at lower dose of 1.25 mg L^{-1} and is about 85% at pH 5. Also, the removal is higher at higher initial concentration of Pb. Guar gum is a biopolymer which does not have any charge of its own and hence the primary mechanism by which guar gum causes flocculation is polymer bridging (Mishra and Bajpai, 2005). At increased concentrations of guar gum, the intermolecular repulsion between the polymer particles will increase causing re-suspension of solids (Abdel-Shafy and O. Abo-El-Wafa, 1987; Mukherjee et al., 2014).The highest removal was obtained at pH 5. At this pH, the number of H^+ ions are less and hence the Pb^{2+} ions can get associated with the active sites at the polymer chain.

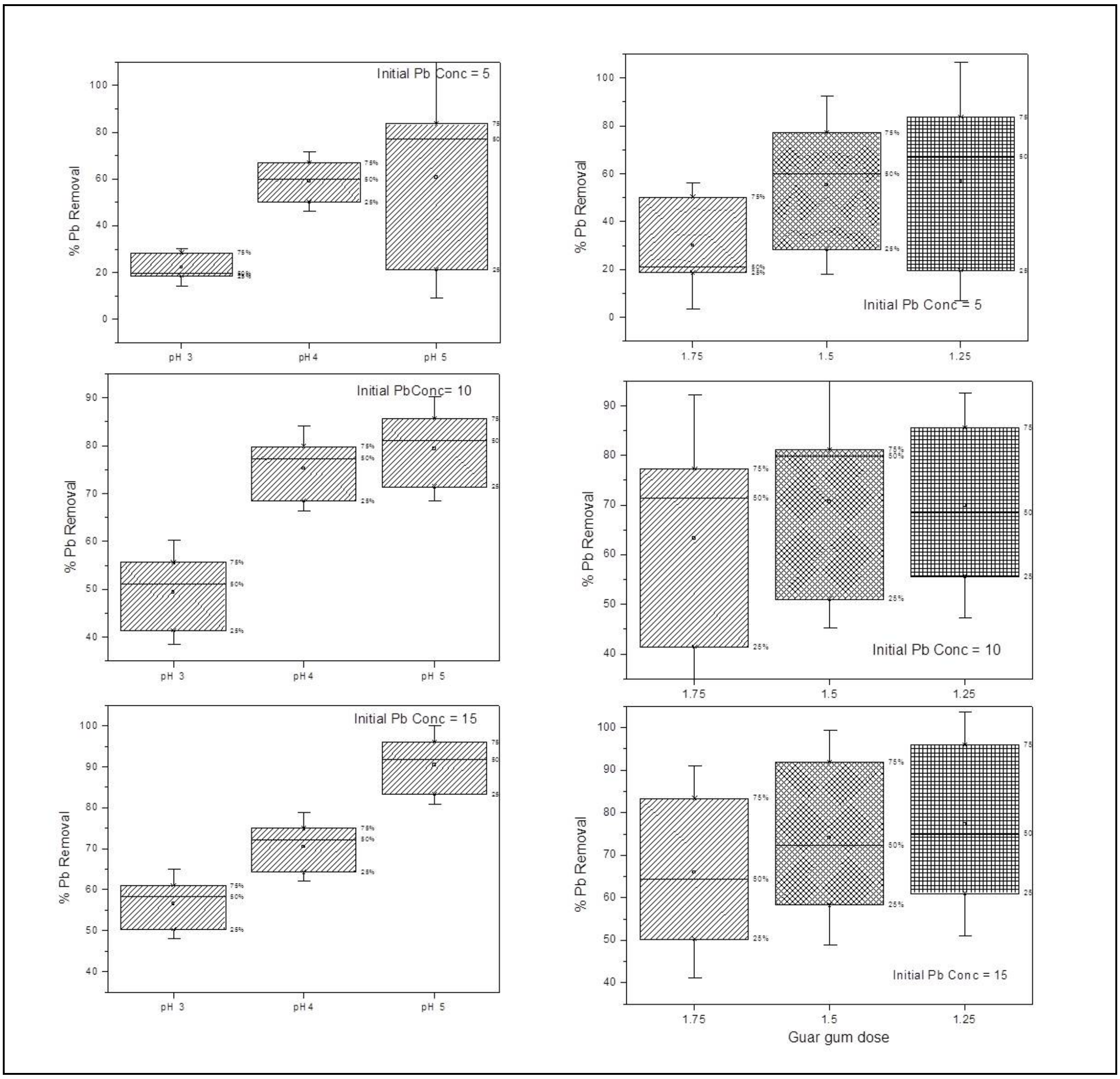

Figure 2. Variation of Pb removal by guar gum at different pH values and guar gum dose at fixed initial Pb concentration. The Box-whisker plot represents maximum score, 75th percentile (Upper Quartile), Median, 25th percentile (Upper Quartile) and Minimum Score

3.2 Settling Velocity distribution curves

The flocculating capability of guar gum and alum is illustrated in Figure 4. The SDVC curves were generated by plotting ‘percent turbidity remaining’ (Table 3) against the corresponding settling velocities. Sampling was carried out at time intervals of 1, 2, 4, 8, 16, 32 and 64 minutes (Gupta and Ako, 2005) and at settling velocities of 2, 1, 0.5, 0.25, 0.125, 0.0625 and

0.03125 cm min^{-1}. The ratio of raw water turbidity remaining at the depth of sampling can be calculated by dividing the raw water turbidity (64 FAU), by the measured turbidity of the samples withdrawn at the depth of sampling at fixed sampling time. The percent of raw water turbidity or the ratio thus defines the proportion of particulate matters that settle at a speed equal to or less than the corresponding settling velocity. The turbidity settled by guar gum and alum at 0.1 cm min^{-1} settling velocity were 33% and 36%, which are similar. Initially, the turbidity removal by guar gum was higher than alum; however after 0.15 cm min^{-1}, settling velocity of alum took over and settled higher percentage of turbidity. Although turbidity removal by alum was much better than guar gum, it was unable to remove significant amount of Pb from the wastewater. Hence, only guar gum was further studied for the optimization.

Table 3. Settling velocity vs measured turbidity at different time intervals and percent turbidity remaining

Min	**velocity (cm/min)**	**Measured Turbidity of Guar gum**	**Measured Turbidity of Alum**	**Percent turbidity remaining Guar gum**	**Percent turbidity remaining Alum**
1	2	47	56	73.44	87.50
2	1	44	60	68.75	93.75
4	0.5	46	54	71.88	84.38
8	0.25	43	51	67.19	79.69
16	0.125	43	41	67.19	64.06
32	0.0625	35	30	54.69	46.88
64	0.03125	34	19	53.13	29.69

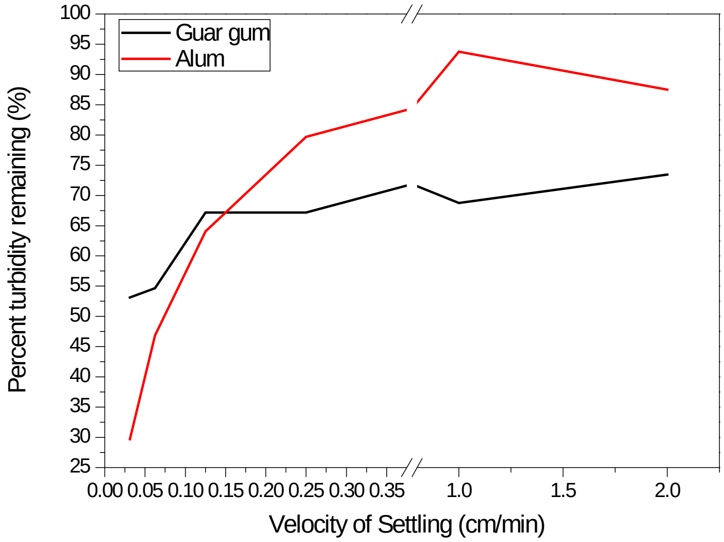

Figure 3. Settling velocity distribution curves for alum and guar gum

3.3 OPTIMIZATION OF GUAR GUM PERFORMANCE

The response surface methodology for optimising different operating parameters for percent Pb removal was used to generate the following reduced second order polynomial equation:

$$\text{Pb Removal} = -193.29 + 96.32 \times \text{Dose} + 73.84 \times \text{pH} + 5.17 \times \text{Pb Conc} + 1.72 \times \text{Dose} \times \text{Pb Conc} - 1.07 \times \text{pH} \times \text{Pb Conc} - 48.06 \times \text{Dose}^2 - 5.87\,\text{pH}^2 - 0.08\,\text{Pb Conc}^2 \qquad (2)$$

To determine the significance of this model, ANOVA was applied which evaluates the variations in different groups of data and adjudge if their mean values are equal (Bezerra et al., 2008). Fisher’s F-test value of 156.06 with a very low probability of (P model > F= 0.0001) (Table A) indicates the model is significant (Liu et al., 2004). In the graph of the predicted values versus actual data show that the 45-degree line should uniformly divide the data points (Figure A).

The accuracy of prediction of response value by a model can also be measured by the predicted R^2. If the predicted and adjusted R^2 values are not within approximately 0.20 then there is an error in the model or the data. In the case of turbidity removal, the predicted R^2 value is 0.96, which is in agreement with the adjusted R^2 value of 0.98. Also the signal to noise ratio of 4 or more is indicates adequate precission, a ratio of 41.46 is indicative of adequate signal (Mason, 2003; Aghamohammadi et al., 2007).

3.3.1 Effect of Dose

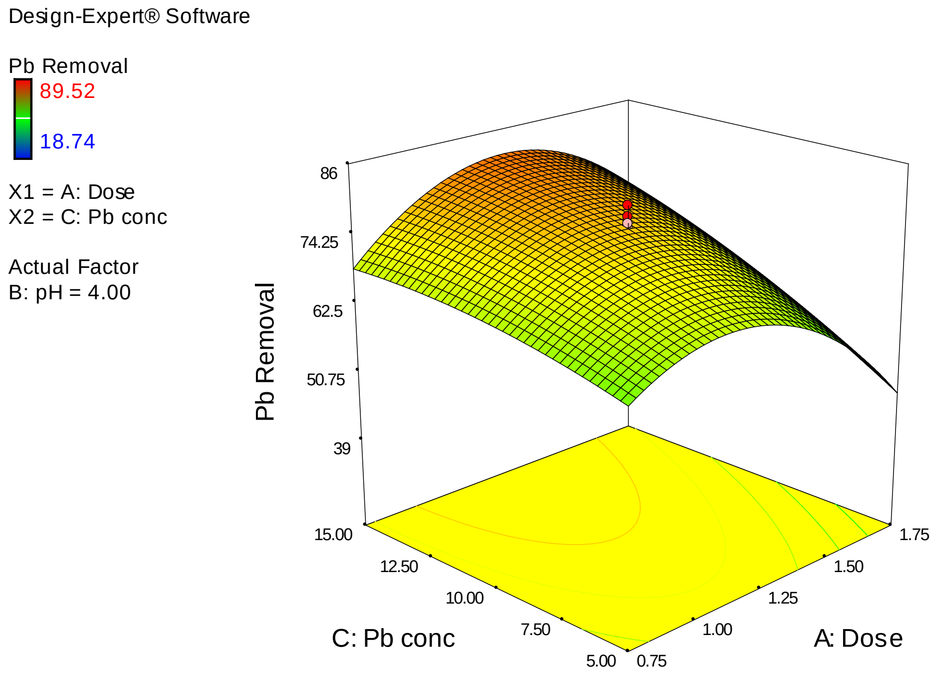

Figure 4. Response surface plot of Pb removal due to addition of Guar gum: Effect of Dose (pH=4.0)

The response surface plot for Pb removal by guar gum with respect to variation of dose is shown in Figure 5. It can be observed that as the guar gum dose is increased from 0.75 mgL^{-1} , the removal of Pb increases. Also, the removal is higher at higher initial concentration of Pb. The highest removal of about 83% is achieved at 1.25 mgL^{-1} of guar gum and high initial dose of 15 mgL^{-1} of Pb. On increasing the dosage, the Pb removal gradually decreased. At higher concentrations of the long chain polymer, the repulsive energy between the polymers increases, resulting in decrease of Pb^{2+} and biopolymer interaction.

3.3.2 Effect of pH

pH has a significant impact on the removal of Pb. The removal is lowest at low pH of 3 and increases at higher pH of 5 (Figure 6). At pH 6, Pb precipitates; hence all experiments were carried out below pH 5 to ascertain efficient removal of Pb^{2+} ions from the wastewater by guar gum. At pH 3, the removal is lowest even though the zeta potential is – 4.92 mV (an increase from – 34.9 mV of the wastewater). A near neutral zeta potential results in better flocculation. However, at very high H^+ ion concentration, there is a competition between Pb^{2+} ions and H^+, and due to their small size H^+ are preferred over the Pb^{2+}. This decreases the Pb^{2+} removal at low pH. However, at higher pH, the H^+ ion concentration decreases and more active sites are available on the polymers for binding Pb^{2+} ions.

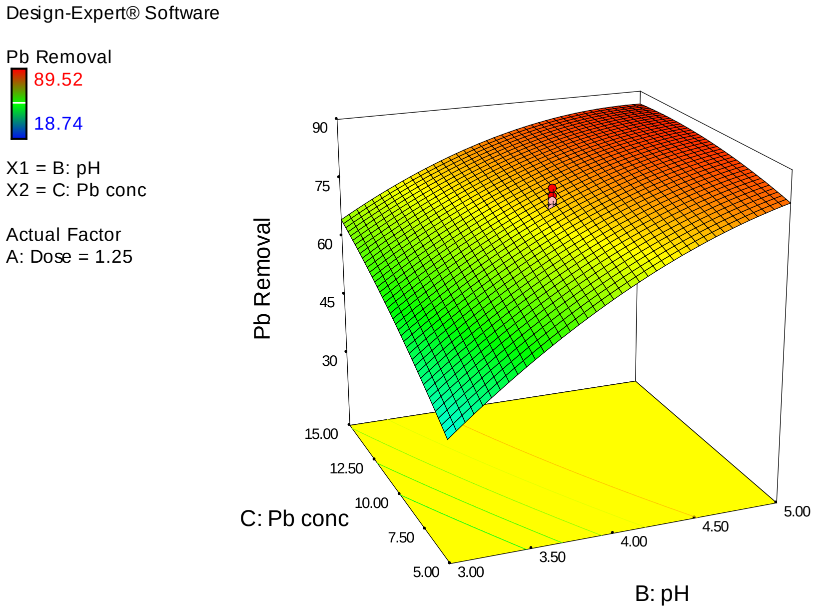

Figure 5. Response surface plot of Pb removal due to addition of Guar gum: Effect of pH

3.3.3 Process optimization and model validation

Optimization of Pb removal was carried out by a multiple response function known as desirability function. The target is to optimize different combinations of process parameters for optimum Pb removal. In order to achieve maximum desiaribility, the pH and initial Pb concentration was kept within the range and guar gum dose was kept at minimum keeping in mind environmental sustainability and econimic constraints. The optimal points of the factors was astertained by additional experiments at the derived optimal conditions. Table 4 shows the optimal conditions and their desirability. It can be said that the model obtained was an adequate prediction of Pb removal with a relatively small error of 3.56% (Table 4).

Table 4. Optimum conditions and their desirability

Flocculant	**Dose**	**pH**	**Pb Conc**	**Optimization**		**Validation**	
				Pb Removal	**Desairability**	**Pb Removal**	**% Error**
Guar gum	0.88	3	15	56.97	0.67	59	3.56%

3.4 PHYSIOCHEMICAL CHARACTERISTICS OF THE FLOCS

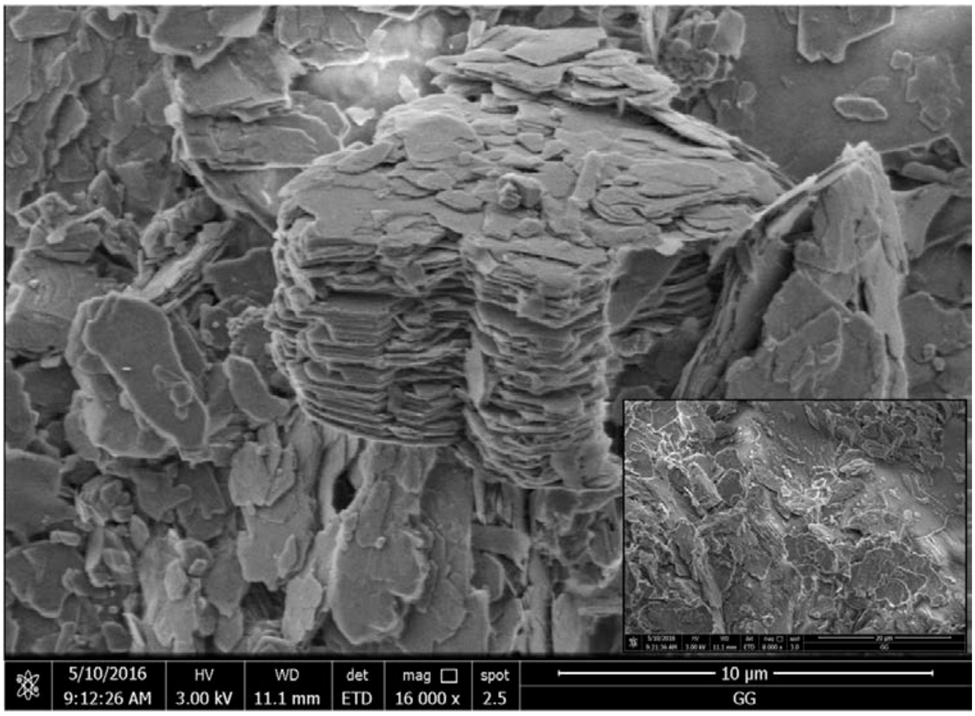

Figure 6. SEM micrographs of guar gum flocs at different resolutions

The SEM micrographs are presented in Figure 6. The figure shows the surface morphology of the flocs. It can be inferred from the micrographs that the flocs formed by guar gum are large and compact. The compactness of the flocs is revealed by the neatly arranged layers of sediments.

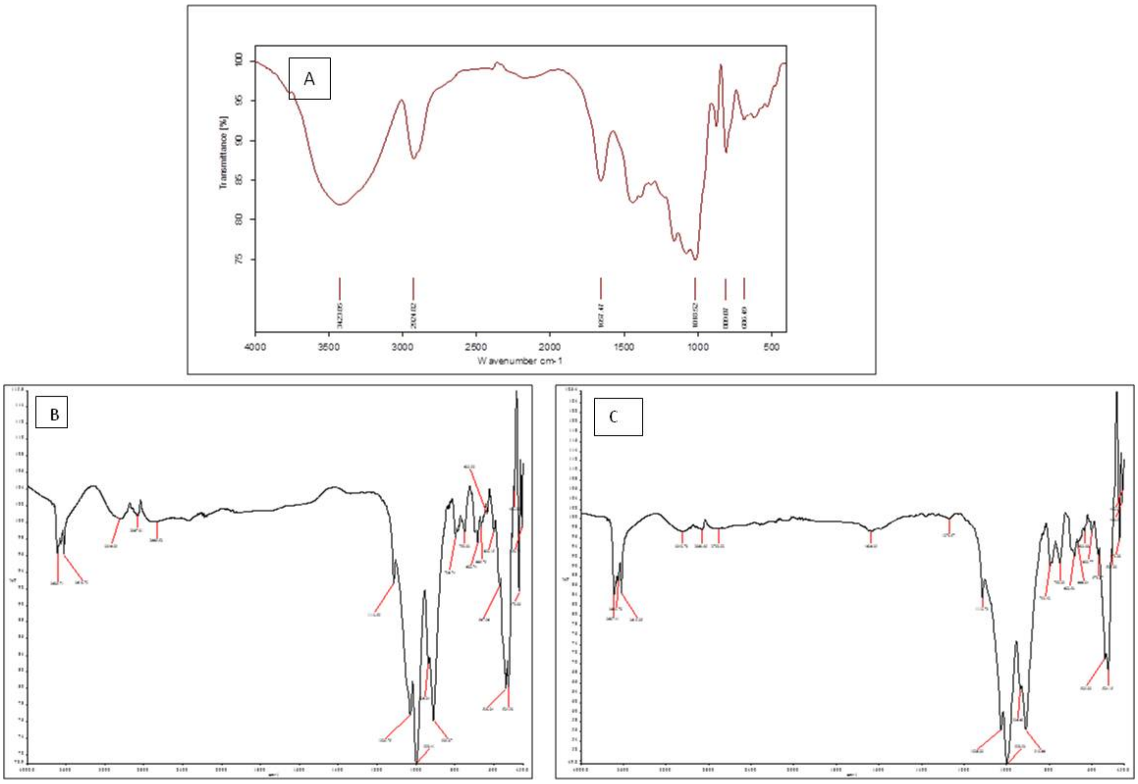

Figure 7. FTIR spectra of (A) Guar gum powder, (B) flocs obtained by Guar gum and (C) flocs obtained by Alum

Figure 7 shows the FTIR spectroscopy of guar gum powder and the flocs obtained by guar gum and alum. The FTIR spectrum of the guar gum flocs show slight shift in the peaks as compared to the guar gum powder, indicating physiochemical interactions between the heavy metal and the polymer which resulted in the removal of Pb^{+2} ions from the solution. The guar gum powder has a peak at 3423.85 cm^{-1} and 1223.5 cm^{-1} indicating O-H and C-O stretch respectively indicating the presence of aliphatic alcohol groups. In the guar gum flocs, the broad peaks of the alcohol groups in guar gum powder is replaced by O-H free stretch at 3685.71 cm^{-1} and O-H hydrogen bonded stretch at 3618.79cm^{-1}. This indicates that H–bonding was an important factor in Pb^{2+} removal. It is worth noting that peaks at 3649 cm^{-1} and 3619 cm^{-1} in alum flocs indicate the Al---O-H stretch marking the presence of kaolinite in the floc sample. In the alum flocs, the broad peaks at 1270 cm^{-1} indicate the presence of sulphate group. The peaks as shown in the flocs is also indicative of kaolinite present in the water samples, which was settled during the flocculation process. The peaks at lower wavelength of 700 to 686 cm^{-1} indicate the presence of Si-O (quartz) bonds. The peaks at υ of 470 cm^{-1} to 452 cm^{-1} indicate the presence of Si-O-Si bending from the kaolinite in both floc samples obtained from alum and guar gum.

4 CONCLUSION

This study shows successful application of biodegradable biopolymer obtained from guar gum for the removal of turbidity and a heavy metal (Pb^{2+}) from wastewater. Statistical design was used to show the leverage of important design parameters such as dose and pH on the removal of Pb. ANOVA showed a high R^2 value of 0.99 for the regression model equation, which has sufficient agreement of the model with the experimental data. 83% removal of Pb was observed at a dose of 1.25 mgL^{-1} and pH 5. Alum on the other hand could remove only 29% Pb due to the interionic repulsion with Al3+ ions and competition for the kaolinite active sites. Zeta potential and FTIR results indicate that physiochemical interaction between the biopolymer and Pb^{2+} ions in the solution was responsible for its removal. Also, the SEM micrographs indicates that guar gum produced compact flocs which are easier to handle. Guar gum is a biodegradable polymer, easily available and inexpensive, and has been proved to be effective in the removal of heavy metals from the wastewater. Further studies should be undertaken to ascertain its efficiency in the removal of other heavy metals.

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APPENDIX

Table A. Statistical models obtained from the ANOVA for turbidity removal

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob> F	
Model	7271.03	8	908.88	156.06	< 0.0001	significant
A-Dose	147.63	1	147.64	25.35	0.0004	
B-pH	3595.84	1	3595.85	617.42	< 0.0001	
C-Pbconc	751.51	1	751.52	129.04	< 0.0001	
AC	148.64	1	148.64	25.52	0.0004	
BC	227.17	1	227.17	39.01	< 0.0001	
A^2	2080.11	1	2080.11	357.16	< 0.0001	
B^2	496.46	1	496.46	85.24	< 0.0001	
C^2	55.88	1	55.88	9.59	0.0102	
Residual	64.06	11	5.82			
Lack of Fit	48.12	6	8.02	2.52	0.1651	not significant
Pure Error	15.94	5	3.19			
Cor Total	7335.09	19				

Std. Dev.	2.41	R-Squared	0.9913
Mean	62.63	Adj R-Squared	0.9849
C.V. %	3.85	Pred R-Squared	0.9601
PRESS	292.80	Adeq Precision	41.456

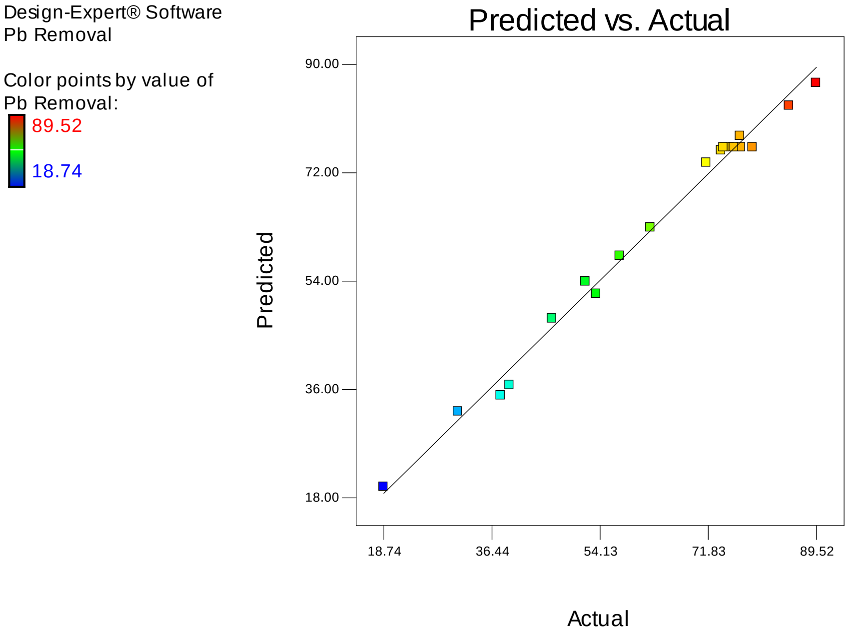

Figure A. Predicted lead removal versus actual experimental values