CHAPTER 6

SUMMARY AND CONCLUSIONS

Population growth is the reason for the development of new and a lot of industries. Industries using heavy metals for their manufacturing processes lead to increased heavy metal contamination and harmful effects on the environment. Surplus amount of red mud production creates a lot of environmental issues such as disposal problem, groundwater contamination and dust generation. In order to overcome the environmental issues, the solid waste red mud can be converted into useful products. In order to overcome these issues, this research investigated the potential usage of red mud and the modified form of red mud as adsorbents to remove the heavy metals such as lead, arsenic and chromium from aqueous solutions. Characterization of adsorbents was performed and mechanism of adsorption was also studied. pH, adsorbent dosage, contact time and initial ion concentration were the parameters optimized for the removal of heavy metals through batch studies. Isotherm models like Langmuir, Freundlich and Dubinin-Radushkevich were assessed to determine the capacity and fitness of the adsorbents in heavy metal removal. Pseudo - first and second - order models were applied to study the rate of reactions of batch studies. Continuous adsorption studies were conducted through column studies. Breakthrough curves were analysed and regressions were analysed using MATLAB software. The performance of columns on metal removal was analysed through Adams-Bohart model. Based on the results of this research, the following conclusions were drawn:
The specific surface area of the adsorbent is a very important parameter for the adsorption process and the surface area for iron oxide coated acid treated activated red mud was 49.44 m$^2$/g and it revealed that the surface area was higher than the acid treated activated red mud and red mud. This concluded that the iron oxide coated acid treated activated red mud might be a potential candidate for effective adsorption. Iron oxides - 73.66 %, aluminum oxides - 25.47 %, titanium oxides - 1.62 % and quartz - 1.12 % were the chemical compounds present in iron oxide coated acid treated activated red mud. Also, powder X – Ray Diffraction analysis obviously confirmed the presence of iron oxide, hematite, quartz and anatase. The results obtained clearly show that higher amount of iron oxide was present in iron oxide coated acid treated activated red mud. The surface morphology of the adsorbent iron oxide coated acid treated activated red mud was rougher and it became irregular in shape after the modification process. High porosity and roughness are the important factors for increasing the adsorption capacity of the adsorbent. Hence, the adsorbate got highly adsorbed on the rough surface and diffused into the pores present in the adsorbent IOCATARM. Hence, a higher percentage of adsorption was expected from iron oxide coated acid treated activated red mud.

The present work has also reported the removal of lead (II) ions with low costs using red mud, acid treated activated red mud and iron oxide coated acid treated activated red mud. The results from the batch experiments have revealed that the iron oxide coated acid treated activated red mud could be an efficient adsorbent for the removal of lead (II) ions from the aqueous solution compared to the other two adsorbents. In addition, the experiments confirmed that the maximum adsorption was attained at pH 6, adsorbent dosage of 0.5 g, 90 minutes of contact time and lower concentration of ions. Fourier transform infrared spectroscopy confirmed the adsorption of lead (II) ions. Isotherm models such as Langmuir, Freundlich and Dubinin-
Radushkevich model were analyzed and the comparative results have been reported. The results showed that the correlation coefficient ($R^2$) for Langmuir, Freundlich and Dubinin- Radushkevich isotherm models were 0.984, 0.997 and 0.875 respectively, which indicated the good agreement with all the isotherm models used. The adsorption capacity ($q_m$) obtained by the Langmuir model was found to be 27.02 mg/g and the separation factor $R_L$ for the adsorption of lead (II) ions on the iron oxide coated acid treated activated red mud was 0.141, which confirmed the favorable uptake of the lead (II) ions. The value of Freundlich constant ‘$n$’ between 1 and 10 indicates a favorable adsorption. The ‘$n$’ value of 2.0 obtained for the Freundlich isotherm represented the good adsorption of lead (II) ions by the adsorbent. Dubinin-Radushkevich model confirmed the physical nature of adsorption for the removal of lead (II) ions. Kinetic models have determined the rate of adsorption of lead (II) ions following the pseudo-second-order model. All the experimental results confirmed the iron oxide coated acid treated activated red mud to be a potential candidate for the removal of lead (II) ions.

Adsorption of arsenic (III) ions by red mud, acid treated activated red mud and iron oxide coated acid treated activated red mud was analyzed and reported. The batch adsorption experiments showed that the iron oxide coated acid treated activated red mud was more efficient in the removal of arsenic (III) ions from aqueous solution. The results revealed that the synthesized Fe$_2$O$_3$ coated red mud enhanced the adsorption ability of red mud. The maximum adsorption of arsenic (III) ions was attained at pH 7, the adsorbent dose of 0.5 g, contact time of 90 min and at lower initial ion concentrations. Arsenic (III) ions binding on the adsorbent were confirmed by Fourier transform infrared spectrometer. Isotherm has been analyzed using the Langmuir, Freundlich and Dubinin- Radushkevich models and the coefficient of determination ($R^2$) was found to be 0.996, 0.979 and 0.946 respectively. The obtained high value of correlation coefficient ($R^2$) showed
the good fit of experimental data with all the isotherm models. The adsorption capacity of the adsorbent obtained by Langmuir model ($q_m$) was 22.22 mg/g, which revealed that the higher adsorption of arsenic (III) ions occurred on iron oxide coated acid treated activated red mud and the separation factor $R_L$ of 0.136, which was less than 1 confirmed the favorable adsorption of arsenic (III) ions on iron oxide coated acid treated activated red mud. The constant n value of Freundlich isotherm within the range of 1-10 indicated a good adsorption. In the present work, the obtained ‘n’ value of iron oxide coated acid treated activated red mud was found to be 2.393, which represented good adsorption of arsenic (III) ions. Dubinin-Radushkevich isotherm suggested that the adsorption of arsenic (III) ions was a physical process. The rate of adsorption followed the pseudo-second-order kinetic model. Batch adsorption results demonstrated that iron oxide coated acid treated activated red mud had a higher adsorption capacity and it could be used as a potential adsorbent for the removal of arsenic (III) ions from aqueous solutions.

The effective removal of chromium (VI) ions from aqueous solutions was conducted through batch experimental studies and the results of the present work had shown that the adsorption of chromium (VI) ions on the iron oxide coated acid treated activated red mud was highly effective and it was found to be suitable adsorbent. The experiments confirmed that the maximum adsorption of chromium (VI) ions was attained at pH 7, adsorbent dosage of 0.6 g, contact time of 90 minutes and at lower concentrations of ions. Fourier transform infrared spectrometer confirmed the adsorption of chromium (VI) ions. The coefficient of determination ($R^2$) was found to be 0.987, 0.996 and 0.895 respectively for Langmuir, Freundlich and Dubinin-Radushkevich models. The obtained high correlation coefficient ($R^2$) indicated experimental data fit with all the isotherm models. Langmuir isotherm showed that the maximum adsorption of adsorbate ($q_m$) per gram was 24.39 mg/g, which showed that the adsorption of chromium (VI) ions
was high the on iron oxide coated acid treated activated red mud. The separation factor $R_L$ for the adsorption of chromium (VI) ions on the iron oxide coated acid treated activated red mud was found to be 0.190, which confirmed the favorable uptake of the chromium (VI) ions. ‘n’ value of the Freundlich isotherm for the removal of chromium (VI) ions was found to be 1.8, which indicated the favorable adsorption. The reaction rate obeyed Pseudo-second order model for the removal of chromium (VI). Hence, it was concluded that the iron oxide coated acid treated activated red mud was an effective adsorbent for the removal of chromium (VI) ions from aqueous solution.

In the present study, continuous adsorption of metals such as, lead (II), arsenic (III) and chromium (VI) was analysed using 7 cm and 5 cm packed adsorbent columns. The performance of column adsorption was explained through the breakthrough curves. In 7 cm column studies, the initial breakthrough curve was observed at 2040 min for lead (II) ions, 1560 min for arsenic (III) ions and 1440 min for chromium (VI) ions on the iron oxide coated acid treated activated red mud, and the equilibrium concentration of the influent was reached after 3900 min, 2880 min and 3240 respectively for lead (II) ions, arsenic (III) ions and chromium (VI) ions on the adsorbent iron oxide coated acid treated activated red mud. Similarly, for 5 cm column studies, the initial breakthrough curve was observed at 1500 min for lead (II) ions, 1020 min for arsenic (III) ions and 1020 min for chromium (VI) ions respectively on the iron oxide coated acid treated activated red mud and the equilibrium concentration of the influent was reached after 2160 min, 1620 min and 1680 min respectively for lead (II) ions, arsenic (III) ions and chromium (VI) ions on the adsorbent iron oxide coated acid treated activated red mud. The results concluded that the breakthrough time and the time of equilibrium for all the three metal ions got delayed on iron oxide coated acid treated activated red mud packed columns compared with acid treated
activated red mud and red mud. The hard coarse surface caused a deeper movement of ions, which led to an increase in the time of analysis. However, in-depth movements of ions offered more time of contact between the adsorbate and the adsorbent. Hence, more adsorption occurred on iron oxide coated acid treated activated red mud. Also, comparing with 7 cm packed adsorbent columns, the initial breakthrough appeared in advance in 5 cm packed adsorbent columns and equilibrium concentration of ions was reached soon in 5 cm columns, which might have been due to the mass of adsorbents packed in the column. The theoretical breakthrough curves of lead (II) ions, arsenic (III) ions and chromium (VI) ions on 7 cm and 5 cm packed adsorbents columns were analysed using the non-linear regression method and modelled by the MATLAB software. The results concluded that the experimental and theoretical breakthrough curves were contiguous with each other and this closeness of curves intimated that the experimental curves fitted well with the non-linear regression model. The theoretical breakthrough curves confirmed that the adsorption of metal ions on the iron oxide coated acid treated activated red mud took some time to attain the saturation level due to the rough and porous surface properties of the adsorbent. However, good quality of adsorption occurred on the iron oxide coated acid treated activated red mud.

The experimental data obtained from column adsorption studies were evaluated using Adams-Bohart model. Performance of column for various bed depths of adsorbents was analysed and saturation capacity was determined using this model. The obtained saturation capacity, $N_0$ of iron oxide coated acid treated activated red mud for 7 cm packed adsorbent columns was 5752 mg/l, 4070 mg/l and 4370 mg/l respectively for lead (II) ions, arsenic (III) ions and chromium (VI) ions. Similarly for 5 cm packed adsorbent columns, $N_0$ was 7642 mg/l, 5848 mg/l and 6106 mg/l respectively for lead (II) ions, arsenic (III) ions and chromium (VI) ions. The results
concluded that the saturation capacity was high for iron oxide coated acid treated activated red mud. Hence, more and perfect adsorption takes place on the iron oxide coated acid treated activated red mud.

The present experimental research study concluded that the solid waste red mud could act as a good adsorbent for metal ion removal. Among the three adsorbents such as red mud, acid treated activated red mud and iron oxide coated acid treated activated red mud, iron oxide coated acid treated activated red mud had a high potential capacity for the removal of heavy metal ions such as, lead (II) ions, arsenic (III) ions and chromium (VI) ions. Lead (II) ions had higher removal efficiency than the other two ions. Moreover, the solid waste disposal of red mud and the associated environmental issues can also be reduced. This research would be a path to utilize the solid waste as low cost adsorbent and to enhance their ability for the metal ion removal and various treatment processes.