



Testing the Suitability of Red Mud Based Systems as Permeable Reactive Barrier (PRB) Materials

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Abstract

This study involved the investigation of using untreated red mud, acid activated red mud and combined acid and heat treated red mud as Permeable Reactive Barrier (PRB) material by firstly equilibrating the different red mud samples alone and in the presence of some local soils, sand and metallic iron with methylene blue (MB) for up to 60 days. The efficiencies of these systems in discoloration of MB as well as their potentials to release iron to solution were evaluated. Secondly, the three red mud samples were equilibrated with distilled water separately for 60 days, the iron released within this period determined and MB was added to the remaining sample solution for duration of 28 days. The discoloration efficiency and released iron were evaluated. These experiments carried out in batch mode (using test tubes) were without agitation, without filtration and all at room temperature. Red mud samples equilibrated directly with MB showed lower discoloration than those pre-equilibrated with water. However, the latter systems showed higher iron release than the former. The presence of soils, sand and metallic iron used significantly enhances the performance of the different red mud samples. Combined acid and heat treated red mud and its systems had best results with high discoloration and almost zero iron release. These results highlight the long term reactivity of different red muds and their different systems, thus, their suitability as PRB material for contaminant removal from polluted water, hence, limiting environmental impacts from red mud disposal.

Keywords: Red mud; Activation; Iron; Permeable reactive barrier; Methylene blue

Introduction

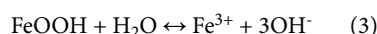
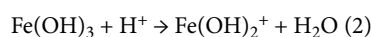
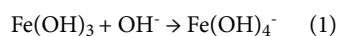
Permeable reactive barrier (PRB) is an *in-situ* method for contaminant remediation [1]. There are engineered reactive passive chemical or biological treatment zones which are placed in the subsurface to provide adequate treatment of contaminants [2]. Different kinds of reactive materials have been used in PRBs to treat

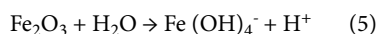
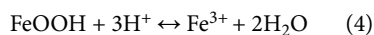
contaminated groundwater. Activated carbon, zero valent iron, bentonite, soil-bentonite mixture, zeolites for treating radionuclides and heavy metals, and transformed red mud are some of reactive materials used. The selection of a particular reactive material for a PRB depends on several factors i.e. reactivity, stability, availability and cost, environmental compatibility, hydraulic performance and safety [1,3]. The contaminants are either degraded or retained in the barrier material, which may require periodic replacement. Reactive materials frequently used are waste products (e.g., mulch, some iron ore slags, red mud) or are recycled (e.g., iron scrap).

Red mud is the insoluble residue resulting from caustic alumina production *via* the Bayer process [4]. Globally, between 60-120 million tons are produced annually [5]. Its disposal may lead to serious pollution of the surrounding soil, air and groundwater due to its high pH (10-13) [6]. However, red mud contains a number of valuable metals and minerals from parent bauxite consisting of gibbsite, diaspore, hematite, goethite and those introduced during the Bayer process such as sodalite, cancrinite etc. [7]. The typical constituents of red mud (% w/w) are: Fe₂O₃ (30-60%), Al₂O₃ (10-20%), SiO₂ (3-5%), Na₂O (2-10%), CaO (2-8%), TiO₂ (trace-10%) [8]. In general, red mud is a very fine material in terms of particle size distribution, having an average particle size <10 μm. In addition, it also presents porous surface [9]. Out of the approximately 120 million tons of red mud produced annually, only about 2-4.5 tons are used annually in some way (cement-500,000 to 1,500,000 tons; raw material/additive in iron and steel production-200,000-1,500,000 tons; roads/landfill capping/soil amelioration-200,000-500,000 tons; construction materials (bricks (tiles, ceramics, etc.)-100,000-300,000 tons; other (refractory, adsorbent, acid mine drainage, catalyst, etc.)-300,000 tons) [10]. The alternative method to disposal is adequate treatment to search for further areas of applications, limiting its environmental impacts.

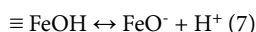
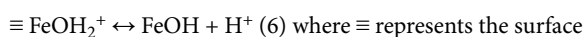
Transformed red mud (TRM) created by mixing red mud with calcium chloride and magnesium chloride brine from solar salt plants [11] has been tested as a PRB material. A TRM PRB was field-tested for the treatment of acid-rock drainage, which included copper, lead, zinc, and manganese, with encouraging results [1,12]. High iron, copper, zinc, nickel, and lead, arsenic removal efficiencies have been shown for TRM in column studies [1,13,14]. The literature review shows easy regeneration of red mud used in the adsorption of some heavy metals, dyes and anions in batch and column modes [15] with acetone easily eluting dyes from red mud surface compared to other solvents. Due to its very high pH and fine texture, red mud by itself is not suitable for PRB applications and needs to be mixed with other materials (e.g. sand or soil) for PRB applications. Few studies have been conducted on the use of soils as the reactive material for PRB [3].

The majority of the oxides found in red mud demonstrate acid/base type behaviour in aqueous solutions, and therefore it is expected that red mud particles will exhibit similar behaviour [16]. The acid/base properties of the particles are believed to be due to the surface hydroxyl groups. Iron oxide like other major ones found in red mud dissolve in acid media to form cationic hydroxo species and in basic media to form anionic hydroxo species as represented by the following equations:





The surface hydroxyl groups (whether they arise from the adsorption of water or from structural OH) are the chemically reactive entities at the surface of red mud in an aqueous environment. They possess a double pair of electrons together with a dissociable hydrogen atom which enables them to react with both acids and bases according to equations:



Equally reactivity of red mud originates from the net surface charge developed due to inter- and intra-particle behaviour in the presence of water (and the inherent dissolved salts). Two origins of mineral surface charge are recognized in red mud: firstly, the mineral composition of bauxite residues reveals they are pH-dependent, and secondly, variably charged surfaces exist (Fe^- , Al^- and $\text{Ti-oxides}+\text{SiO}_2$) alongside permanently negatively-charged surfaces [7]. Treatment of red mud introduces further charges to the solid. The surface charge properties are generally defined by the point of zero charge (PZC) which is the pH at which the net charge on the surface is zero [17]. The PZC of red mud varies significantly due to the different origins of bauxite, and variability in Bayer process variables, the addition of different types of flocculants and the composition of the background electrolyte [18]. A PZC of 7.09 was obtained for the raw red mud used for this study [19] but was not determined for other samples. Thus, the variable charge surfaces on red mud also gives them the ability to adsorb different species; anions, metal cations and dyes [20]. The reactivity of red mud originating from the acid/base behaviour of its constituents and surface charge can probably lead to the leaching of some of its constituents in to solution. Literature review shows that there are limited studies on the use of red mud as PRB reactive material. Thus, in this paper we report the investigation of the use of raw, acid and combined acid and heat treated mud alone and in the presence of some local clay soil, andosols and metallic iron as possible PRB materials using methylene blue (MB) as the adsorbate. The discoloration of methylene blue and the iron released into solution will be used to characterize each system. These results will permit us evaluate the reactivity, stability and safety of using red mud as a PRB reactive zone material as it is available in large quantity at low cost around the world.

Experimental

Sampling of bauxite and preparation of red mud samples: Red mud used for this study was produced in our laboratory from bauxite collected at Minim-Martap deposit as described in [18]. Accordingly, 10 g of water-washed and dried red mud was boiled in 200 mL of corresponding HCl concentration (2.25 M, 2 M) for 20 min. The acid slurry was then filtered on a Whatman filter paper N°1, the residue washed with distilled water and dried at 40°C. The 2M acidified sample was placed in a muffle furnace for calcination at 900°C in air for 4 h (this sample was designated RMAC), while the 2.25 M acidified sample was designated RMA and untreated red mud designated RM. These three samples were used in the study. Their properties are presented in [21] with BET surface areas of 13.15, 23.80 and 26.46 m²/g for RM, RMA and RMAC respectively. The mixing with soils and sand will improve the reactive sites as they are also rich in different oxides and also limit clogging resulting from red mud iron and metallic iron corrosion, thus improving long term reactivity and permeability. The characteristics of 2.25 M HCl treated red mud and 2 M HCl treated

and calcinated red mud had been determined in our previous study [21], and showed good adsorbent properties; thus their use in this study.

Sampling of andosol, sand and clay: The white and yellow andosols used were sampled from the Bamboutous massif (West Cameroon in Central Africa) area (N 05° 38' 15.0" E 010° 00' 29.2" and N 05° 37' 55, 7" E 009° 59' 28.2" respectively). The major oxides present in these soil samples are $\text{SiO}_2 > \text{Al}_2\text{O}_3 > \text{Fe}_2\text{O}_3$ [22,23]. The sand and clay were collected in the town of Maroua where its soil is principally sandy and clayed. The different soil samples were washed with distilled water and dried in air (35-40°C) for 7 days.

Preparation of solutions and discoloration of methylene blue (MB):

A 10.0 mg/L MB test solution used was obtained by diluting a stock solution of 1000 mg/L (prepared by dissolving 1000 mg of MB in 1 L of distilled water). MB was used because it has been widely used as model contaminant to characterize the suitability of various systems for water treatment [24] and particularly because it has a low affinity adsorption onto red mud surfaces [6,9,25-27]. The used initial concentration (10 mg/L) was selected to approach the concentration range of natural waters [28].

Two sets of red mud systems were used. In the first system, RM, RMA and RMAC were used. Six separate 20 ml solutions were prepared in test tubes for each red mud sample with following composition; i) sample + MB ii) sample + MB + sand iii) sample + MB + white andosol iv) sample + MB + yellow andosol v) sample + MB + clay and vi) sample + MB + ZVI or Fe⁰ (metallic iron, commercial grade). 0.7 g of each red mud sample, 20 mL of 10 mg/L MB, 0.4 g of sand, 0.4 g of Fe⁰ and 0.4 g each of different soils were used in each case. Each mixture was characterized by evaluating the discoloration of MB after 28 and 60 days of contact (MB and material or materials) and determining the concentration of iron released into solution after 60 days of contact. In the second system, each of the red mud samples (RM, RMA and RMAC, 0.7 g of each) were equilibrated with 20 mL of distilled water for 60 days. After which 10 mL of solution was used to determine the concentration of iron released into solution. A 20 mg/L MB was added to the remaining 10 mL solution (to bring MB concentration to 10 mg/L) and equilibrated for 28 days, then the MB discoloration and released iron concentration were evaluated. These experiments carried out in batch mode were without agitation, without filtration and all at room temperature. The proportions of mixing were chosen by adapting the study of [29], with optimal Fe⁰/sand volumetric ratio of 25/75 with the aim of evaluating the effects of using more red mud in the mixture.

Analytical methods

MB and aqueous iron concentrations were determined by a UV-Vis spectrophotometer Spectro 23 RS, LaboMed.inc. The working wavelength for MB was 664 nm. Dissolved iron was determined at 510 nm. Cuvettes with 1.0 cm light path were used. The iron determination followed the 1, 10 orthophenanthroline method [30]. The spectrophotometer was calibrated for MB concentrations $\leq 10 \text{ mg L}^{-1}$ and iron concentrations $\leq 10 \text{ mg L}^{-1}$. All chemicals were of analytical grades.

Presentation of experimental results: After the determination of the residual MB concentration (C), the discoloration efficiency (E) was calculated (Equation 1) in order to characterize the magnitude of tested systems for MB discoloration.

$$E = [1 - (C/C_0)]^* 100 \dots\dots\dots (1)$$

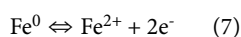
Where C_0 is the initial aqueous MB concentration (10.0 mgL^{-1}), while C is the residual MB concentration.

Results and Discussion

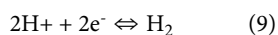
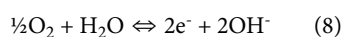
The long term reactivity of the different red mud samples and their safety in water treatment was evaluated in this study by determining their efficiencies in decolourising methylene and also evaluating the leaching of iron (the main constituent of red mud) into solution. These results are presented in Tables 1-4.

Untreated red mud (RM) systems

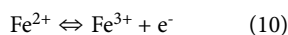
From Table 1 presenting the use of untreated red mud alone, with sand, white soil, yellow soil, clay and metallic iron in MB aqueous media, it is seen that, there was an increase in discoloration of MB from 28 to 60 days for systems with red mud alone, red mud and sand, red mud and yellow soil, and red mud and Fe^0 (zero valent iron) but a decrease in discoloration for systems with red mud and white soil and red mud with clay soil. This decrease shows that the mechanism of discoloration was mainly by physical adsorption in the case of white and clay soils. Highest results were however observed for systems containing soil and sand samples. This is definitely stemming from the porous character of these soils. RM used has a total volume of $0.063 \text{ cm}^3/\text{g}$ and BET surface area of $13.15 \text{ m}^2/\text{g}$ [21] compared to the andosol with total pore volume of $0.083 \text{ cm}^3/\text{g}$ and BET surface area of $50.12 \text{ m}^2/\text{g}$ [22]. Thus mixing increased the porosity and surface area for reaction. Previous studies with sand have shown high discoloration of MB [31]. Metallic iron has been shown to enhance the discoloration of MB in the long term due to the production of corrosion products [32]. Red mud corrosion products result from reactions shown in equations 1-6. Also metallic Fe^0 corrodes in aqueous media due to differences in the electrical potential on anodic and cathodic sites on the Fe^0 surface [33]. The metal oxidizes at the anode, where corrosion occurs according to equation:



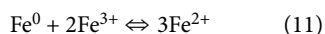
Simultaneously, a reduction reaction occurs at cathodic sites as shown in equations below.



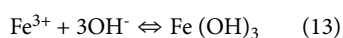
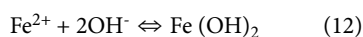
Fe^{2+} ions from Eq. 7 might be further oxidized (e.g. by O_2 , MnO_2 or contaminants like CrO_4^{2-}) to Fe^{3+} ions according to equation:



While, Fe^{3+} from Eq. 10 is an oxidizing agent for Fe^0 according to equation:



Finally, the generated Fe^{2+} and Fe^{3+} will form hydroxides according to equations 12 and 13 and the hydroxides will be progressively transformed to amorphous and crystalline oxides, equation 14.



This was the primary motive on adding metallic iron to systems studied. Its addition to untreated red mud increased discoloration by about 7% in 28 days compared to red mud alone and only by less than

3% in 60 days. Methylene blue is commonly used in different research areas involving solid Fe species (Fe and oxides) for corrosion protection [34]. Despite the high discoloration potentials of red mud in the presence of soil samples they result in the release of iron from red mud in to solution; 1.90 mg/L for red mud and white soil sample, 1.65 mg/L for red mud and yellow soil and 4.29 mg/L for red mud and clay soil. The WHO limit of iron in drinking water is 0.3 mg/L [35]. The addition of metallic iron to red mud also significantly contaminates the solution with 3.89 mg/L of iron. However, untreated red mud alone and in the presence of sand show significant reactivity; 82.85 to 92.21% and 47.64 to 95.08% in MB discoloration respectively with zero iron released for RM/sand and 0.163 mg/L for RM alone. This study confirms ITRC findings that red mud by itself is not suitable for PRB applications and needs to be mixed with other materials (e.g. sand or soil) for PRB applications [1]. The use of red mud in the presence of sand showed high reactivity and safety (zero iron release) in our study. The use of red mud in the presence of different soils also showed high reactivity but releases much iron in to solution.

Reaction medium + MB	MB discoloration (%)		[Fe] mg/L
	28 days	60 days	60 days
RM	82.85	92.21	0.16
RM + sand	47.64	95.08	0
RM + white soil	99.22	98.36	1.9
RM + yellow soil	98.76	100	1.65
RM + clay	100.43	98.01	4.29
RM + Fe^0	89.11	91.52	3.89
RM=untreated red mud			

Table 1: MB discoloration efficiency and released iron in different RM media.

Acid treated red mud (RMA) systems

Table 2 involving the use of acid treated red mud shows low MB discoloration of RMA alone (43.08% in 60 days) and in the presence of sand (87.79% in 60 days). However, RMA in the presence of white soil, yellow soil clay and metallic iron showed high discoloration (100.00% in all soils to 98.07% in metallic iron). Nonetheless, all the RMA systems significantly released iron in to solution (16.00 mg/L with Fe^0 , 13.09 mg/L with white soil, over 7.61 mg/L with yellow soil and about 3.27 mg/L with RMA alone). Wang et al., also showed that nitric acid treated red mud exhibits much lower adsorption compared with untreated red mud [9]. This low adsorption may be due to the repulsive forces resulting from the positive surface of RMA and cationic MB. Iron is soluble in acid medium (equations 2 and 4). This is the likely cause of the high iron released in all the systems studied especially with Fe^0 . There is however a reduction in iron released by mixing RMA with sand and clay. Sand and clay are negatively charged and partly neutralizes the acidic red mud with pH tending basic. This reduces iron dissolution thus reducing the quantity in solution. These results show that acid treated red mud alone cannot be a good PRB material but can be improved when combined with other materials (sand and clay soil). However, the quantity of iron released when RMA is used alone or in combination is significant.

Reaction medium + MB	MB discoloration (%)		[Fe] mg/L
	28 days	60 days	60 days
RMA	29.43	43.08	3.27
RMA+ sand	51.03	87.79	2.17
RMA + white soil	100	100	13.09
RMA + yellow soil	97.04	100	7.61
RMA + clay	100	100	1.12
RMA + Fe ⁰	94.74	98.07	16
RMA=Red mud treated with 2.25 mol/L hydrochloric acid			

Table 2: MB discoloration efficiency and released iron in different RMA media.

Combined acid and heat treated red mud (RMAC) systems

The results of the combined acid and heat treated red mud (RMAC) presented in Table 3 shows that it is the most promising form of red mud that can be used as PRB material. This is shown by nearly a 100.00% discoloration in 28 days when mixed with sand, soils and even metallic iron accompanied by zero or negligible release of iron even in 60 days. RMAC used has a total volume of 0.111 cm³/g and BET surface area of 26.46 m²/g [21]; efficiency enhanced by mixing with andosol, sand, clay as well as metallic iron that probably increased its porosity, composition and surface area. This sample contain mostly oxides and no water molecules as the hydroxides and water are removed during acid treatment and heating. These oxides are more stable thus (equation 14), thus limiting the release of its iron.

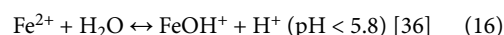
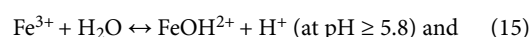
Reaction medium + MB	MB discoloration (%)		[Fe] mg/L
	28 days	60 days	60 days
RMAC	79.46	88.88	0.1
RMAC + sand	78.16	90.32	0.09
RMAC + white soil	100	100	0
RMAC + yellow soil	100	100	0
RMAC + clay	100	100	0.34
RMAC + Fe ⁰	96.63	100	0.04
RMAC=Red mud treated with 2.00 mol/L HCl and heated at 900°C			

Table 3: MB discoloration efficiency and released iron in different RMAC media.

Influence of treatment of RM, RMA and RMAC with water

Results presented in Table 4 show that the efficiency of the untreated red mud, acid treated red mud and combined acid and heat treated red mud in decolourising MB can be highly improved by equilibrating the red mud sample with water for a length of time prior to utilization in discoloration studies. However, this procedure release a significant quantity of iron into solution especially for the RMA sample with 9.36 mg/L compared to 1.61 mg/L in RM and zero mg/L in RMAC after 60 days of contact with distilled water. This same trend with release of

iron continued when MB was added to the respective red mud samples water solutions for equilibration time of 28 days (88 days in total). This indicates continuous reactivity of red mud samples over a long period of time. The discoloration efficiencies were higher for this water treated red mud samples than when they were mixed with MB directly. For example, the following discoloration efficiencies were obtained for samples treated with water when they were equilibrated with MB for 28 days; 97.04% for RM, 81.07% for RMA and 98.87% for RMAC. Meanwhile discoloration efficiencies of 92.21% for RM, 43.08% for RMA and 88.88% for RMAC were obtained when MB was equilibrated directly with respective samples for duration of 60 days (confirming MB as corrosion protection species). The increased reactivity of the water treated red mud samples is likely due to the generation of intermediate species such as FeOH²⁺, FeOH⁺ resulting from the following reactions on red mud surface;



As well as processes shown in equations 1-7. The generated protons are thus responsible for the leaching of iron as they continuously acidify the medium.

Reaction medium	[Fe] mg/L, after 60 days equilibration of sample with H ₂ O	MB discoloration (%) and [Fe] mg/L after 28 days of contact (using samples equilibrated with H ₂ O for 60 days)	
	[Fe] mg/L	MB discoloration (%)	[Fe] mg/L
RMAC+H ₂ O	0	*	**
RMA+H ₂ O	9.36	*	**
RMA+H ₂ O+MB	*	81.07	11.32
RM+H ₂ O	1.61	*	**
RM+H ₂ O+MB	*	97.04	2.17
*: Absence of MB during the first 60 days, **: Absence of only water containing systems after the 60th day			

Table 4: MB discoloration and iron release using RM, RMA and RMAC pre-treated with water.

Conclusion

Results show all the red mud samples used alone as well as their mixtures increasing ability to decolourize MB and release of iron in to solution. The presence of sand, soils and metallic iron enhanced the discoloration. Equilibrating the different red muds with water for a long time greatly increased their ability to decolour MB although they release much iron in to solution more than those directly mixed with MB. However, these results show that red mud treated with acid and heat (RMAC) has best results especially in the presence of sand, soils and Fe⁰ with high discoloration efficiencies and almost zero iron released. The untreated red (RM) mud also shows similar results especially in the presence of sand with zero iron released. The acid treated red mud (RMA) show lowest results of discoloration, 43% in 60 days although increased in the presence of sand, soil and metallic iron and when treated with distilled water. But all these acid treated red mud systems release high amounts of iron in to solution [37].

The increasing trend of MB discoloration and iron release is an indication of the increased reactivity of red mud and its different systems studied over a long time. However, release of iron and other major elements on red mud (e.g. Al, Na, Si, Ti) should be monitored to avoid contamination of the treated water. The choice of red mud sample and reaction medium (mixing with other materials) can be used to control the iron release and reactivity. This work should provide basis for construction of red mud PRB systems which to date are rare. This will reduce dumping of this residue with its corresponding environmental impacts and provide cheaper water treatment systems in developing countries like Cameroon.

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