

# Application of modified red mud in environmentally-benign applications: A review

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#### ABSTRACT

Red mud (RM) is a waste product that results from bauxite refining via the Bayer process. Its disposal remains an issue which raises significant environmental concerns, particularly if disposed on land or water bodies. Much research has been done on the use of red mud for environmentally-benign applications such as wastewater treatment, catalysis, the production of construction materials and glass ceramics, and for the recovery of metals. This paper reviews the current efforts made in the utilization of red mud as a valuable industrial by-product, which in turn should minimize its harmful impact on the environment. This detailed review compiles and highlights a variety of novel applications of modified red mud as a coagulant, an adsorbent for wastewater treatment, as well as, its use in catalytic processes and in building materials. The physico-chemical properties of red mud can be tuned by a range of treatment methods include acidification, neutralization and heat treatment. As revealed from the literature reviewed, modifications on red mud for the removal of various types of contaminants have shown promising results. However, further amendment and modifications on red mud are needed to utilize this industrial waste in many other industrial applications.

Keywords: Disposal, Red Mud, Utilization, Water treatment

# 1. Introduction

The alumina industry frequently generates a bauxite residue of commercial value namely red mud (RM). On average, between 1 and 1.5 tonne of red mud is generated for every tonne of alumina produced. Since the demand for alumina is increasing worldwide, the generation of red mud is estimated to be 4 billion tonnes by 2015 based on its current production rate [1]. Every tonne of alumina produced roughly generates between 1 and 2 tonne of dry bauxite residues, which varies according to the bauxite source and alumina extraction efficiencies [2]. The nature of red mud depends on the ore source and the technological process parameters used for the production of bauxite. It consists of iron oxides, primarily hematite (Fe<sub>2</sub>O<sub>3</sub>), boehmite (AlOOH), and goethite (FeOOH), titanium oxides, calcium oxides, aluminium hydroxides, and sodalite [3]. Chemical analyses has shown that it also contains radionuclides (e.g.  $^{40}$ K,  $^{226}$ Ra, and  $^{230}$ Th), as well as, heavy metals such as Cd, Co, Cr,

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Ni and V [4].

Due to its alkaline nature (pH 10.0 to 12.5) and the presence of the chemical and mineralogical species, this solid waste causes a significant impact on the environment. Storing red mud in large quantities, however, could prove to be hazardous. Studies have revealed that disposing red mud in the sea has a significant impact on the aquatic ecosystem. The issues regarding the massive generation and subsequent disposal of red mud (Fig. S1) leading to negative impacts continue to be of global concern for the alumina industry, as well as, for the regulatory authorities. Therefore, proper disposal or treatment of waste red mud is necessary in the region where the alumina refinery plants are located. Countless attempts have been made to determine an environmentally safe method to dispose or utilize the red mud waste [5, 6].

Various investigators around the world are currently researching new methods for treatment and utilization of red mud. In an attempt to redefine the utilization of red mud, potential applications are

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being investigated and developed. Current strategies include its use as an adsorbent and coagulant material in water and wastewater treatment [7-11], as a catalyst [12, 13], as a building material, for metal recovery, and for ceramic production.

This review focuses on the modifications of the red mud material and its use in wastewater treatment and summarizes the studies made in other areas of interest which utilize red mud as a valuable resource.

# 2. Generation of Red Mud

In 1888, Karl Josef Bayer developed and patented the Bayer process for alumina production. Although alumina can be obtained from bauxite ore by several processes such as the Deville Pechiney process (using sodium carbonate), the Lime Sinter process (using lime), and the Serpeck process (at high temperature with coke and nitrogen), the Bayer process (using sodium hydroxide) is the most economical method, which is in practice for the refinement of bauxite, particularly if this contains a considerable amount of Fe<sub>2</sub>O<sub>3</sub> [14]. The Bayer process (Fig. S2) involves the digestion of crushed bauxite in concentrated sodium hydroxide (caustic) solution, at elevated temperature and pressure. Under these conditions, the aluminium oxides dissolves, leaving a residue which is known as red mud [15]. The amount of the red mud produced, per tonne of alumina generated, varies greatly depending on the origin of bauxite, from 0.3 tonnes for high grade bauxite to 2.5 tonnes for the very low grade.

Wang and Liu [16] have documented that red mud from the Bayer process consists of dispersive particles compared to sintering red mud. The specific gravity of the Bayer red mud (2.64) determined by pycnometry is higher than that of the sintering red mud (2.47). Fig. S3 shows the typical morphology of red mud [13], which contains a range of particles with different sizes and shapes, mixed with crystals. The major components of Bayer red mud are crystal-line boehmite ( $\gamma$ -AlO(OH)), hematite (Fe<sub>2</sub>O<sub>3</sub>), gypsum (CaSO<sub>4</sub>.2H<sub>2</sub>O), sodalite (Na<sub>4</sub>Al<sub>3</sub>Si<sub>3</sub>O<sub>12</sub>Cl), and quartz (SiO<sub>2</sub>) with a minor presence of gibbsite Al(OH)<sub>3</sub>, calcite (CaCO<sub>3</sub>), and whewellite (CaC<sub>2</sub>O<sub>4</sub>.H<sub>2</sub>O) [17]. Table 1 shows that the composition of red mud from different locations can vary significantly.

# 3. Applications of Red Mud in Wastewater Treatment

#### 3.1. Modifications of Red Mud for Adsorption Processes

The physico-chemical properties of red mud can be tuned by a range of methods including acidification, neutralization and heat treatment (Table 2). Acidification methods improve the removal capacity of red mud of water contaminants by dissolving the calcium and acid-soluble salts, which in turn create new cavities and increase the surface area. Acids used for this purpose include concentrated hydrochloric acids, dilute hydrogen chloride or nitric acids [11, 13, 27-29]. However, contrasting results have also been reported with regards to acid treatment, which was found to dissolve a portion of cancrinite and another type of compounds responsible for adsorption sites [30]. Another study on dye adsorption reports that the acidification treatment which neutralises hydroxide ions on the basic surface favours the removal of basic dyes [18].

Heat treatment on red mud is able to decompose unstable compounds and organics, improving the physico-chemical properties which resulted in higher adsorption capacity. Temperatures ranging from 200°C to 1,000°C have been investigated in the heat treatment of red mud for the removal of phosphate [28]. In general, heat treatment reduces the specific surface area of red mud (e.g. 700°C) but enhances the adsorption capacity of phosphate removal. During heating phase transition usually occurs (XRD patterns, Fig. S4). For example for the red mud with composition calcite (CaCO<sub>3</sub>), dicalcium silicate (Ca<sub>2</sub>SiO<sub>4</sub>), hematite (Fe<sub>2</sub>O<sub>3</sub>), gibbsite (Al(OH)<sub>3</sub>), perovskite (CaTiO<sub>3</sub>), and CaO [28], the gibbsite decomposes into  $Al_2O_3$  and  $H_2O$  in the temperature range 300 - 550°C, and between 600 - 800°C, the calcite phase decomposes into CaO and CO<sub>2</sub>. The phases of tricalcium aluminate (Ca<sub>3</sub>Al<sub>2</sub>O<sub>6</sub>) and Gehlenite (Ca<sub>2</sub>Al<sub>2</sub>SiO<sub>7</sub>) emerge in the 800 - 900°C interval without obvious mass change or phase change above 900°C. The acid-heat combined treatment decomposes goethite into a new phase of magnetite. The intensities of hematite also showed a significant enhancement, making them dominant phases in RM-HNO3-700°C and RM-HCl-700°C samples. However, Liu [31] observed a loss of acid-soluble fractions such as Fe<sub>2</sub>O<sub>3</sub> and CaCO<sub>3</sub> during the acid

| Table | 1. | Different | Compositions | of | Red | Mud | from | Different | Locations |
|-------|----|-----------|--------------|----|-----|-----|------|-----------|-----------|
|-------|----|-----------|--------------|----|-----|-----|------|-----------|-----------|

| Aroa   |           | Composition wt% |                  |                  |                   |       |      |                  |      |
|--|-----------|-----------------|------------------|------------------|-------------------|-------|------|------------------|------|
| Alta   | $Fe_2O_3$ | $Al_2O_3$       | SiO <sub>2</sub> | TiO <sub>2</sub> | Na <sub>2</sub> O | CaO   | MgO  | K <sub>2</sub> O | Ref. |
| HINDALCO, India  | 38.80     | 17.28           | 9.64             | 18.80            | 6.86              | _     | _    | -                | [7]  |
| Queensland Alumina Ltd. Australia                          | 34.05     | 25.45           | 17.06            | 4.90             | 2.74              | 3.69  | 1.86 | 0.20             | [8]  |
| Slurry pond from Worsley Alumina, Australia                | 60.00     | 15.00           | 5.00             | 5.00             | 16.00             | _     | _    | _                | [18] |
| Aluminium de Gréce S.A.                                    | 45.58     | 15.65           | 6.96             | 7.07             | 3.26              | 14.84 | _    | 0.07             | [19] |
| Eurallumina alumina plant, Italy                           | 30.45     | 17.19           | 9.58             | 8.61             | 12.06             | 7.77  | 0.86 | 0.03             | [20] |
| Aluminum de Grece  | 40.80     | 19.95           | 6.80             | 5.80             | 2.70              | 12.60 | 0.20 | 0.14             | [21] |
| Shandong Aluminium Corporation, China                      | 12.76     | 6.93            | 19.14            | 3.43             | 2.37              | 46.02 | 1.15 | 1.20             | [22] |
| Seydiehir Aluminium Plant, Konya, Turkey                   | 35.73     | 23.29           | 12.08            | 4.08             | 7.40              | 2.81  | 0.76 | 0.28             | [23] |
| Eurallumina (Porto Vesme, Cagliari, Italy)                 | 35.20     | 20.00           | 11.60            | 9.20             | 7.50              | 6.70  | 0.40 | _                | [24] |
| Alpart factory and the Alcan Ewarton red mud pond, Jamaica | 45.30     | 18.80           | 4.30             | 6.40             | 1.50              | 3.10  | _    | _                | [25] |
| ALCOA factory, San Cibrao (Northwest of Spain)             | 37.00     | 12.00           | 9.00             | 20.00            | 5.00              | 6.00  | -    | -                | [26] |

| Treatment                   | Red mud modification scheme   | Target pollutant                  | Red Mud   | Ref  |
|-----------------------------|---|-----------------------------------|---|------|
| Acid heat treatment         | Acid-heat treatment; refluxing red mud in HCl; Addition of $\rm NH_3,$ calcining at 500°C for 2 h   | As(V)                             | HINDALCO, India   | [8]  |
| Acid treatment              | Acid treatment (0.25-2 M); Heat treatment (200, 400, 600, 800°C);   | As(III)                           | Seyisehir Aluminium Plant<br>(Konya, Turkey)                            | [34] |
| Acid treatment              | Acid treatment; seawater neutralization; acid and heat treatment; ferric sulphate or aluminium sulphate added to neutralize red mud   | As(V)                             | Queensland Alumina Ltd.<br>Refinery, Gladstone, Australia               | [35] |
| Acid treatment              | Acid treated with 0.05M HCl at ratio 1:25 (wt/wt) of red mud/ HCl   | Pb(II)<br>Cd(II)<br>Zn(II)        | Eurallumina plant (Portovesme,<br>Sardinia, Italy)                      | [30] |
| Acid treatment              | Treated with 2 M HCl or HNO3 at liquid/solid ratio of 20 ml g^1; Calcined the acid pre-treated red mud at $700^{\circ}\rm C$  | Phosphate                         | Worsley Alumina, Australia  | [28] |
| Acid treatment              | Acid treatment $% 1000\%$ with 0.25M HCl; Heat treatment at $700\%$   | Phosphate                         | Shandong Aluminum Cop. Ltd.,<br>China                                   | [36] |
| Acid treatment              | Acid-heat treatment at $80^{\rm o}{\rm C}$ with 0.25 mol L^1; heat treated at $700^{\rm o}{\rm C}$  | Phosphate                         | Shandong Aluminum Cop. Ltd.,<br>China                                   | [37] |
| Acid treatment              | Activated with 10.20 mol $\mathrm{L}^{\text{-1}}$ of HCl  | Phosphate                         | Shandong Aluminum Industry<br>Corporation (Zibo, China)                 | [11] |
| Acid treatment              | Treated with 0.5 M HCl, 32% HCl, 0.5 M HNO <sub>3</sub> , 70% HNO <sub>3</sub> , 0.5 M H <sub>2</sub> SO <sub>4</sub> or 98% H <sub>2</sub> SO <sub>4</sub> , respectively. | Fluoride                          | Australian alumina refinery   | [29] |
| Acid treatment              | Soaked in 1 M HNO3 solution at the 1:2 ratio of red mud and nitric acid (w/v), activated at $150^{\circ}C$ for 4 h.   | Acid Blue 113<br>Reactive black 5 | Bauxite mill, Iran  | [10] |
| Acid treatment              | $10~g$ of red mud boiled with $20\%$ wt of HCl, dried at $40^{\rm o}{\rm C}$  | Congo red                         | Etibank Seydisehir Aluminium<br>Plant (Konya, Turkey)                   | [38] |
| Acid treatment              | Red mud and 0.5 mol $L^{\text{-}1}\text{HCl}$ at a solid liquid ratio of 1/20.  | Crystal violet<br>Malachite green | Shandong Aluminum Corporation   | [39] |
| Acid treatment              | $10~g$ of red mud boiled with $20\%$ wt of HCl, dried at $40^{\circ}\mathrm{C}$   | Phenol                            | Seyisehir Aluminium Plant<br>(Konya, Turkey)                            | [40] |
| Addition of metal<br>halide | $10~g$ of red mud in $1~L$ of water, add $40~mL$ 0.5 M $\rm FeCl_3\cdot 6H_2O,~aged$ for $1~d.$   | As(V)                             | Shandong Aluminium<br>Corporation, China                                | [41] |
| Composite mixture           | Mixture of red mud (58.7 wt%), kaolin (25.2 wt%), sodium silicate solution (11.7 wt%), fly ash (2.9 wt%), and MgCl <sub>2</sub> (1.5 wt%); heat treatment at $600^\circ$ C  | Cu(II)<br>Cd(II)<br>Pb(II)        | Korea General Chemical<br>Corporation, Daebul Industrial<br>Park, Korea | [42] |
| Composite mixture           | Mixing dewatered red mud, bentonite and starch at mass ratios (95:5:5)  | Phosphate                         | Shandong Aluminum Cop. Ltd.,<br>China                                   | [43] |
| Composite mixture           | Mixture of red mud (15 g), fly ash (2 g), sodium carbonate (1 g), sodium silicate (1.2 g), powdered quicklime (0.8 g); roast at 400°C for 2 h, calcined at 900°C for 0.5 h  | Cd(II)                            | Shandong Aluminum Cop. Ltd.,<br>China                                   | [44] |
| Composite mixture           | Mixture of neutralized red mud (15 g), dried fly<br>ash (2 g), sodium carbonate (1 g), powdered quicklime<br>(0.8 g) and sodium silicate (1.2 g)                            | Fluoride                          | Etibank Aluminium Plant, Konya,<br>Turkey                               | [45] |
| Heat treatment              | Treated with $\mathrm{H_2O_2}$ and heat treatment at 500°C  | Pb(II)<br>Cr(II)                  | HINDALCO, India   | [7]  |
| Heat treatment              | Treated with $\mathrm{H_2O_2}$ and heat treatment at 500°C  | Cd(II)<br>Zn(II)                  | HINDALCO, India   | [46] |

Table 2. Modification Methods on Red Mud Tailored to the Adsorption of Selected Water Contaminants

| Treatment      | Red mud modification scheme   | Target pollutant                            | Red Mud  | Ref  |
|----------------|---|---|--|------|
| Heat treatment | Treated with $H_2O_2$ , activate at 500°C   | Fast green<br>Methylene blue<br>Rhodamine B | Hindustan Aluminium Company<br>(HINDALCO), Renukoot, India | [47] |
| Heat treatment | Heat treatment at $800^{\rm o}\text{C}$ and acid treatment with 1 M HNO_3                                     |   | Worsley Alumina, Australia.                                | [18] |
| Heat treatment | Seawater to Bayer liquor (v/v) (4.5:1), Heat treatment at $400^{\rm o}{\rm C}$                                | Reactive blue 19                            | Alumina plant, Aluminio City, São<br>Paulo State (Brazil)  | [48] |
| Neutralization | Neutralization using sequestration of $\rm CO_2$ gas; calcination of neutralized sample at $500^{\circ}\rm C$ | As(V)                                       | R & D Laboratory of NALCO,<br>Damanjodi, Orissa, India     | [33] |
| Raw usage      | Filtrate was obtained from red mud slurry (liquid/solid = $2.5$ )   | As(V)                                       | Etibank Aluminium Plant, Konya,<br>Turkey                  | [49] |
|                |   |   |  |      |

#### Table 2. Continued

heating process, particularly when the acid concentration or the activation temperature (>  $700^{\circ}$ C) were too high, or the activation time was too long (> 2 h).

Seawater neutralization treatment is also used to reduce the alkalinity of the red mud without losing the acid neutralization capacity. Thermally activated seawater neutralised red mud was found to remove at least twice the concentration of anionic species than thermally activated red mud alone [32]. Neutralised red mud using CO<sub>2</sub> treatment has been successfully applied for the removal of arsenate with promising results. XRD analysis indicated significant differences among RM, CO<sub>2</sub> neutralised RM and activated CO<sub>2</sub> neutralised red mud [33]. An increase in the gibbsite fraction and the formation of a new mineral ilmenite (FeTiO<sub>3</sub>) was revealed as a result of CO<sub>2</sub> treatment. Table 2 summarizes physico-chemical treatments of red mud, tailored to the adsorption of target water contaminants.

#### 3.2. Coagulant Production with Red Mud

Red mud has been shown to be a promising material for the production of coagulants, due to the presence of a porous structure with a high content of Fe and Al [50] and Table 3 reveals a wide range of wastewater contaminants that can be treated using coagulants produced from red mud. Several advantages have been attributed to coagulants produced from red mud in comparison to commercial Fe and Al salts. These include: (i) one-step coagulation/flocculation process which avoids the use of coagulant aids, or other chemicals; (ii) negligible change of pH during the purification process; (iii) single step removal of the anionic and cationic species from the wastewater; (iv) one dose usage of coagulant for up to five adsorption contaminants removal cycles; (v) negligible leaching of heavy metals from the waste mud under normal environmental conditions; (vi) safe transport, storage and handling. The activation of red mud for the production of coagulants can be easily obtained using 30% wt of H<sub>2</sub>SO<sub>4</sub> with a solid/liquid ratio of 1:5 and contact time 9 h, followed by the neutralisation with waste base [51]. This coagulant has been found effective for the treatment of wastewater generated from pressure washing of boats in marinas.

A highly soluble coagulant (both in solid or concentrated liquid form) with high amounts of Al and Fe has been produced by the treatment of red mud in an acidic and saline medium [52]. The optimal conditions for the production coagulant involved the treatment of red mud (20% w/v) using 1,765 kg  $H_2SO_4$ /ton of treated red mud (trm) and 469 kg NaCl/trm at 110°C for 2 h. This coagulant promoted 98% phosphate removal from a synthetic effluent containing KH<sub>2</sub>PO4, which was similar to the removal obtained with commercial coagulants containing alum, ferric chloride, and ferric sulphate.

The removal of dyes such as acid red (B), direct blue ( $B_2R_L$ ), and reactive blue (KNR) by coagulation using MgCl<sub>2</sub>/red mud (MRM) has been reported to be superior to the removal with PAC/RM and PAC/NaOH coagulants [50]. The effective coagulation effect of MRM on dyes in this case is favoured from the alkalinization of the dyeing solution by the addition of red mud. At pH higher than 12, most of the magnesium ions were converted into precipitable magnesium hydroxide, which exhibited adsorptive coagulating behaviour with a large surface area.

The removal phosphate from biologically pre-treated municipal wastewater and eutrophic water by optimized red mud coagulants (hydrochloric pickle liquor of bauxite with w/v 35:100, a calcination temperature at 700°C, reaction temperature 80°C for 4 h) has been reported to be 5 to 10% more efficient than conventional polyaluminum chloride (PACl) (Fig. S5) [53]. Furthermore, leaching test of potential heavy metals from the red mud coagulant confirmed that the coagulant to be non-hazardous.

Efforts have also been made to produce effective polymer-based coagulants from red mud. A novel polyaluminium ferric chloride, PAFC coagulant has been prepared from red mud using 30% of hydrochloric acid leaching and polymerization processes [54]. Ca(AlO<sub>2</sub>)<sub>2</sub> and NaOH were used as the polymerization adjuster (alkali). In this product, Ca(AlO<sub>2</sub>)<sub>2</sub> and NaOH increased the content of aluminium in the coagulant and improved the coagulant quality. The optimum dosage of PAFC coagulant (0.8 g L<sup>-1</sup>) which was used for the treatment of wastewater from the printing and dyeing industry, achieved residual chemical oxygen demand (COD) lower than 100 mg L<sup>-1</sup> and residue turbidity lower than 5 NTU. Red mud has also been used as an alternative alkali to adjust the basicity of the semi-product of polyaluminium chloride (ACl), producing a composite coagulant RMPACl comprised polymeric aluminium species and residual red mud particles with a higher surface area than the raw red mud [55]. Through this process, basicity increased

| Target pollutant   | Coagulant              | Red mud  | Coagulant production   | Suggested applications of the coagulants  | Ref  |
|--|------------------------|--|--|---|------|
| Phosphate  | Composite<br>coagulant | Shandong Aluminum<br>Corporation,<br>Shandong, China.                      | Calcination temperature of RM (700°C), w/v ratio of red mud and 200 mL hydrochloric pickle liquor of bauxite (35:100), reaction temperature (80°C), pH (6.2)             | This coagulant could be effectively<br>used in tertiary treatment of<br>biologically pre-treated municipal<br>sewage while in eutrophic wastewater.<br>Its performance was better compared<br>to PACl | [53] |
| Phosphate  | RMPACl                 | Shandong Aluminum<br>Corporation,<br>Shandong, China.                      | w/v ratio of red mud to ACl (0.25), water bath temperature (80°C), 2 h   | Phosphate removal from the Xiang Xi<br>river water in the Hubei province was<br>performed.<br>RMPACl performed better than PACl<br>at a low dosage in the phosphate<br>removal from real water.       | [55] |
| Phosphorus   | J1<br>coagulant        | Vaudreuil<br>Aluminium Factory<br>in Jonquière<br>(QC, Canada)             | $\rm H_2SO_4$ concentration (6.0 N), NaCl (93.8 g $\rm L^{-1}$ ), leaching period (120 min), solids concentration (200 g $\rm L^{-1})$ , temperature (110°C).            | The performance of this coagulant<br>was similar to the commercially<br>available coagulant   | [52] |
| Pretreated oily sewage,<br>printing and dyeing<br>wastewater | PAFC                   | Shandong Weiqiao<br>aluminium &<br>electricity Co.Ltd.,<br>Shandong, China | 30% of HCl (300 mL) and RM (100 g), mother liquor and washing liquor (100 mL) were mixed with Ca(AlO <sub>2</sub> ) <sub>2</sub> (1.5 g) and NaOH (1.2 g), $80^{\circ}C$ | Application in the pretreated oily<br>sewage and in printing and dyeing<br>wastewater treatments.   | [54] |
| Direct blue, reactive<br>blue, acid red dyes                 | MRM                    | Shandong Aluminum<br>Corporation,<br>Shandong, China.                      | Mg powder and 20% HCl (Solid: liquid ratio (g/L)=175:1); mixture of $MgCl_2$ and $RM$  | MRM coagulant could be effectively<br>used as an alternative to some of the<br>conventional treatments, particularly,<br>in the textile wastewater industry.  | [50] |

Table 3. Production of Various Types of Red Mud-based Coagulants

from 2.1% to 77.3% as the RM/ACl ratio increased from 0 to 0.5. As a result, RMPACl (147.5 mgL<sup>-1</sup>) showed better coagulation performance (94.9%) than PACl (175 mg L<sup>-1</sup>) which yielded only 92.3% in the treatment of synthetic and natural phosphate contaminated wastewater.

#### 3.3. Adsorbent Development

3.3.1. Removal of heavy metals and metal ions with red mud Red mud has been used as a viable adsorbent for heavy metals adsorption such as As(III), As(V), Cd(II), Cr(V), Cu(II), Ni(II), Pb(II), Zn(II) in wastewater. Toxicity characteristic leaching procedure (TCLP) tests before and after metals removal have shown that red mud is an environmentally compatible material that could be used for wastewater treatment [56]. Modifications of raw red mud with heat treatment, acid treatment, and other developing methods have been reported to improve the removal of heavy metals from aqueous system.

Arsenic is a toxic element at higher concentration, commonly found in the groundwater of certain countries such as Bangladesh, Brazil, Canada, China, India, and Nepal. Mining, smelting of arsenic-bearing minerals are the main causes of the high abundance of arsenic species (-III, 0, +III and +V) in groundwater. Inorganic As(III) and As(IV) are known to be more toxic compared to its methylated forms monomethyl arsenic acid (MMA) and dimethyl arsenic acid (DMA) [57-59], while arsenate (As(V)) is highly toxic. The adsorption of arsenic from water with acid and heat treated red mud is pH dependent. The optimum pH range has been reported to be 5.8 - 7.5 for As(III) adsorption (exothermic process) and 1.8-3.5 for As(V) (endothermic process) [34, 60]. A process for the removal of As(V) using liquid phase red mud (LPRM, 2.5 liquid/slurry ratio) and coagulation has been proposed [49]. The As(V) removal comprises the two steps of neutralization of LPRM-arsenical solution mixtures in acidic condition followed by air-agitation and CO<sub>2</sub>-neutralization. As(v) can be removed effectively from the mixture of LPRM-As(v) solution using an optimal Al/As (V) molar ratio of 6-8. Arsenate can also be effectively removed using seawater-neutralized red mud (bauxsol) [8] in adsorption columns packed with bauxsol coated sand (BCS) (1.64 mg g<sup>-1</sup>) and activated bauxsol coated sand (ABCS) (3.14 mg g<sup>-1</sup>) (Fig. S6). Most of the sorbed As(V) (0.39-8.76 mmol kg<sup>-1</sup>) is usually associated with amorphous and crystalline Al and Fe oxides (24.1 - 43.8% and 24.7 -59.0% of total sorbed arsenic) [61] with the percentage distribution related to the surface coverage of arsenic.

The adsorption of arsenate is usually significantly affected by the pH of the water and the adsorption capacity increases as pH decreases, however, the highest absorption capacity of FeCl<sub>3</sub> modified red mud (68.5 mg  $g^{-1}$ ) is obtained at pH 6 [41]. Among the ions present in the water, nitrate ion has little impact, Ca<sup>2+</sup> enhances the adsorption process, whereas HCO<sub>3</sub><sup>-</sup> decreases the adsorption of arsenate. The spent FeCl<sub>3</sub> modified red mud can be regenerated up to 92% by using 0.2 mol L<sup>-1</sup> NaOH. Using activated CO<sub>2</sub>-neutralized red mud (ANRM) [33] the most effective removal of arsenate is obtained at pH 4. The high adsorption of arsenate on ARNM is attributed to the hydroxyl surfaces mixture of Fe, Al, and Ti oxides, which provides strong adsorption affinity by forming inner-sphere complexes. Again, the arsenate-adsorbed ANRM can be easily regenerated using NaOH solution at pH 12.0. Effective removal of other heavy metals (Cr<sup>2+</sup>, Pb<sup>2+</sup>, Cd<sup>2+</sup> and

Zn<sup>2+</sup>) in both batch and column configurations can be achieved using activated red mud (ARM) [7, 46]. High capacity ARM is made by treating red mud with H<sub>2</sub>O<sub>2</sub> and calcination at 500°C. The adsorption capacity for chromium has been reported to be 1.3 times higher than that for lead, while the presence of other metal ions (Na<sup>+</sup>, Cd<sup>2+</sup>, Zn<sup>2+</sup>) and surfactants (manaxol 1B, cetyltrimethyl ammonium bromide) reduces the removal of Cr<sup>2+</sup> and Pb<sup>2+</sup> [7]. At low ions concentrations, remarkable removal of efficiency of Cd<sup>2+</sup> (0.02 mM) and Zn<sup>2+</sup> (0.03 mM) has been reported at pH 4 using 10 g L<sup>-1</sup> of ARM [46].

A new pellet type adsorbent produced with red mud, kaolin, sodium silicate solution, fly ash, and MgCl<sub>2</sub> at 600°C has been shown to be highly effective for the removal (> 95%) of Cu<sup>2+</sup>, Cd<sup>2+</sup> and Pb<sup>2+</sup> from aqueous systems [42]. Continuous adsorption experiments confirmed that this adsorbent is more effective in the removal of Pb<sup>2+</sup> among the heavy metals tested. Granular red mud (GRM) has also been examined for the removal of cadmium from aqueous solutions [44]. The adsorption process in the GRM-Cd<sup>2+</sup>system at initial pH 6.0 was found to be controlled primarily by intraparticle-diffusion. The maximum adsorption capacities of GRM were determined to be 38.2 mg g<sup>-1</sup> at 20°C, 43.4 mg g<sup>-1</sup> at 30°C and 52.1 mg g<sup>-1</sup> at 40°C.

Acid treated (HCl) red mud containing a high amount of cancrinite, however, has been reported deleterious for the adsorption of heavy metals( $Cd^{2+}$ ,  $Pb^{2+}$ , and  $Zn^{2+}$ ) in comparison to untreated red mud [30]. The adsorption capacity of the untreated red mud for  $Cd^{2+}$ ,  $Pb^{2+}$ , and  $Zn^{2+}$  was 1.35 mmol g<sup>-1</sup>, 1.88 mmol g<sup>-1</sup>, and 2.47 mmol g<sup>-1</sup>, respectively, while, it decreased by 30% using HCl treated red mud. Acid treatment in this case decreases the amount (by 8.2%) and pore structure of cancrinite and other phases of the red mud, which are responsible for adsorption sites. In contrast, the presence of a higher amount of cancrinite in the untreated red mud facilitates the incorporation of Pb, Cd, and Zn in the cages and channels of its lattice.

Boron as borate is a problematic ion to be removed from aqueous systems. Neutralized red mud is highly effective for the removal of boron from aqueous systems [62]. The adsorption of boron as borate anions is negligibly affected in the pH range from 2 to 7 and equilibrium is readily achieved within 20 min of contact time. The results are more accurately modelled by the Freundlich isotherm rather than by the Langmuir isotherm, which indicated a heterogeneous adsorption process. Table 4 compares the Freundlich isotherm constants (k, n) for the adsorption of boron using a range of adsorbents and it shows a several order increase in the adsorption capacity of neutralized red mud.

 
 Table 4. The Freundlich Isotherm Constants (k, n) for Adsorption of Boron by Different Adsorbents [62]

| 1                           |                                |     |      |
|-----------------------------|--------------------------------|-----|------|
| Adsorbents                  | <i>k</i> (mg g <sup>-1</sup> ) | n   | Ref  |
| Activated carbon            | 0.19                           | 2.5 | [63] |
| Activated alumina           | 0.44                           | 1.4 | [63] |
| Minespoils (Wooley Edge)    | 0.004                          | 1.4 | [64] |
| Minespoils (Hoyland Common) | 0.005                          | 1.6 | [64] |
| Minespoils (Crowedge)       | 0.002                          | 1.9 | [64] |
| Neutralized red mud         | 5.996                          | 2.2 | [62] |

#### 3.3.2. Removal of inorganic ions with red mud

Phosphate: The removal of phosphate has been reported using heat activated and acid activated red mud [37]. The optimum activation of red mud is obtained after calcination at 700°C for 2 h, while in the acid-heat activated process (RMAH), the highest performance is obtained after treatment at 80°C with 0.25 mol L<sup>-1</sup> HCl for 2 h. At pH 7, the RMAH and RM700 achieved 31.0 and 30.7 mg g<sup>-1</sup> removal from a solution with an initial phosphate concentration of 155 mg L<sup>-1</sup>. The Langmuir isotherm model indicated that the maximum sorption capacities of phosphate by the RMAH and RM700 were 203 mg g<sup>-1</sup> and 155 mg g<sup>-1</sup>. The loss of acid-soluble fractions such as  $Fe_2O_3$  and CaO in the residue was observed during the acid-heat process when either the HCl concentration or the activation temperature was too high. In a comparative study between raw RM and ARM [28], the greatest adsorption capacity of ARM was 0.58 mg g<sup>-1</sup> at pH 5.5 (40°C) while raw RM only yielded 0.23 mg g<sup>-1</sup> under similar experimental conditions. The adsorption of phosphate was improved by 25% when the temperature increased from 30 to 40°C. The authors demonstrated that the adsorption of phosphate was a heterogeneous adsorption with two major phosphate species, H<sub>2</sub>PO<sub>4</sub><sup>-</sup> and HPO<sub>4</sub><sup>2-</sup>.

Red mud granular adsorbents (RMGA) prepared using different mass proportion of raw materials (red mud, bentonite and starch) at different sintering temperatures (ST) have been assessed for the adsorption of phosphate at selected aquatic temperatures (AT) (17°C, 27°C, 37°C) [65]. The RM ratio in the RMGA and ST influenced the characteristics of the RMGA more significantly than other factors. The optimum parameters, under which the largest adsorption capacities could be achieved, varied with different AT. The optimum ST was 1,080°C, 1,050°C and 1,030°C for RMGA-85% under AT of 17°C, 27°C, and 37°C, respectively, and for RMGA-90%, it was 1,050°C, 1,010°C, and 980°C, respectively, at different AT. In the following study, the regeneration of RMGA (RM, bentonite, and starch at a ratio of 95:5:5) used for phosphate removal using various desorption reagents was investigated [43]. The generation of the sorbent was found optimal using a 0.01 mol  $L^{-1}$  NaOH solution, considering both an optimum regeneration capacity and the process economics. Another study, reported the mechanism of adsorption of phosphate from aqueous solution using RMGA, which involved two stages of adsorption and precipitation [66].

Recently, the interaction between acid activated-neutralized red mud (AaN-RM) and phosphate was examined [11]. The phosphate adsorption capacity of AaN-RM was found to be 492 mg g<sup>-1</sup>. The phosphate adsorption was described as the chemisorption of phosphate on AaN-RM and the process was described as heterogeneous. The formation of phosphate complexes (Al-P, Al–P–H<sub>3</sub>PO<sub>4</sub>, Fe-P, and Fe–P–H<sub>3</sub>PO<sub>4</sub>) on the AaN-RM surface can be attributed to surface deposition, ion exchange, and precipitation mechanisms. 60% of the sorbed phosphate onto AaN-RM was through ion exchange and precipitation with strong chemical bonds, while the remaining phosphate was adsorbed via surface deposition with weak chemical bonds.

*Fluorides and Nitrates:* Batch and column studies have been conducted using granular red mud (GRM) on fluoride removal [45]. The maximum adsorption of fluoride in batch experiments was 0.644 mg g<sup>-1</sup> (pH 4.7) and equilibrium was reached after 6h. The results indicated that the sorption capacities determined from columns studies were higher (0.773-1.274 mg g<sup>-1</sup> for 5 g L<sup>-1</sup> GRM

dosage) than in batch tests. The discrepancy was explained by the presence of GRM pores that favour improved solid state diffusion in the column tests relative to the batch tests. However, concentrated acids were found to have a negative effect on fluoride adsorption due to the loss of active sites [29]. The ionic charge of aluminium and iron oxide/hydroxides on the surface of the red mud strongly influenced the adsorption of fluoride. The acidification of red mud with strong acids transforms the  $\equiv$ SOH/ $\equiv$ SO sites to  $\equiv$ SOH<sub>2</sub>+ which replaces a proton (H<sup>+</sup>) with fluoride.

The removal of nitrate using HCl activated red mud has been reported in batch adsorption experiments [67]. The nitrate adsorption capacity of activated red mud (5.86 mmol  $g^{-1}$ ) was found to be higher than that of the non-activated red mud (1.86 mmol  $g^{-1}$ ) and decreased above pH 7. The nitrate saturation capacity of activated red mud was three times higher when compared to non-activated red mud.

#### 3.3.3. Dye adsorption on red mud

Growing concern has been reported with regards to the potential adverse effects of textile dyes on aquatic ecosystems and humans due to the exposure of contaminated drinking and recreational waters [68]. The use of modified red mud for dyes adsorption has yielded promising results and has been reported in numerous studies. The chemistry of the dye molecules and of activated red mud in aqueous solution is strongly influenced by the pH. The removal of fast green, methylene blue, and rhodamine B has been reported 94.0, 75.0 and 92.5% respectively, using 10.0 g L<sup>-1</sup> of modified red mud [47], and the optimum pH for the removal were 8.0, 7.0, and 1.0, respectively. The adsorption of dyes decreased as the temperature increased from  $30^{\circ}$ C to  $50^{\circ}$ C. The presence of anionic and cationic surfactants [manoxol 1B and cetyltrim-ethylammonium bromide (CTAB), respectively] in dye solutions resulted in a decrease in the adsorption of the dyes.

The effect of pH and the temperature was also studied for the adsorption of methylene blue from aqueous solutions using fly ash and red mud [18]. Raw fly ash showed greater adsorption than red mud with adsorption capacity of 14.0 and 7.8  $\mu$ mol g<sup>-1</sup>, respectively. Acid treatment and heat treatment of red mud at 800°C exhibited lower adsorption capacity compared to virgin red mud. The treatment at high temperature on red mud decomposes organic compounds and hydroxyl groups, which may create effective sites for adsorption. Acid treatment also reduced the basicity of red mud, which favours the adsorption of basic dyes. The adsorption of methylene blue on red mud was an endothermic reaction with  $\Delta$ H° of 10.8 kJ mol<sup>-1</sup>.

The adsorption of cationic dyes on red mud is favoured under basic conditions. The removal of crystal violet (CV) and malachite green (MG) with acid-activated sintering red mud (ASRM) [39] is a rapid process and was completed in 90 min and 180 min for CV and MG respectively. The Langmuir isotherm model described the adsorption of these dyes more accurately than the Freundlich isotherm model, with adsorption capacities of 60.5 mg g<sup>-1</sup> and 336.4 mg g<sup>-1</sup> for CV and MG, respectively. The adsorption of these dyes was favoured at pH higher than the pH<sub>pzc</sub> of ASRM (3.2) as a result of the electrostatic interaction between the positively charged (-N<sup>+</sup>) groups of the cationic dyes and the negatively charged surface of ASRM presented by ion exchange Reaction (1) or Si-O-Si structures Reaction (2).

ASRM-OH + N<sup>+</sup> ((CH<sub>3</sub>)<sub>2</sub>)-dye  $\rightarrow$  ASRM-O-N((CH<sub>3</sub>)<sub>2</sub>)-dye + H<sup>+</sup> (1)

ASRM-Si-O<sup>-</sup> + N<sup>+</sup> ((CH<sub>3</sub>)<sub>2</sub>)-dye  $\rightarrow$  ASRM-Si-O-N((CH<sub>3</sub>)<sub>2</sub>)-dye (2)

In contrast to cationic dyes, the adsorption of anionic dyes is favoured at pH lower than the pH<sub>pzc</sub> of the sorbent. The adsorption of reactive black 19 (RB19) onto seawater-neutralised red mud (SWNRM) which have pH<sub>pzc</sub> (9.0  $\pm$  0.2) was investigated [48]. Red mud samples were treated with seawater as shown in Table 2. The highest removal of RB19 was obtained for the SWNRM sample heated to 400°C, and at pH less than the pH<sub>pzc</sub>. From the adsorption data, the maximum adsorption capacities were 250.0 mg g<sup>-1</sup>, 416.7 mg g<sup>-1</sup> and 384.6 mg g<sup>-1</sup> for SWNRM, SWNRM400 and SWNRM500, respectively.

The adsorption capacities of modified red mud for various types of dyes are summarized in Table 5. The removal of a diazo dye, congo red from aqueous solution with activated red mud [38] was optimum at pH 7.0 and equilibrium was reached in 90 min. The maximum adsorption capacity of congo red on ARM was 7.08 mg g<sup>-1</sup>.

In further studies, the removal of anionic dyes, acid blue 113 (AB113) and reactive black 5 (RB5) using acid activated red (ARM) mud after 60 min were 3871 mg kg<sup>-1</sup> and 2406 mg kg<sup>-1</sup>, respectively [10]. The removal of AB113 and RB5 decreased from 97% to 88% and 58% to 11%, respectively, when the pH of the solution pH increased from 3 to 11. This phenomenon can be described by the amphoteric behaviour of adsorbent which has  $pH_{pzc}$  (8.96). The presence of aniline and phenol groups on RB5 lessens its interaction with the positively charged surface of ARM especially below pH 8.96. The removal of AB113 was higher than RB5 because of the greater molecular size of RB5 which prevents it from approaching to the adsorbent surface. The maximum adsorption capacities were 83.3 mg g<sup>-1</sup> and 35.6 mg g<sup>-1</sup> at pH 3 for AB113 and RB5, respectively.

#### 3.3.4. Adsorption of phenolic compounds on red mud

Effluents containing phenol and derivative compounds generated from industrial operations such as pharmaceutical production, polymer production, and petrochemicals operations are often toxic and carcinogenic due to the stability of phenolics species in aqueous systems. The removal of phenol using HCl activated red mud was found to have negligible effect in comparison to unmodified red mud [72]. The authors explained that changes in the electrostatic, hydrophilic and hydrophobic characteristics of red mud imparted by HCl treatment, resulted in weak interactions between the sorbed phenol molecules and the surface of the red mud and this facilitated the desorption of the bonded phenols. A contrasting study reported the removal of phenol by 33% with neutralized red mud and 70% with acid activated neutralized red mud [45]. Another study using neutralized red mud reported that the removal of phenol was obtained in a wide pH range from 1 to 9 though a spontaneous process. The maximum monolayer sorption capacity for the adsorption of phenol was found to be 4.12 mg g<sup>-1</sup>. The higher selectivity of metal oxides present in the red mud showed that an increasing chloride dosage had no effect on the phenol adsorption, as compared to sulphate and nitrate ions [40].

The adsorption of phenol, 2-chlorophenol, 4-chlorophenol and

| Classification of dye | Dye                    | Adsorbent                        | рН   | Adsorption (mg g <sup>-1</sup> )  | Ref. |  |  |
|-----------------------|------------------------|----------------------------------|--|---|------|--|--|
|                       | Acid blue 113          | RM-HNO <sub>3</sub>              | 3  | 35.58   | [10] |  |  |
|                       | Congo red              | RM-HCl                           | 7  | 7.08  | [38] |  |  |
| A                     | Remazol brilliant blue | $RM-H_2SO_4$                     | sorbentpHAdsorption (mg g'1)Ref. $4$ -HNO33 $35.58$ [10] $M$ -HCl7 $7.08$ [38] $1-H_2SO_4$ 2-6 $27.80$ [69] $4$ -HNO33 $83.33$ [10]WNRM4 $250.00$ [48]NRM-4004 $416.70$ [48]M-HCl> $3.2$ $60.50$ [39] $M$ -H2O28 $16.72$ [47]M-Heat10 $0.48$ [18] $A$ -HNO310 $1.02$ [18]GRM11 $5.13$ [70] |   |      |  |  |
| Anionic               | Reactive black 5       | RM-HNO <sub>3</sub>              | 3  | 83.33   | [10] |  |  |
|                       | Parativa blue 10       | SWNRM                            | 4  | 3 $3335$ $[10]$ $7$ $7.08$ $[38]$ $2-6$ $27.80$ $[69]$ $3$ $83.33$ $[10]$ $4$ $250.00$ $[48]$ $4$ $416.70$ $[48]$ $4$ $416.70$ $[48]$ $5$ $3.2$ $60.50$ $[39]$ $8$ $16.72$ $[47]$ $10$ $0.48$ $[18]$ $10$ $1.02$ $[18]$ |      |  |  |
|                       | Reactive blue 19       | SWNRM-400                        | 4  |   | [48] |  |  |
|                       | Crystal violet         | RM-HCl                           | > 3.2  | 60.50   | [39] |  |  |
|                       |                        | $RM-H_2O_2$                      | 8  | 16.72   | [47] |  |  |
|                       |                        | <b>RM-Heat</b>                   | 10   | 0.48  | [18] |  |  |
| Basic                 | Methylene blue         | RM-HNO <sub>3</sub>              | 10   | 1.02  | [18] |  |  |
|                       |                        | GRM                              | 11   | 5.13  | [70] |  |  |
|                       |                        | RM-500°C                         | 2-4  | 178.40  | [71] |  |  |
|                       | Rhodamine B            | RM-H <sub>2</sub> O <sub>2</sub> | 1  | 5.56  | [47] |  |  |
|                       |                        |                                  |  |   |      |  |  |

Table 5. Adsorption Capacity of Modified Red Mud for Different Class of Dyes

2,4-dichlorophenol from wastewater using  $H_2O_2$  treated red mud evolved through a particle diffusion mechanism [73]. The removal of 2,4-dichlorophenol and 4-chlorophenol ranged between 94 and 97%, while the removal of 2-chlorophenol and phenol ranged between 50 and 81%. Column experiments with a flow rate of 0.5 mL min<sup>-1</sup> removed 98% phenols and its derivatives in the following order 2,4-dichlorophenol > 4-chlorophenol > 2-chlorophenol > phenol.

#### 3.4. Applications in Catalysis

Red mud features in a wide range of catalytic applications, such as hydrochlorination, hydroliquefaction, hydrogenation and oxidation. Physico-chemical treatments such as acid activation, calcination, reduction, and sulphidation influence the catalytic activity of red mud [5, 12]. Metallic oxides such as iron oxides in red mud are less susceptible to poisoning by sulphur, however, the low level of dispersion and low surface area of red mud are detrimental to the catalytic activity. The interaction of calcium and sodium oxides in the red mud with the major components (Fe<sub>2</sub>O<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, SiO<sub>2</sub>) leads to morphologic and crystallographic changes under reaction conditions required for catalytic activity. Pratt and Christoverson [74] have proposed a dissolution-precipitation method to reduce the Na and Ca content in red mud. This method involved the dissolution of red mud in strong acid, HCl and precipitation with ammonia at pH 8, which resulted in a material with high surface area and enhanced catalytic activity. Table 6 shows selected treatment methods that result in an increase in the surface area of red mud.

The removal of volatile organic compounds (VOCs), such as alkanes, aromatics, and oxygenated compounds have been investigated using iron-based catalysts prepared from red mud by dissolution-precipitation methods, followed by calcination in air at 500°C [75]. ARM prepared from Pratt and Christoverson method was found to be more active than PARM prepared by dissolving red mud in a mixture of hydrochloric acid and ortho-phosporic acid. The catalytic activity was observed to be similar to that of pure Fe<sub>2</sub>O<sub>3</sub> and Cu-Cr-Ti commercial catalysts.

The catalytic activity of red mud can also be improved by impregnation with metals such as Au, Cu, Cr etc., which in addition to acting as support materials, they also contribute to increasing the catalytic activity [12]. Acid treatment and calcination at 400°C was found to increase both the BET surface area of red mud from 23.0 m<sup>2</sup> g<sup>-1</sup> to 124.9 m<sup>2</sup> g<sup>-1</sup> and its catalytic activity [76]. HCl treated red mud (HRM) with platinum loading (Pt/HRM) prepared through an impregnation method was found to be more active than platinum supported  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (Pt/Al) catalysts. An increase in the platinum loading from 0.1% to 1% on HRM (400) resulted in an increase

Table 6. Effect of Different Treatment Methods on the Surface Area of the Red Mud [12]

| Catalyst          | Surface area, $m^2$ g <sup>-1</sup> (before treatment, $A_0$ ) | Surface area, $m^2$ g <sup>-1</sup> (after treatment, $A_i$ ) | $[(A_i - A_0)/A_0] \ge 100, \%$ |
|-------------------|--|---|---------------------------------|
| ARM <sup>a</sup>  | 64.0   | 155.0   | 1.42                            |
| ARM <sup>a</sup>  | 25.5   | 184.1   | 6.21                            |
| ARM <sup>a</sup>  | 29.4   | 60.7  | 1.06                            |
| ARM <sup>a</sup>  | 24.3   | 82.4  | 2.39                            |
| SARM <sup>c</sup> | 24.3   | 85.4  | 2.51                            |
| $SRM^{c}$         | 24.3   | 29.5  | 0.21                            |
| ARM <sup>a</sup>  | 28.3   | 131.1   | 3.63                            |
| PARM <sup>b</sup> | 28.3   | 111.7   | 2.94                            |

<sup>a</sup>ARM-HCl activated red mud.

<sup>b</sup>PARM-HCl +  $H_3PO_4$  activated red mud.

<sup>c</sup>SRM-Sulphided red mud.

in the toluene  $T_{50}$  conversion from 289°C to 253°C and  $T_{90}$  conversion from 330 C to 253°C, which was accredited to an augmentation of the redox properties of the catalyst. Benzene, hexane, toluene, and o-xylene were completely oxidized over the 1 wt% Pt/HRM(400) catalysts at a temperature less than 280°C.

Red mud and fly ash have also been used in the preparation of Ru-based catalysts, which were tested for the catalytic ammonia decomposition to hydrogen [77]. In this case, the red mud supported Ru catalysts exhibited higher ammonia conversion of 11% and hydrogen production of 7.4% compared to the fly-ash-supported catalyst which yielded 7% ammonia conversion and 4.2% of hydrogen production.

#### 3.5. Red Mud Use in Building Materials

Building materials (bricks, cement, lime and their subsidiaries) are becoming increasingly uneconomical because of obsolescence, exhaustion of raw materials, low plant efficiencies and increasing costs [78]. The use of red mud as a replacement for cement in the production of cementitious with mechanical, microstructure, and hygroscopic properties which is suitable to use in the civil construction sector has been demonstrated [79]. The incorporation of industrial by-products in building materials may lead to concern regarding the presence of natural radionuclides in the component materials. However, bauxite and red mud contents in special cement appear to be viable from radiological aspect [80]. Naturally occurring radioactive materials (NORM) such as  ${}^{40}$ K,  ${}^{232}$ Th, and  ${}^{226}$ Ra in the construction materials were evaluated using 68 red mud samples and 27 clay samples collected from different Hungarian building material processing plants [81]. The samples surveyed using gamma spectrometry and screened in accordance with European Basic Safety Standards (BSS) I-index were classified as bulk building materials (those having I-index < 1) while those sample with large I-index (1.3 to 3.0) were proposed for mixing with cement in proportions between 12-39% of red mud (on average 25%).

Cement produced from bauxite, lime, and red mud, or bauxite, gypsum, lime and red mud, usually exhibit strengths equivalent

Table 7. Various Applications Involving Red Mud as Catalyst [12, 75-77]

or greater than ordinary Portland cement. The cementitious behaviour of red mud derived from the bauxite-calcination (400-900°C) method has been investigated [82]. Red mud calcined at 600°C possesses good cementitious properties, which results from a poorly crystallized Ca<sub>2</sub>SiO<sub>4</sub> metastable phase. This metastable phase transforms into highy-crystallized Ca<sub>2</sub>SiO<sub>4</sub> when the calcination temperature increased from 700°C to 900°C. Figure S7 shows the XRD patterns of Ca<sub>2</sub>SiO<sub>4</sub> in calcined and uncalcined red mud, at temperatures ranging from 400°C to 900°C.

The possibility of partial replacement of Portland cement in concrete with red mud and the properties of the hardened concrete have been reported and compared with the conventional concrete [83]. It was revealed that up to 15% of cement may be replaced with red mud before split tensile strength, comprehensive strength and flexural strength began to decrease, particularly with regards to the comprehensive strength at 20, 25 and 30% of red mud. Another study has shown that the addition of 3.5% of red mud in the raw meal for the production of Portland cement clinkers had no effect on the mineralogical characteristics and quality of the Portland cement clicker produced [21].

A new alkali-slag-red mud cementitious material (ASRC), with both high early and ultimate strength and excellent resistance against chemical attacks, has been described [84]. The hydration products of ASRC cement are made by a C-S-H gel with low Ca/Si ratio of 0.8-1.2 in very fine size and irregular shapes. Neither Ca(OH)<sub>2</sub> and Aft (alumina, ferric oxide, and tri-sulfate), which are usually present in Portland cement, nor zeolite-like products were found in ASRC. The hydration products of the final material remained similar, irrespective of the type of activator used (simple or composite) and curing condition (ambient temperature curing or steam curing).

Conventional bricks are usually produced from ordinary Portland cement or from concrete clay with high temperature kiln firing, and thus contain high embodied energy and have a large carbon footprint. Recently, extensive studies on brick production from waste materials evolved from the shortage of natural source material for the production of the conventional bricks. The alkaline content

| Catalyst            | Application                                     | Temperature, °C | Conversion, % |
|---------------------|---|-----------------|---------------|
| ARM                 | Methane combustion                              |                 | 50            |
| ARM                 | M Naphthalene hydrogenation                     |                 | 80            |
| ARM                 | Naphthalene hydrogenation                       | 350             | 49            |
| PARM                | Methane combustion                              | 557             | 50            |
| Ru/RMHNO3-700       | Ammonia conversion                              | 550             | 17            |
| Cu-RM               | Nitric oxide oxidation                          | 350             | 50            |
| Calcined-RM         | Organochlorinated compounds hydrodechlorination | 300             | 39            |
| Sulphur promoted RM | Coal liquefaction                               | 450             | 7.2 mol       |
| RM                  | Methane combustion                              | > 650           | 50            |
| RM                  | Coal hydrogenation                              | 400             | > 90          |
| RM                  | $SO_2$ reduction                                | 640             | 30            |
| Pt/HRM-400          | Toluene conversion                              | 253             | 90            |
| Pt/HRM-400          | Hexane coversion                                | 240             | 90            |
| Pt/HRM-400          | Benzene   | 266             | 90            |
| Pt/HRM-400          | o-xylene  | 265             | 90            |

in red mud (4 - 5%) provides good fluxing action in good plasticity and better bonding in bricks. The pale brown or golden yellow colour of the bricks from red mud depend on upon the raw material composition and firing temperature [5]. To explore the possibility of producing building materials for commercial applications, paving blocks using FARM10 and FARM20 compositions have been produced on 100 kg scale (Fig. S8). Kumar and Kumar [85] mixed the red mud and fly ash together with 6 M of NaOH and Na<sub>2</sub>SiO<sub>3</sub>.9H<sub>2</sub>O (SiO<sub>2</sub>/Na<sub>2</sub>O molar ratio = 1.5) into 1:1 and ratio. After mixing the dough was cured at ambient temperature for 28 d. The developed paving blocks using 10 - 20% red mud was found to meet IS 15658 specifications. These blocks were also found to be environmentally safe with regards to the leaching of toxic and non-toxic metals.

# 4. Conclusions

This review article has underlined that raw red mud poses a significant threat to the environment and public health and that it is therefore critical to find feasible approaches to reduce the environmental impact of this industrial waste product. The hydroxides content in red mud make it highly caustic and current disposal practice in landfills creates ecological problems. Red mud has been observed to be a useful by-product for the removal of various types of metal ions, inorganic ions, and dye molecules from wastewater, however, fewer studies have focused on the removal of phenols and other organic water contaminants. It is a well-known fact that the red mud works far superior for pollutants removal if it is first activated with acids, CO<sub>2</sub>, H<sub>2</sub>O<sub>2</sub> and by calcination at high temperatures. The modifications of unprocessed red mud with strong acids or heat treatment below 700°C have been found to remarkably enhance the sorption capacities in numerous studies. Among different parameters, pH is an essential factor influencing the sorption process. There are still a few issues that need more consideration, such as improvement of sorption limit through alteration and assessment of sorbent for multi-component pollutants.

Even though red mud offers a wide field of applications in catalysis, the rapid deactivation of its catalytic activity means that little efforts have been made to improve its use in catalysis. Red mud also has the capability to be used as a catalyst support. Extensive use of red mud in the production of building materials such as bricks, cement, and cement clinkers are environmentally beneficial and economically feasible. Tests have demonstrated that these products are safe to the environment. Further investigations on the mechanism of adsorption and precipitation that governs the removal of pollutants in solid and liquid phase should also be intensively conducted, particularly in pilot and field trials, to promote these new processes. In doing so, we may have an opportunity of turning a hazardous waste to a useful wealthy product.

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# Author Contributions

C.G.J. (Associate Professor) supervised the student, visualised, wrote and edited the manuscript. T-Y.Y.H (Professor) made funding acquisition, wrote and edited the manuscript. V.K. (M.Sc. student) conducted the research and investigation process and wrote the original draft. G.L.P (Professor) visualised, wrote, reviewed and edited the manuscript.

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