



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

Collin G. Joseph^{1,4†}, Yun Hin Taufiq-Yap^{2,3}, Vigneswar Krishnan¹, Gianluca Li Puma^{5†}

¹Sonophotochemistry Research Group, Faculty of Science and Natural Resources, Universiti Malaysia Sabah, 88400 Kota Kinabalu, Sabah, Malaysia

²Chancellery Office, Universiti Malaysia Sabah, 88400 Kota Kinabalu, Sabah, Malaysia

³Catalysis Science and Technology Research Centre, Faculty of Science, Universiti Putra Malaysia, Serdang, Malaysia

⁴Water Research Unit, Faculty of Science and Natural Resources, Universiti Malaysia Sabah, 88400 Kota Kinabalu, Sabah, Malaysia

⁵Environmental Nanocatalysis & Photoreaction Engineering, Department of Chemical Engineering, Loughborough University, Loughborough, LE11 3TU, UK

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



This is an Open Access article distributed under the terms of the Creative Commons Attribution-Non-Commercial License (<http://creativecommons.org/licenses/by-nc/3.0/>)

which permits unrestricted non-commercial use, distribution, and reproduction in any medium, provided the original work is properly cited.

Received September 6, 2019 Accepted November 18, 2019

[†] Corresponding Author

E-mail: collin@ums.edu.my (Collin) g.lipuma@lboro.ac.uk (Gianluca)

Tel: +6-088-320000 ext. 2117 (Collin) +44(0)1509 222510 (Gianluca)

Orchid: 0000-0002-0199-4735

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_2O_3), 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, 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 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_2O_3 [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 dissolve, 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

crystalline boehmite (γ -AlO(OH)), hematite (Fe_2O_3), gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), sodalite ($\text{Na}_4\text{Al}_3\text{Si}_3\text{O}_{12}\text{Cl}$), and quartz (SiO_2) with a minor presence of gibbsite $\text{Al}(\text{OH})_3$, calcite (CaCO_3), and whewellite ($\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$) [17]. Table 1 shows that the composition of red mud from different locations can vary significantly.

Table 1. Different Compositions of Red Mud from Different Locations

Area	Composition wt%								Ref.
	Fe ₂ O ₃	Al ₂ O ₃	SiO ₂	TiO ₂	Na ₂ O	CaO	MgO	K ₂ O	
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 Grèce 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]

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 1000°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_3), dicalcium silicate (Ca_2SiO_4), hematite (Fe_2O_3), gibbsite ($\text{Al}(\text{OH})_3$), perovskite (CaTiO_3), 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_2 . The phases of tricalcium aluminate ($\text{Ca}_3\text{Al}_2\text{O}_6$) and Gehlenite ($\text{Ca}_2\text{Al}_2\text{SiO}_7$) 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 Fe₂O₃ and CaCO₃ during the acid heating process, particularly when the acid concentration or the activation temperature was too high (> 700°C), 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 CO₂ treatment has been successfully applied for the removal of arsenate with promising results. XRD analysis indicated significant differences among RM, CO₂ neutralised RM and activated CO₂ neutralised red mud [33]. An increase in the gibbsite fraction and the formation of a new mineral ilmenite (FeTiO₃) was revealed as a result of CO₂ treatment. Table 2 summarizes physico-chemical treatments of red mud, tailored to the adsorption of target water contaminants.

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
Acid heat treatment	Acid-heat treatment; refluxing red mud in HCl; Addition of 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 (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. Refinery, Gladstone, Australia	[35]
Acid treatment	Acid treated with 0.05M HCl at ratio 1:25 (wt/wt) of red mud/ HCl	Pb(II) Cd(II) Zn(II)	Eurallumina plant (Portovesme, Sardinia, Italy)	[30]
Acid treatment	Treated with 2 M HCl or HNO ₃ at liquid/solid ratio of 20 ml g ⁻¹ ; Calcined the acid pre-treated red mud at 700°C	Phosphate	Worsley Alumina, Australia	[28]
Acid treatment	Acid treatment with 0.25M HCl; Heat treatment at 700°C	Phosphate	Shandong Aluminum Cop. Ltd., China	[36]

Acid treatment	Acid-heat treatment at 80°C with 0.25 mol L ⁻¹ ; heat treated at 700°C	Phosphate	Shandong Aluminum Cop. Ltd., China	[37]
Acid treatment	Activated with 10.20 mol L ⁻¹ of HCl	Phosphate	Shandong Aluminum Industry Corporation (Zibo, China)	[11]
Acid treatment	Treated with 0.5 M HCl, 32% HCl, 0.5 M HNO ₃ , 70% HNO ₃ , 0.5 M H ₂ SO ₄ or 98% H ₂ SO ₄ , respectively.	Fluoride	Australian alumina refinery	[29]
Acid treatment	Soaked in 1 M HNO ₃ solution at the 1:2 ratio of red mud and nitric acid (w/v), activated at 150°C for 4 h.	Acid Blue 113 Reactive black 5	Bauxite mill, Iran	[10]
Acid treatment	10 g of red mud boiled with 20% wt of HCl, dried at 40°C	Congo red	Etibank Seydisehir Aluminium Plant (Konya, Turkey)	[38]
Acid treatment	Red mud and 0.5 mol L ⁻¹ HCl at a solid liquid ratio of 1/20.	Crystal violet Malachite green	Shandong Aluminum Corporation	[39]
Acid treatment	10 g of red mud boiled with 20% wt of HCl, dried at 40°C	Phenol	Seyisehir Aluminium Plant (Konya, Turkey)	[40]
Addition of metal halide	10 g of red mud in 1 L of water, add 40 mL 0.5 M FeCl ₃ .6H ₂ O, aged for 1 d.	As(V)	Shandong Aluminium Corporation, China	[41]
Composite	Mixture of red mud (58.7 wt%), kaolin (25.2 wt%), sodium silicate	Cu(II)	Korea General Chemical	[42]

mixture	solution (11.7 wt%), fly ash (2.9 wt%), and MgCl ₂ (1.5 wt%); heat treatment at 600°C	Cd(II) Pb(II)	Corporation, Daebul Industrial Park, Korea	
Composite mixture	Mixing dewatered red mud, bentonite and starch at mass ratios (95:5:5)	Phosphate	Shandong Aluminum Cop. Ltd., 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., China	[44]
Composite mixture	Mixture of neutralized red mud (15 g), dried fly ash (2 g), sodium carbonate (1 g), powdered quicklime (0.8 g) and sodium silicate (1.2 g)	Fluoride	Etibank Aluminium Plant, Konya, Turkey	[45]
Heat treatment	Treated with H ₂ O ₂ and heat treatment at 500°C	Pb(II) Cr(II)	HINDALCO, India	[7]
Heat treatment	Treated with H ₂ O ₂ and heat treatment at 500°C	Cd(II) Zn(II)	HINDALCO, India	[46]
Heat treatment	Treated with H ₂ O ₂ , activate at 500°C	Fast green Methylene blue Rhodamine B	Hindustan Aluminium Company (HINDALCO), Renukoot, India	[47]

Heat treatment	Heat treatment at 800°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°C	Reactive blue 19	Alumina plant, Aluminio City, São Paulo State (Brazil)	[48]
Neutralization	Neutralization using sequestration of CO ₂ gas; calcination of neutralized sample at 500°C	As(V)	R & D Laboratory of NALCO, Damanjodi, Orissa, India	[33]
Raw usage	Filtrate was obtained from red mud slurry (liquid/solid = 2.5)	As(V)	Etibank Aluminium Plant, Konya, Turkey	[49]

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 H₂SO₄ 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 1765 kg H₂SO₄/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 KH₂PO₄, 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 (B₂R_L), and reactive blue (KNR) by coagulation using MgCl₂/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 alkalization 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]. $\text{Ca}(\text{AlO}_2)_2$ and NaOH were used as the polymerization adjuster (alkali). In this product, $\text{Ca}(\text{AlO}_2)_2$ 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^{-1}) 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^{-1} 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 from 2.1% to 77.3% as the RM/ACl ratio increased from 0 to 0.5. As a result, RMPACl (147.5 mg L^{-1}) showed better coagulation performance (94.9%) than PACl (175 mg L^{-1}) which yielded only 92.3% in the treatment of synthetic and natural phosphate contaminated wastewater.

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

Target pollutant	Coagulant	Red mud	Coagulant production	Suggested applications of the coagulants	Ref
Phosphate	Composite coagulant	Shandong Aluminum Corporation, 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 used in tertiary treatment of biologically pre-treated municipal sewage while in eutrophic wastewater. Its performance was better compared to PACl	[53]
Phosphate	RMPACl	Shandong Aluminum Corporation, Shandong, China.	w/v ratio of red mud to AlCl (0.25), water bath temperature (80°C), 2 h	— Phosphate removal from the Xiang Xi river water in the Hubei province was performed. — RMPACl performed better than PACl at a low dosage in the phosphate removal from real water.	[55]
Phosphorus	JI coagulant	Vaudreuil Aluminium Factory in Jonquièrre	H ₂ SO ₄ concentration (6.0 N), NaCl (93.8 g L ⁻¹), leaching period (120 min), solids concentration (200 g L ⁻¹), temperature	— The performance of this coagulant was similar to the commercially available coagulant	[52]

		(QC, Canada)	(110°C).		
Pretreated oily sewage, printing and dyeing wastewater	PAFC	Shandong Weiqiao aluminium & electricity Co.Ltd., Shandong, China	30% of HCl (300 mL) and RM (100 g), mother liquor and washing liquor (100 mL) were mixed with Ca(AlO ₂) ₂ (1.5 g) and NaOH (1.2 g), 80°C	— Application in the pretreated oily sewage and in printing and dyeing wastewater treatments.	[54]
Direct blue, reactive blue, acid red dyes	MRM	Shandong Aluminum Corporation, 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 used as an alternative to some of the conventional treatments, particularly, in the textile wastewater industry.	[50]

1 **3.3. Adsorbent Development**

2 3.3.1. Removal of heavy metals and metal ions with red mud

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

9 Arsenic is a toxic element at higher concentration, commonly found in the groundwater
10 of certain countries such as Bangladesh, Brazil, Canada, China, India, and Nepal. Mining,
11 smelting of arsenic-bearing minerals are the main causes of the high abundance of arsenic
12 species (-III, 0, +III and +V) in groundwater. Inorganic As(III) and As(IV) are known to be
13 more toxic compared to its methylated forms monomethyl arsenic acid (MMA) and dimethyl
14 arsenic acid (DMA) [57-59], while arsenate (As(V)) is highly toxic. The adsorption of arsenic
15 from water with acid and heat treated red mud is pH dependent. The optimum pH range has been
16 reported to be 5.8 - 7.5 for As(III) adsorption (exothermic process) and 1.8-3.5 for As(V)
17 (endothermic process) [34] [60]. A process for the removal of As(V) using liquid phase red mud
18 (LPRM, 2.5 liquid/slurry ratio) and coagulation has been proposed [49]. The As(V) removal
19 comprises the two steps of neutralization of LPRM-arsenical solution mixtures in acidic
20 condition followed by air-agitation and CO₂-neutralization. As(v) can be removed effectively
21 from the mixture of LPRM-As(v) solution using an optimal Al/As (V) molar ratio of 6-8.
22 Arsenate can also be effectively removed using seawater-neutralized red mud (bauxsol) [8] in

1 adsorption columns packed with bauxsol coated sand (BCS) (1.64 mg g^{-1}) and activated bauxsol
2 coated sand (ABCS) (3.14 mg g^{-1}) (Fig. S6). Most of the sorbed As(V) ($0.39\text{-}8.76 \text{ mmol kg}^{-1}$) is
3 usually associated with amorphous and crystalline Al and Fe oxides (24.1 - 43.8% and 24.7-59.0%
4 of total sorbed arsenic) [61] with the percentage distribution related to the surface coverage of
5 arsenic.

6 The adsorption of arsenate is usually significantly affected by the pH of the water and the
7 adsorption capacity increases as pH decreases, however, the highest absorption capacity of FeCl_3
8 modified red mud (68.5 mg g^{-1}) is obtained at pH 6 [41]. Among the ions present in the water,
9 nitrate ion has little impact, Ca^{2+} enhances the adsorption process, whereas HCO_3^- decreases the
10 adsorption of arsenate. The spent FeCl_3 modified red mud can be regenerated up to 92% by using
11 0.2 mol L^{-1} NaOH. Using activated CO_2 -neutralized red mud (ANRM) [33] the most effective
12 removal of arsenate is obtained at pH 4. The high adsorption of arsenate on ANRM is attributed
13 to the hydroxyl surfaces mixture of Fe, Al, and Ti oxides, which provides strong adsorption
14 affinity by forming inner-sphere complexes. Again, the arsenate-adsorbed ANRM can be easily
15 regenerated using NaOH solution at pH 12.0.

16 Effective removal of other heavy metals (Cr^{2+} , Pb^{2+} , Cd^{2+} and Zn^{2+}) in both batch and
17 column configurations can be achieved using activated red mud (ARM) [7] [46]. High capacity
18 ARM is made by treating red mud with H_2O_2 and calcination at 500°C . The adsorption capacity
19 for chromium has been reported to be 1.3 times higher than that for lead, while the presence of
20 other metal ions (Na^+ , Cd^{2+} , Zn^{2+}) and surfactants (manaxol 1B, cetyltrimethyl ammonium
21 bromide) reduces the removal of Cr^{2+} and Pb^{2+} [7]. At low ions concentrations, remarkable
22 removal of efficiency of Cd^{2+} (0.02 mM) and Zn^{2+} (0.03 mM) has been reported at pH 4 using 10

1 g L⁻¹ of ARM [46].

2 A new pellet type adsorbent produced with red mud, kaolin, sodium silicate solution, fly
3 ash, and MgCl₂ at 600°C has been shown to be highly effective for the removal (> 95%) of Cu²⁺,
4 Cd²⁺ and Pb²⁺ from aqueous systems [42]. Continuous adsorption experiments confirmed that
5 this adsorbent is more effective in the removal of Pb²⁺ among the heavy metals tested. Granular
6 red mud (GRM) has also been examined for the removal of cadmium from aqueous solutions
7 [44]. The adsorption process in the GRM-Cd²⁺ system at initial pH 6.0 was found to be controlled
8 primarily by intraparticle-diffusion. The maximum adsorption capacities of GRM were
9 determined to be 38.2 mg g⁻¹ at 20°C, 43.4 mg g⁻¹ at 30°C and 52.1 mg g⁻¹ at 40°C.

10 Acid treated (HCl) red mud containing a high amount of cancrinite, however, has been
11 reported deleterious for the adsorption of heavy metals (Cd²⁺, Pb²⁺, and Zn²⁺) in comparison to
12 untreated red mud [30]. The adsorption capacity of the untreated red mud for Cd²⁺, Pb²⁺, and
13 Zn²⁺ was 1.35 mmol g⁻¹, 1.88 mmol g⁻¹, and 2.47 mmol g⁻¹ respectively, while, it decreased by
14 30% using HCl treated red mud. Acid treatment in this case decreases the amount (by 8.2%) and
15 pore structure of cancrinite and other phases of the red mud, which are responsible for adsorption
16 sites. In contrast, the presence of a higher amount of cancrinite in the untreated red mud
17 facilitates the incorporation of Pb, Cd, and Zn in the cages and channels of its lattice.

18 Boron as borate is a problematic ion to be removed from aqueous systems. Neutralized
19 red mud is highly effective for the removal of boron from aqueous systems [62]. The adsorption
20 of boron as borate anions is negligibly affected in the pH range from 2 to 7 and equilibrium is
21 readily achieved within 20 min of contact time. The results are more accurately modelled by the
22 Freundlich isotherm rather than by the Langmuir isotherm, which indicated a heterogeneous

1 adsorption process. Table 4 compares the Freundlich isotherm constants (k , n) for the adsorption
 2 of boron using a range of adsorbents and it shows a several order increase in the adsorption
 3 capacity of neutralized red mud.

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

Adsorbents	$k(\text{mg g}^{-1})$	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]

7
 8 3.3.2. Removal of inorganic ions with red mud

9 *Phosphate:* The removal of phosphate has been reported using heat activated and acid activated
 10 red mud [37]. The optimum activation of red mud is obtained after calcination at 700°C for 2 h,
 11 while in the acid-heat activated process (RMAH), the highest performance is obtained after
 12 treatment at 80°C with 0.25 mol L⁻¹ HCl for 2 h. At pH 7, the RMAH and RM700 achieved 31.0
 13 and 30.7 mg g⁻¹ removal from a solution with an initial phosphate concentration of 155 mg L⁻¹.
 14 The Langmuir isotherm model indicated that the maximum sorption capacities of phosphate by
 15 the RMAH and RM700 were 203 mg g⁻¹ and 155 mg g⁻¹. The loss of acid-soluble fractions such

1 as Fe_2O_3 and CaO in the residue was observed during the acid-heat process when either the HCl
2 concentration or the activation temperature was too high. In a comparative study between raw
3 RM and ARM [28], the greatest adsorption capacity of ARM was 0.58 mg g^{-1} at pH 5.5 (40°C)
4 while raw RM only yielded 0.23 mg g^{-1} under similar experimental conditions. The adsorption of
5 phosphate was improved by 25% when the temperature increased from 30 to 40°C . The authors
6 demonstrated that the adsorption of phosphate was a heterogeneous adsorption with two major
7 phosphate species, H_2PO_4^- and HPO_4^{2-} .

8 Red mud granular adsorbents (RMGA) prepared using different mass proportion of raw
9 materials (red mud, bentonite and starch) at different sintering temperatures (ST) have been
10 assessed for the adsorption of phosphate at selected aquatic temperatures (AT) (17°C , 27°C , 37°C)
11 [65]. The RM ratio in the RMGA and ST influenced the characteristics of the RMGA more
12 significantly than other factors. The optimum parameters, under which the largest adsorption
13 capacities could be achieved, varied with different AT. The optimum ST was 1080°C , 1050°C
14 and 1030°C for RMGA-85% under AT of 17°C , 27°C , and 37°C , respectively, and for RMGA-
15 90%, it was 1050°C , 1010°C , and 980°C , respectively, at different AT. In the following study, the
16 regeneration of RMGA (RM, bentonite, and starch at a ratio of 95:5:5) used for phosphate
17 removal using various desorption reagents was investigated [43]. The generation of the sorbent
18 was found optimal using a 0.01 mol L^{-1} NaOH solution, considering both an optimum
19 regeneration capacity and the process economics. Another study, reported the mechanism of
20 adsorption of phosphate from aqueous solution using RMGA, which involved two stages of
21 adsorption and precipitation [66].

22 Recently, the interaction between acid activated-neutralized red mud (AaN-RM) and

1 phosphate was examined [11]. The phosphate adsorption capacity of AaN-RM was found to be
2 492 mg g^{-1} . The phosphate adsorption was described as the chemisorption of phosphate on AaN-
3 RM and the process was described as heterogeneous. The formation of phosphate complexes
4 (Al-P, Al-P-H₃PO₄, Fe-P, and Fe-P-H₃PO₄) on the AaN-RM surface can be attributed to
5 surface deposition, ion exchange, and precipitation mechanisms. 60% of the sorbed phosphate
6 onto AaN-RM was through ion exchange and precipitation with strong chemical bonds, while the
7 remaining phosphate was adsorbed via surface deposition with weak chemical bonds.

8 *Fluorides and Nitrates:* Batch and column studies have been conducted using granular
9 red mud (GRM) on fluoride removal [45]. The maximum adsorption of fluoride in batch
10 experiments was 0.644 mg g^{-1} (pH 4.7) and equilibrium was reached after 6h. The results
11 indicated that the sorption capacities determined from columns studies were higher ($0.773\text{-}1.274$
12 mg g^{-1} for 5 g L^{-1} GRM dosage) than in batch tests. The discrepancy was explained by the
13 presence of GRM pores that favour improved solid state diffusion in the column tests relative to
14 the batch tests. However, concentrated acids were found to have a negative effect on fluoride
15 adsorption due to the loss of active sites [29]. The ionic charge of aluminium and iron
16 oxide/hydroxides on the surface of the red mud strongly influenced the adsorption of fluoride.
17 The acidification of red mud with strong acids transforms the $\equiv\text{SOH}/\equiv\text{SO}^-$ sites to $\equiv\text{SOH}_2^+$
18 which replaces a proton (H^+) with fluoride.

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

1 to non-activated red mud.

2

3 3.3.3. Dye adsorption on red mud

4 Growing concern has been reported with regards to the potential adverse effects of textile dyes
5 on aquatic ecosystems and humans due to the exposure of contaminated drinking and
6 recreational waters [68]. The use of modified red mud for dyes adsorption has yielded promising
7 results and has been reported in numerous studies. The chemistry of the dye molecules and of
8 activated red mud in aqueous solution is strongly influenced by the pH. The removal of fast
9 green, methylene blue, and rhodamine B has been reported 94.0, 75.0 and 92.5% respectively;
10 using 10.0 g L⁻¹ of modified red mud [47], and the optimum pH for the removal were 8.0, 7.0,
11 and 1.0, respectively. The adsorption of dyes decreased as the temperature increased from 30°C,
12 40°C, and 50°C. The presence of anionic and cationic surfactants [manoxol 1B and cetyltrim-
13 ethylammonium bromide (CTAB), respectively] in dye solutions resulted in a decrease in the
14 adsorption of the dyes.

15 The effect of pH and the temperature was also studied for the adsorption of methylene
16 blue from aqueous solutions using fly ash and red mud [18]. Raw fly ash showed greater
17 adsorption rather than red mud with adsorption capacity of 14.0 and 7.8 μmol g⁻¹, respectively.
18 Acid treatment and heat treatment of red mud at 800°C exhibited lower adsorption capacity
19 compared to virgin red mud. The treatment at high temperature on red mud decomposes organic
20 compounds and hydroxyl groups, which may create effective sites for adsorption. Acid treatment
21 also reduced the basicity of red mud, which favours the adsorption of basic dyes. The adsorption
22 of methylene blue on red mud was an endothermic reaction with ΔH° of 10.8 kJ mol⁻¹.

1 The adsorption of cationic dyes on red mud is favoured under basic conditions. The
 2 removal of crystal violet (CV) and malachite green (MG) with acid-activated sintering red mud
 3 (ASRM) [39] is a rapid process and was completed in 90 min and 180 min for CV and MG
 4 respectively. The Langmuir isotherm model described the adsorption of these dyes more
 5 accurately than the Freundlich isotherm model, with adsorption capacities of 60.5 mg g⁻¹ and
 6 336.4 mg g⁻¹ for CV and MG, respectively. The adsorption of these dyes was favoured at pH
 7 higher than the pH_{pzc} of ASRM (3.2) as a result of the electrostatic interaction between the
 8 positively charged (-N⁺) groups of the cationic dyes and the negatively charged surface of
 9 ASRM presented by ion exchange Eq. (1) or Si-O-Si structures Eq. (2).

10



13

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

21 The adsorption capacities of modified red mud for various types of dyes are summarized
 22 in Table 5. The removal of a diazo dye, congo red from aqueous solution with activated red mud

1 [38] was optimum at pH 7.0 and equilibrium was reached in 90 min. The maximum adsorption
 2 capacity of congo red on ARM was 7.08 mg g⁻¹.

3 In further studies, the removal of anionic dyes, acid blue 113 (AB113) and reactive black
 4 5 (RB5) using acid activated red (ARM) mud after 60 min were 3871 mg kg⁻¹ and 2406 mg kg⁻¹,
 5 respectively [10]. The removal of AB113 and RB5 decreased from 97% to 88% and 58% to 11%,
 6 respectively, when the pH of the solution pH increased from 3 to 11. This phenomenon can be
 7 described by the amphoteric behaviour of adsorbent which has p*H*_{pzc} (8.96). The presence of
 8 aniline and phenol groups on RB5 lessens its interaction with the positively charged surface of
 9 ARM especially below pH 8.96. The removal of AB113 was higher than RB5 because of the
 10 greater molecular size of RB5 which prevents it from approaching to the adsorbent surface. The
 11 maximum adsorption capacities were 83.3 mg g⁻¹ and 35.6 mg g⁻¹ at pH 3 for AB113 and RB5,
 12 respectively.

13
 14 **Table 5.** Adsorption Capacity of Modified Red Mud for Different Class of Dyes

Classification of dye	Dye	Adsorbent	pH	Adsorption (mg g ⁻¹)	Ref.
Anionic	Acid blue 113	RM-HNO ₃	3	35.58	[10]
	Congo red	RM-HCl	7	7.08	[38]
	Remazol brilliant blue	RM-H ₂ SO ₄	2-6	27.80	[69]
	Reactive black 5	RM-HNO ₃	3	83.33	[10]
	Reactive blue 19	SWNRM	4	250.00	[48]
		SWNRM-400	4	416.70	[48]

Basic	Crystal violet	RM-HCl	> 3.2	60.50	[39]
	Methylene blue	RM-H ₂ O ₂	8	16.72	[47]
		RM-Heat	10	0.48	[18]
		RM-HNO ₃	10	1.02	[18]
		GRM	11	5.13	[70]
		RM-500°C	2-4	178.40	[71]
	Rhodamine B	RM-H ₂ O ₂	1	5.56	[47]

1

2 3.3.4. Adsorption of phenolic compounds on red mud

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

1 phenol adsorption, as compared to sulphate and nitrate ions [40].

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

9 **3.4. Applications in Catalysis**

10 Red mud features in a wide range of catalytic applications, such as hydrochlorination,
11 hydroliquefaction, hydrogenation and oxidation. Physico-chemical treatments such as acid
12 activation, calcination, reduction, and sulphidation influence the catalytic activity of red mud [5,
13 12]. Metallic oxides such as iron oxides in red mud are less susceptible to poisoning by sulphur,
14 however, the low level of dispersion and low surface area of red mud are detrimental to the
15 catalytic activity. The interaction of calcium and sodium oxides in the red mud with the major
16 components (Fe_2O_3 , Al_2O_3 , TiO_2 , SiO_2) leads to morphologic and crystallographic changes under
17 reaction conditions required for catalytic activity. Pratt and Christoverson [74] have proposed a
18 dissolution-precipitation method to reduce the Na and Ca content in red mud. This method
19 involved the dissolution of red mud in strong acid, HCl and precipitation with ammonia at pH 8,
20 which resulted in a material with high surface area and enhanced catalytic activity. Table 6
21 shows selected treatment methods that result in an increase in the surface area of red mud.

22 The removal of volatile organic compounds (VOCs), such as alkanes, aromatics, and

1 oxygenated compounds have been investigated using iron-based catalysts prepared from red mud
 2 by dissolution-precipitation methods, followed by calcination in air at 500°C [75]. ARM
 3 prepared from Pratt and Christoverson method was found to be more active than PARM prepared
 4 by dissolving red mud in a mixture of hydrochloric acid and ortho-phosphoric acid. The catalytic
 5 activity was observed to be similar to that of pure Fe₂O₃ and Cu-Cr-Ti commercial catalysts.

6

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

Catalyst	Surface area, m ² g ⁻¹ (before treatment, A ₀)	Surface area, m ² g ⁻¹ (after treatment, A _i)	[(A _i - A ₀)/ A ₀] x 100, %
ARM ^a	64.0	155.0	1.42
ARM ^a	25.5	184.1	6.21
ARM ^a	29.4	60.7	1.06
ARM ^a	24.3	82.4	2.39
SARM ^c	24.3	85.4	2.51
SRM ^c	24.3	29.5	0.21
ARM ^a	28.3	131.1	3.63
PARM ^b	28.3	111.7	2.94

8

9 ^aARM-HCl activated red mud.

10 ^bPARM-HCl + H₃PO₄ activated red mud.

11 ^cSRM-Sulphided red mud.

12 The catalytic activity of red mud can also be improved by impregnation with metals such
 13 as Au, Cu, Cr etc., which in addition to acting as support materials, they also contribute to

1 increasing the catalytic activity [12]. Acid treatment and calcination at 400°C was found to
 2 increase both the BET surface area of red mud from 23.0 m² g⁻¹ to 124.9 m² g⁻¹ and its catalytic
 3 activity [76]. HCl treated red mud (HRM) with platinum loading (Pt/HRM) prepared through an
 4 impregnation method was found to be more active than platinum supported γ -Al₂O₃ (Pt/Al)
 5 catalysts. An increase in the platinum loading from 0.1% to 1% on HRM (400) resulted in an
 6 increase in the toluene T₅₀ conversion from 289°C to 253°C and T₉₀ conversion from 330 C to
 7 253°C, which was accredited to an augmentation of the redox properties of the catalyst. Benzene,
 8 hexane, toluene, and o-xylene were completely oxidized over the 1 wt% Pt/HRM(400) catalysts
 9 at a temperature less than 280°C.

10 Red mud and fly ash have also been used in the preparation of Ru-based catalysts, which
 11 were tested for the catalytic ammonia decomposition to hydrogen [77]. In this case, the red mud
 12 supported Ru catalysts exhibited higher ammonia conversion of 11% and hydrogen production of
 13 7.4% compared to the fly-ash-supported catalyst which yielded 7% ammonia conversion and 4.2%
 14 of hydrogen production.

15
 16 **Table 7.** Various Applications Involving Red Mud as Catalyst [12, 75-77]

Catalyst	Application	Temperature, °C	Conversion, %
ARM	Methane combustion	530	50
ARM	Naphthalene hydrogenation	405	80
ARM	Naphthalene hydrogenation	350	49
PARM	Methane combustion	557	50
Ru/RMHNO ₃ -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 conversion	240	90
Pt/HRM-400	Benzene	266	90
Pt/HRM-400	o-xylene	265	90

1

2 **3.5. Red Mud Use in Building Materials**

3 Building materials (bricks, cement, lime and their subsidiaries) are becoming increasingly
4 uneconomical because of obsolescence, exhaustion of raw materials, low plant efficiencies and
5 increasing costs [78]. The use of red mud as a replacement for cement in the production of
6 cementitious with mechanical, microstructure, and hygroscopic properties which is suitable to
7 use in the civil construction sector has been demonstrated [79]. The incorporation of industrial
8 by-products in building materials may lead to concern regarding the presence of natural
9 radionuclides in the component materials. However, bauxite and red mud contents in special
10 cement appear to be viable from radiological aspect [80]. Naturally occurring radioactive
11 materials (NORM) such as ⁴⁰K, ²³²Th, and ²²⁶Ra in the construction materials were evaluated

1 using 68 red mud samples and 27 clay samples collected from different Hungarian building
2 material processing plants [81]. The samples surveyed using gamma spectrometry and screened
3 in accordance with European Basic Safety Standards (BSS) I-index were classified as bulk
4 building materials (those having I-index < 1) while those sample with large I-index (1.3 to 3.0)
5 were proposed for mixing with cement in proportions between 12-39% of red mud (on average
6 25%).

7 Cement produced from bauxite, lime, and red mud, or bauxite, gypsum, lime and red mud,
8 usually exhibit strengths equivalent or greater than ordinary Portland cement. The cementitious
9 behaviour of red mud derived from the bauxite-calcination (400-900°C) method has been
10 investigated [82]. Red mud calcined at 600°C possesses good cementitious properties, which
11 results from a poorly crystallized Ca_2SiO_4 metastable phase. This metastable phase transforms
12 into highly-crystallized Ca_2SiO_4 when the calcination temperature increased from 700°C to 900°C.
13 Figure S7 shows the XRD patterns of Ca_2SiO_4 in calcined and uncalcined red mud, at
14 temperatures ranging from 400°C to 900°C.

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

1 A new alkali-slag-red mud cementitious material (ASRC), with both high early and
2 ultimate strength and excellent resistance against chemical attacks, has been described [84]. The
3 hydration products of ASRC cement are made by a C-S-H gel with low Ca/Si ratio of 0.8-1.2 in
4 very fine size and irregular shapes. Neither $\text{Ca}(\text{OH})_2$ and Aft (alumina, ferric oxide, and tri-
5 sulfate), which are usually present in Portland cement, nor zeolite-like products were found in
6 ASRC. The hydration products of the final material remained similar, irrespective of the type of
7 activator used (simple or composite) and curing condition (ambient temperature curing or steam
8 curing).

9 Conventional bricks are usually produced from ordinary Portland cement or from
10 concrete clay with high temperature kiln firing, and thus contain high embodied energy and have
11 a large carbon footprint. Recently, extensive studies on brick production from waste materials
12 evolved from the shortage of natural source material for the production of the conventional
13 bricks. The alkaline content in red mud (4 - 5%) provides good fluxing action in good plasticity
14 and better bonding in bricks. The pale brown or golden yellow colour of the bricks from red mud
15 depend on upon the raw material composition and firing temperature [5]. To explore the
16 possibility of producing building materials for commercial applications, paving blocks using
17 FARM10 and FARM20 compositions have been produced on 100 kg scale (Fig. S8). Kumar and
18 Kumar [85] mixed the red mud and fly ash together with 6 M of NaOH and $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$
19 ($\text{SiO}_2/\text{Na}_2\text{O}$ molar ratio = 1.5) into 1:1 and ratio. After mixing the dough was cured at ambient
20 temperature for 28 d. The developed paving blocks using 10 - 20% red mud was found to meet
21 IS 15658 specifications. These blocks were also found to be environmentally safe with regards to
22 the leaching of toxic and non-toxic metals.

1

2 **4. Conclusions**

3 This review article has underlined that raw red mud poses a significant threat to the environment
4 and public health and that it is therefore critical to find feasible approaches to reduce the
5 environmental impact of this industrial waste product. The hydroxides content in red mud make
6 it highly caustic and current disposal practice in landfills creates ecological problems. Red mud
7 has been observed to be a useful by-product for the removal of various types of metal ions,
8 inorganic ions, and dye molecules from wastewater, however, fewer studies have focused on the
9 removal of phenols and other organic water contaminants. It is a well-known fact that the red
10 mud works far superior for pollutants removal if it is first activated with acids, CO₂, H₂O₂ and by
11 calcination at high temperatures. The modifications of unprocessed red mud with strong acids or
12 heat treatment below 700°C have been found to remarkably enhance the sorption capacities in
13 numerous studies. Among different parameters, pH is an essential factor influencing the sorption
14 process. There are still a few issues that need more consideration, such as improvement of
15 sorption limit through alteration and assessment of sorbent for multi-component pollutants.

16 Even though red mud offers a wide field of applications in catalysis, the rapid
17 deactivation of its catalytic activity means that little efforts have been made to improve its use in
18 catalysis. Red mud also has the capability to be used as a catalyst support. Extensive use of red
19 mud in the production of building materials such as bricks, cement, and cement clinkers are
20 environmentally beneficial and economically feasible. Tests have demonstrated that these
21 products are safe to the environment. Further investigations on the mechanism of adsorption and
22 precipitation that governs the removal of pollutants in solid and liquid phase should also be

1 intensively conducted, particularly in pilot and field trials, to promote these new processes. In
2 doing so, we may have an opportunity of turning a hazardous waste to a useful wealthy product.

3

4 **Acknowledgment**

5 This research was supported by the Research Management Centre, Universiti Putra Malaysia in
6 collaboration with the Centre for Research & Innovation of Universiti Malaysia Sabah (Grant No.
7 RACE0008-ST-2013) and is gratefully acknowledged.

8

9 **References**

- 10 1. Zhu X, Li W, Guan X. An active dealkalization of red mud with roasting and water leaching. *J.*
11 *Hazard. Mater.* 2015;286:85-91.
- 12 2. Kobya M, Oncel MS, Demirbas E, Şik E, Akyol A, Ince M. The application of
13 electrocoagulation process for treatment of the red mud dam wastewater from Bayer's process. *J.*
14 *Environ. Chem. Eng.* 2014;2:2211-2220.
- 15 3. Antunes MLP, Couperthwaite SJ, Da Conceição FT, et al. Red mud from Brazil: Thermal
16 behavior and physical properties. *Ind. Eng. Chem. Res.* 2012;51:775-779.
- 17 4. Mišík M, Burke IT, Reismüller M, et al. Red mud a byproduct of aluminum production
18 contains soluble vanadium that causes genotoxic and cytotoxic effects in higher plants. *Sci. Total*
19 *Environ.* 2014;493:883-890.
- 20 5. Samal S, Ray AK, Bandopadhyay A. Proposal for resources, utilization and processes of red
21 mud in India - A review. *Int. J. Miner. Process.* 2013;118:43-55.
- 22 6. Liu Y, Naidu R. Hidden values in bauxite residue (red mud): Recovery of metals. *Waste*

- 1 *Manag.* 2014;34:2662-2673.
- 2 7. Gupta VK, Gupta M, Sharma S. Process Development for the Removal of Lead and
3 Chromium from Aqueous Solutions using Red Mud an Aluminium Industry Waste. *Water Res.*
4 2001;35:1125-1134.
- 5 8. Genç-Fuhrman H, Bregnhøj H, McConchie D. Arsenate removal from water using sand-red
6 mud columns. *Water Res.* 2005;39:2944-2954.
- 7 9. Sahu MK, Mandal S, Dash SS, Badhai P, Patel RK. Removal of Pb(II) from aqueous solution
8 by acid activated red mud. *J. Environ. Chem. Eng.* 2013;1:1315-1324.
- 9 10. Shirzad-Siboni M, Jafari SJ, Giahhi O, Kim I, Lee SM, Yang JK. Removal of acid blue 113
10 and reactive black 5 dye from aqueous solutions by activated red mud. *J. Ind. Eng. Chem.*
11 2014;20:1432-1437.
- 12 11. Ye J, Cong X, Zhang P, et al. Interaction between phosphate and acid-activated neutralized
13 red mud during adsorption process. *Appl. Surf. Sci.* 2015;356:128-134.
- 14 12. Sushil S, Batra VS. Catalytic applications of red mud, an aluminium industry waste: A
15 review. *Appl. Catal. B Environ.* 2008;81:64-77.
- 16 13. Wang S, Ang HM, Tadé MO. Novel applications of red mud as coagulant, adsorbent and
17 catalyst for environmentally benign processes. *Chemosphere.* 2008;72:1621-1635.
- 18 14. Rai S, Wasewar KL, Mukhopadhyay J, Yoo CK, Uslu H. Neutralization and utilization of red
19 mud for its better waste management. *Arch. Environ. Sci.* 2012;6:13-33.
- 20 15. Ma S hua, Wen Z guo, Chen J ning, Zheng S li. An environmentally friendly design for low-
21 grade diasporic-bauxite processing. *Miner. Eng.* 2009;22:793-798.
- 22 16. Wang P, Liu DY. Physical and Chemical Properties of Sintering Red Mud and Bayer Red

- 1 Mud and the Implications for Beneficial Utilization. *Materials (Basel)*. 2012;5:1800-1810.
- 2 17. Brunori C, Cremisini C, Massanisso P, Pinto V, Torricelli L. Reuse of a treated red mud
3 bauxite waste: Studies on environmental compatibility. *J. Hazard. Mater.* 2005;117:55-63.
- 4 18. Wang S, Boyjoo Y, Choueib A, Zhu ZH. Removal of dyes from aqueous solution using fly
5 ash and red mud. *Water Res.* 2005;39:129-138.
- 6 19. Komnitsas K, Bartzas G, Paspaliaris I. Efficiency of limestone and red mud barriers:
7 Laboratory column studies. *Miner. Eng.* 2004;17:183-194.
- 8 20. Bertocchi AF, Ghiani M, Peretti R, Zucca A. Red mud and fly ash for remediation of mine
9 sites contaminated with As, Cd, Cu, Pb and Zn. *J. Hazard. Mater.* 2006;134:112-119.
- 10 21. Tsakiridis PE, Agatzini-Leonardou S, Oustadakis P. Red mud addition in the raw meal for
11 the production of Portland cement clinker. *J. Hazard. Mater.* 2004;116:103-110.
- 12 22. Li P, Miser DE, Rabiei S, Yadav RT, Hajaligol MR. The removal of carbon monoxide by
13 iron oxide nanoparticles. *Appl. Catal. B Environ.* 2003;43:151-162.
- 14 23. Yalçın N, Sevinç V. Utilization of bauxite waste in ceramic glazes. *Ceram. Int.* 2000;26:485-
15 493.
- 16 24. Sglavo VM, Campostrini R, Maurina S, et al. Bauxite "red mud" in the ceramic industry. Part
17 1: thermal behaviour. *J. Eur. Ceram. Soc.* 2000;20:235-244.
- 18 25. Jústiz-Smith N, Buchanan VE, Oliver G. The potential application of red mud in the
19 production of castings. *Mater. Sci. Eng. A.* 2006;420:250-253.
- 20 26. Collazo A, Fernández D, Izquierdo M, Nóvoa XR, Pérez C. Evaluation of red mud as surface
21 treatment for carbon steel prior painting. *Prog. Org. Coatings.* 2005;52:351-358.
- 22 27. Kurtoğlu SF, Soyer-Uzun S, Uzun A. Tuning structural characteristics of red mud by simple

- 1 treatments. *Ceram. Int.* 2016;42:17581-17593.
- 2 28. Huang W, Wang S, Zhu Z, et al. Phosphate removal from wastewater using red mud. *J.*
3 *Hazard. Mater.* 2008;158:35-42.
- 4 29. Liang W, Couperthwaite SJ, Kaur G, Yan C, Johnstone DW, Millar GJ. Effect of strong
5 acids on red mud structural and fluoride adsorption properties. *J. Colloid. Interface. Sci.*
6 2014;423:158-165.
- 7 30. Santona L, Castaldi P, Melis P. Evaluation of the interaction mechanisms between red muds
8 and heavy metals. *J. Hazard. Mater.* 2006;136:324-329.
- 9 31. Liu Y, Lin C, Wu Y. Characterization of red mud derived from a combined Bayer Process
10 and bauxite calcination method. *J. Hazard. Mater.* 2007;146:255-261.
- 11 32. Palmer SJ, Nothling M, Bakon KH, Frost RL. Thermally activated seawater neutralised red
12 mud used for the removal of arsenate, vanadate and molybdate from aqueous solutions. *J.*
13 *Colloid. Interface. Sci.* 2010;342:147-154.
- 14 33. Sahu RC, Patel RK, Ray BC. Neutralization of red mud using CO₂ sequestration cycle. *J.*
15 *Hazard. Mater.* 2010;179:28-34.
- 16 34. Altundoan HS, Altundoan S, Tümen F, Bildik M. Arsenic adsorption from aqueous solutions
17 by activated red mud. *Waste Manag.* 2002;22:357-363.
- 18 35. Genç H, Tjell JC, McConchie D, Schuiling O. Adsorption of arsenate from water using
19 neutralized red mud. *J. Colloid. Interface. Sci.* 2003;264:327-334.
- 20 36. Li Y, Liu C, Luan Z, et al. Phosphate removal from aqueous solutions using raw and
21 activated red mud and fly ash. *J. Hazard. Mater.* 2006;137:374-383.
- 22 37. Liu CJ, Li YZ, Luan ZK, Chen ZY, Zhang ZG, Jia ZP. Adsorption removal of phosphate

- 1 from aqueous solution by active red mud. *J Environ Sci.* 2007;19:1166-1170.
- 2 38. Tor A, Cengeloglu Y. Removal of congo red from aqueous solution by adsorption onto acid
3 activated red mud. *J. Hazard. Mater.* 2006;138:409-415.
- 4 39. Zhang L, Zhang H, Guo W, Tian Y. Removal of malachite green and crystal violet cationic
5 dyes from aqueous solution using activated sintering process red mud. *Appl. Clay Sci.* 2014;93-
6 94:85-93.
- 7 40. Tor A, Cengeloglu Y, Aydin ME, Ersoz M. Removal of phenol from aqueous phase by using
8 neutralized red mud. *J. Colloid. Interface. Sci.* 2006;300:498-503.
- 9 41. Zhang S, Liu C, Luan Z, Peng X, Ren H, Wang J. Arsenate removal from aqueous solutions
10 using modified red mud. *J. Hazard. Mater.* 2008;152:486-492.
- 11 42. Han SW, Kim DK, Hwang IG, Bae JH. Development of pellet-type adsorbents for removal
12 of heavy metal ions from aqueous solutions using red mud. *J. Ind. Eng. Chem.* 2002;8:120-125.
- 13 43. Zhao Y, Yue Q, Li Q, Gao B, Han S, Yu H. The regeneration characteristics of various red
14 mud granular adsorbents (RMGA) for phosphate removal using different desorption reagents. *J.*
15 *Hazard. Mater.* 2010;182:309-316.
- 16 44. Zhu C, Luan Z, Wang Y, Shan X. Removal of cadmium from aqueous solutions by
17 adsorption on granular red mud (GRM). *Sep. Purif. Technol.* 2007;57:161-169.
- 18 45. Tor A, Danaoglu N, Arslan G, Cengeloglu Y. Removal of fluoride from water by using
19 granular red mud: Batch and column studies. *J. Hazard. Mater.* 2009;164:271-278.
- 20 46. Gupta VK, Sharma S. Removal of cadmium and zinc from aqueous solutions using red mud.
21 *Environ. Sci. Technol.* 2002;36:3612-3617.
- 22 47. Gupta VK, Suhas, Ali I, Saini VK. Removal of rhodamine B, fast green, and methylene blue

- 1 from wastewater using red mud, an aluminum industry waste. *Ind Eng Chem Res.* 2004;43:1740-
2 1747.
- 3 48. de Souza KC, Antunes MLP, Couperthwaite SJ, da Conceição FT, de Barros TR, Frost R.
4 Adsorption of reactive dye on seawater-neutralised bauxite refinery residue. *J. Colloid. Interface.*
5 *Sci.* 2013;396:210-214.
- 6 49. Altundoğan HS, Tümen F. As(V) removal from aqueous solutions by coagulation with liquid
7 phase of red mud. *J. Environ. Sci. Health A Tox. Hazard. Subst. Environ. Eng.* 2003;38:1247-
8 1258.
- 9 50. Wang Q, Luan Z, Wei N, Li J, Liu C. The color removal of dye wastewater by magnesium
10 chloride/red mud (MRM) from aqueous solution. *J. Hazard. Mater.* 2009;170:690-698.
- 11 51. Orescanin V, Nad K, Mikelic L, Mikulic N, Lulic S. Utilization of bauxite slag for the
12 purification of industrial wastewaters. *Process Saf. Environ. Prot.* 2006;84:265-269.
- 13 52. Poulin É, Blais JF, Mercier G. Transformation of red mud from aluminium industry into a
14 coagulant for wastewater treatment. *Hydrometallurgy.* 2008;92:16-25.
- 15 53. Zhao Y, Zhang LY, Ni F, et al. Evaluation of a novel composite inorganic coagulant
16 prepared by red mud for phosphate removal. *Desalination.* 2011;273:414-420.
- 17 54. Lu R, Zhang Y, Zhou F, Wang X, An Q, Meng Z. Novel polyaluminum ferric chloride
18 composite coagulant from Bayer red mud for wastewater treatment. *Desalin. Water Treat.*
19 2014;52:7645-7653.
- 20 55. Ni F, He J, Wang Y, Luan Z. Preparation and characterization of a cost-effective red
21 mud/polyaluminum chloride composite coagulant for enhanced phosphate removal from aqueous
22 solutions. *J. Water Process. Eng.* 2015;6:158-165.

- 1 56. Vaclavikova M, Misaelides P, Gallios G, Jakabskya S, Hredzaka S. Removal of cadmium,
2 zinc, copper and lead by red mud, an iron oxides containing hydrometallurgical waste. *Stud Surf*
3 *Sci Catal.* 2005;155:517-525.
- 4 57. Sanchez TR, Perzanowski M, Graziano JH. Inorganic arsenic and respiratory health, from
5 early life exposure to sex-specific effects: A systematic review. *Environ. Res.* 2016;147:537-555.
- 6 58. Schlebusch CM, Gattepaille LM, Engström K, Vahter M, Jakobsson M, Broberg K. Human
7 adaptation to arsenic-rich environments. *Mol. Biol. Evol.* 2015;32:1544-1555.
- 8 59. Benramdane L, Accominotti M, Fanton L, Malicier D, Vallon JJ. Arsenic speciation in
9 human organs following fatal arsenic trioxide poisoning-a case report. *Clin. Chem.* 1999;45:301-
10 306.
- 11 60. Altundoğan HS, Altundoğan S, Tümen F, Bildik M. Arsenic Removal from Aqueous
12 Solutions by Adsorption on Red Mud. *Waste Manag.* 2000;20:761-767.
- 13 61. Rubinos DA, Arias M, Dáz-Fierros F, Barral MT. Speciation of adsorbed arsenic(V) on red
14 mud using a sequential extraction procedure. *Mineral Mag.* 2005;69:591-600.
- 15 62. Cengeloglu Y, Tor A, Arslan G, Ersoz M, Gezgin S. Removal of boron from aqueous
16 solution by using neutralized red mud. *J. Hazard. Mater.* 2007;142:412-417.
- 17 63. H. Genc-Fuhrman, PhD Thesis, Environment & Resources DTU Technical University of
18 Denmark, Denmark, 2004
- 19 64. L. Sigg, in: W. Stumm (Ed.), Aquatic Surface Chemistry, Chemical Processes at the Particle
20 Water-Interface, Wiley, New York, 1987, p. 325.
- 21 65. Yue Q, Zhao Y, Li Q, et al. Research on the characteristics of red mud granular adsorbents
22 (RMGA) for phosphate removal. *J. Hazard. Mater.* 2010;176:741-748.

- 1 66. Zhao Y, Yue Q, Li Q, et al. Characterization of red mud granular adsorbent (RMGA) and its
2 performance on phosphate removal from aqueous solution. *Chem. Eng. J.* 2012;193-194:161-168.
- 3 67. Cengeloglu Y, Tor A, Ersoz M, Arslan G. Removal of nitrate from aqueous solution by using
4 red mud. *Sep. Purif. Technol.* 2006;51:374-378.
- 5 68. Carneiro PA, Umbuzeiro GA, Oliveira DP, Zanoni MVB. Assessment of water
6 contamination caused by a mutagenic textile effluent/dyehouse effluent bearing disperse dyes. *J.*
7 *Hazard. Mater.* 2010;174:694-699.
- 8 69. Ratnamala GM, Shetty KV. Removal of Remazol Brilliant Blue Dye from Dye-
9 Contaminated Water by Adsorption Using Red Mud : Equilibrium, Kinetic, and Thermodynamic
10 Studies. *Water Air Soil Pollut.* 2012;223:6187-6199.
- 11 70. Le TQX, Wang H, Ju S, Peng J, Zhou L, Dai L. Column absorption and regeneration
12 behavior of a granular red mud for treating wastewater containing methylene blue. *Desalin.*
13 *Water Treat.* 2016;57:728-737.
- 14 71. de Jesus CPC, Antunes MLP, da Conceição FT, Navarro GRB, Moruzzi RB. Removal of
15 reactive dye from aqueous solution using thermally treated red mud. *Desalin. Water Treat.*
16 2015;55:1040-1047.
- 17 72. Tor A, Cengeloglu Y, Ersoz M. Increasing the phenol adsorption capacity of neutralized red
18 mud by application of acid activation procedure. *Desalination.* 2009;242:19-28.
- 19 73. Gupta VK, Ali I, Saini VK. Removal of chlorophenols from wastewater using red mud: An
20 aluminum industry waste. *Environ. Sci. Technol.* 2004;38:4012-4018.
- 21 74. Pratt KC, Christoverson V. Hydrogenation of a model hydrogen-donor system using
22 activated red mud catalyst. *Fuel.* 1982;61:460-462.

- 1 75. Paredes JR, Ordóñez S, Vega A, Déz FV. Catalytic combustion of methane over red mud-
2 based catalysts. *Appl. Catal. B Environ.* 2004;47:37-45.
- 3 76. Kim SC, Nahm SW, Park Y-K. Property and performance of red mud-based catalysts for the
4 complete oxidation of volatile organic compounds. *J. Hazard. Mater.* 2015;300:104-113.
- 5 77. Pei FN, Li L, Wang S, Zhu Z, Lu G, Yan Z. Catalytic ammonia decomposition over
6 industrial-waste-supported Ru catalysts. *Environ. Sci. Technol.* 2007;41:3758-3762.
- 7 78. Sawant AB, Kumthekar MB, Sawant SG, Mud AR. Utilization of Neutralized Red Mud
8 (Industrial Waste) in Concrete. *Int. J. Inven. Eng. Sci.* 2013;1:9-13.
- 9 79. Manfroi EP, Cheriaf M, Rocha JC. Microstructure, mineralogy and environmental evaluation
10 of cementitious composites produced with red mud waste. *Constr. Build Mater.* 2014;67:29-36.
- 11 80. Somlai J, Jobbágy V, Kovács J, Tarján S, Kovács T. Radiological aspects of the usability of
12 red mud as building material additive. *J. Hazard. Mater.* 2008;150:541-545.
- 13 81. Sas Z, Somlai J, Szeiler G, Kovács T. Usability of clay mixed red mud in Hungarian building
14 material production industry. *J. Radioanal Nucl. Chem.* 2015;306:271-275.
- 15 82. Liu X, Zhang N, Sun H, Zhang J, Li L. Structural investigation relating to the cementitious
16 activity of bauxite residue - Red mud. *Cem. Concr. Res.* 2011;41:847-853.
- 17 83. Linora Metilda D, Selvamony C, Anandakumar R, Seeni A. Experimental investigation on
18 optimum possibility of replacing cement by redmud. *Int. J. Appl. Eng. Res.* 2015;10:4569-4578.
- 19 84. Pan Z, Cheng L, Lu Y, Yang N. Hydration products of alkali-activated slag-red mud
20 cementitious material. *Cem Concr Res.* 2002;32:357-362.
- 21 85. Kumar A, Kumar S. Development of paving blocks from synergistic use of red mud and fly
22 ash. *Constr. Build. Mater.* 2013;38:865-871.