



# A review on the potential uses of red mud as amendment for pollution control in environmental media

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## Abstract

Red mud is a solid waste of bauxite processing by Bayer process which involves caustic digestion of Al-containing mineral for alumina production. The global inventory of red mud waste reached an estimated amount of 4 billion tons in 2015, increasing at an approximate rate of 120 million tons per year. Therefore, its management is becoming a global environmental issue for the protection of environment, and the need for awareness in this regard is becoming crucial. Although red mud is not considered as a hazardous material in many countries, its high alkalinity and fine particle size may pose significant environmental threat, and it is found to be an interesting material for environmental remediation purposes due to rich iron content. This paper provides a review of possible remedial applications of red mud in various environmental compartments. Modification of red mud creates novel opportunities for cost-effective and efficient removal of metal ions, inorganic anions, dyes, and phenols from wastewater and acid mine drainage. Re-vegetation of red mud disposal sites, treatment of metal-contaminated acidic soils presents the usefulness of this material but less research has been done so far to investigate its use in the stabilization of polluted sediments. On the other hand, leaching and eco-toxicological tests have also revealed that red mud does not pose high toxicity to the environment making it suitable for the treatment of contaminated media. Nevertheless, neutralization of red mud is recommended for its safe disposal and secure application in any environmental media.

**Keywords** Red mud · Neutralization · Low-cost adsorbent · Heavy metals · Environment · Ecotoxicity

## Introduction

Metallurgy industry is one of the important industries in the world. It produces metals and metal alloys using ores and metallic scraps as raw materials. Extraction of metals from ores and metallic scrap generates large amounts of gaseous, liquid, and solid by-products (Panias et al. 2001). Global production of aluminum, iron, copper, and zinc generates

approximately 2000 megatons of by-products annually. Therefore, metallurgy industry is regarded as one of the major contributors in the generation of solid by-products. By-products generated during the extraction of metals are of little or no economic value depending on their composition and can be classified as hazardous or non-hazardous depending upon the leaching of constituents from them into environmental media. According to the decision about industrial by-product management, the characterization of solid by-products according to globally accepted protocols and regulations is mandatory. Hence, solid by-product valorization and further scientific advances are indispensable for their utilization in various applications (Kumar et al. 2006; Panias et al. 2001; Siddique 2014; Zheng and Kozinsk 1996).

Alumina industry generates huge quantities of waste red mud, i.e., 1–1.5 tons of red mud per ton of alumina (Genç et al. 2003). Over the last few decades, many efforts have been made to find the cost-effective and sustainable solutions for by-product minimization and utilization such as re-use or recycling has the potential to reduce the risk of environmental pollution and space for disposal (Bandopadhyay et al. 2002;

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Siddique 2014). In the present article, we attempt to present a review of the uses of an alumina industry by-product called red mud (RM), focusing on the different treatments applied to red mud to make it suitable for specific re-use, its applications for treatment of contaminated water, soil and sediment with regards to the contaminant types, and finally the ecotoxicity investigations.

## Properties of by-product from alumina extraction industry

Alumina is industrially extracted from bauxite ore by applying Bayer process. This process consists in digestion of bauxite mineral with concentrated sodium hydroxide under high temperature and pressure conditions which results in the dissolution of aluminum oxide and generation of solid residue. After separation from residue (by settling and/or precipitation), aluminum trihydroxide ( $\text{Al}(\text{OH})_3$ ) is precipitated by cooling and seeding the solution. Then, it is washed and calcinated to get pure aluminum. Extraction residue is commonly called red mud (RM) due to its specific reddish brown color. Application of Bayer process to bauxite produces from 0.3 to 2.5 tons of red mud per ton of alumina, depending on the quality of ore (Power et al. 2011; Wang et al. 2008). Red mud generation is comparatively high to other metallurgical wastes (i.e., 1 ton pig iron produces 300–400 kg of slag), and therefore, its global inventory approaches to 4 billion tons in 2015 (Kumar et al. 2006; Power et al. 2011). Red mud is a highly alkaline material (pH 10–13), with 90% of particles having a size below 75  $\mu\text{m}$  and a specific surface area (BET) between 10 and 25  $\text{m}^2/\text{g}$  (Nadaroglu et al. 2010). Physical, chemical, and mineralogical properties of red mud are dependent on the bauxite ore source and refining process (Table 1). The main mineralogical fractions present in red mud are hematite ( $\text{Fe}_2\text{O}_3$ ), goethite ( $\alpha\text{-FeOOH}$ ), boehmite ( $\gamma\text{-AlOOH}$ ), quartz ( $\text{SiO}_2$ ), titania ( $\text{TiO}_2$ ), sodalite ( $\text{Na}_4\text{Al}_3\text{Si}_3\text{O}_{12}\text{Cl}$ ), and gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ), with a minor presence of calcite ( $\text{CaCO}_3$ ), whewellite ( $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ ), gibbsite ( $\text{Al}(\text{OH})_3$ ), and minor constituents like Na, K, Cr, V, Ni, Ba, Cu, Mn, and Zn (Brunori et al. 2005; Genç et al. 2003; Liu et al. 2011; Palmer et al. 2009; Snars and Gilkes 2009; Wang et al. 2008).

Considering the legislative requirements of by-product management, alumina industries are facing a challenging environmental issue. Until 1980s, sea dumping and lagooning were considered as the major options for red mud disposal; later on, dry stacking and dry cake stacking was preferred because it can reduce potential leakage to groundwater and land use. However, certain limitations are associated with this

method such as significant compaction density limit vegetation and as it is difficult to apply in areas of high rainfall and low evaporation. While land-based disposal in lagoons is favored even for refineries on the seaboard in case of North America (Power et al. 2011), sea dumping has been practiced in France, UK, Germany, Greece, and Japan, but it is stopped in France in 2015 due to a national regulation (article 4.5 of the decree of 24 May 1994). Now, red mud is adequately stored on land in the industrial site area (Mange Garri Basin) which is large enough to store it for 6 years (Dauvin 2010). Ajka (Hungary) disaster revealed that some red mud suspensions could be really irritant and corrosive (hazardous properties H4 and H8, respectively, as defined in Directive 2008/98/CE (European Union 2008). However, US Environment Protection Agency (EPA) evaluated red mud in terms of four hazardous waste characteristics including corrosivity, reactivity, ignitability, and extraction procedure (EP) toxicity. All the EP constituents (except selenium) were below EPA regulatory levels and the red mud was classified as non-hazardous (US EPA 1984; US EPA 1990). In numerous other jurisdictions (USA, Canada, and the EU), red mud has been characterized as non-hazardous waste (European Commission 2000; Klauber et al. 2011).

Despite its high alkalinity, red mud appears to be an interesting material due to its mineralogical composition, particularly its high proportion of hematite and, goethite. Investigations on single minerals have shown that hematite surface sites are able to form strong surface complexes with toxic trace elements such as As and Cd (Giménez et al. 2007; Jiang et al. 2013; Mamindy-Pajany et al. 2009). In line with previous studies on single minerals, red mud has been investigated for toxic metal removal from aqueous and solid environmental media (Brunori et al. 2005; Lombi et al. 2002b; Nadaroglu et al. 2010), but highly alkalinity limits its direct use and pre-treatment is often necessary. After pH neutralization, red mud can be used for various remediation purposes (Wang et al. 2008).

## Neutralization of red mud

Adequate neutralization of red mud can decrease its negative impacts on the environment and provide better material for various applications. A range of methods have been used for neutralization such as acid treatment (neutralization or activation), thermal activation, washing with seawater or saline brines, addition of gypsum or phosphogypsum,  $\text{CO}_2$  sequestration, microbial neutralization, and a combination of some of these treatments. The objectives of neutralization include (i) to lower the initial pH of the material, (ii) to increase the surface area, and (iii) to provoke neo-formed phases (Genç-Fuhrman et al. 2004a; Krishna et al. 2005; Lopes et al. 2013; Sahu et al. 2013; Sahu et al. 2010; Santona et al. 2006).

**Table 1** Major constituents (%wt), pH, EC, and SSA of bauxite residue generated in different parts of the world

Country	Plant	Fe <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub>	SiO <sub>2</sub>	Na <sub>2</sub> O	CaO	pH	EC (mS/cm)	S <sub>BET</sub> (m <sup>2</sup> /g)	Ref
Australia	AICOAKwinana	28.5	24.0	3.11	18.8	3.4	5.26	11.45	2.98	28	(Snars and Gilkes 2009)
	AICOAPinjarra	31.7	18.8	3.17	20.2	4.2	4.44	11.63	6.09	25	
	AICOAWagerup	29.6	17.3	2.65	30.0	3.2	3.64	11.99	2.69	24	
	AICOAWorsley	56.9	15.6	4.46	3.0	2.2	2.39	12.56	6.28	25	
	Nabalco	34.8	23.2	8.03	9.2	7.1	2.25	12.44	10.75	29	
	QAL	30.7	18.6	7.01	16.0	8.6	2.51	10.22	8.15	29	
	QAL (Bauxsol)	34.05	25.45	4.90	17.06	2.74	3.69	10.00	-	30	
USA	Reynolds Metal Company	35.5	18.4	6.31	8.5	6.1	7.73	11.04	3.59	27	(Snars and Gilkes 2009)
China	Shandong Aluminum Industry Co., Ltd	21	12	1.4	9.4	7.0	3.0	10.8	-	21.6	(Luo et al. 2011)
France	ALTEO Gardanne Bauxaline®	14	50	11.5	6	3.5	5.5	10.60	0.919	23.06	(Taneez et al. 2015)
Turkey	Seydisehir Aluminum Plant	35.04	20.20	4.0	17.29	9.40	5.30	12–13	-	10–25	(Nadaroglu et al. 2010)
India	NALCO	54	13	3.5	7	8	-	11.8	-	31.7	(Sahu et al. 2010)
Brazil	Alunorte	45.6	15.1	4.29	15.6	7.5	1.16	12.21	3.26	15	(Snars and Gilkes 2009)
Germany	Aluminium Oxid Stade GmbH	44.8	16.2	12.3	5.4	4.0	5.22	12.08	2.57	23	(Snars and Gilkes 2009)
Spain	Alcoa	37.5	21.2	11.4	4.4	3.6	5.51	12.58	2.34	21	(Snars and Gilkes 2009)
Italy	Eurallumina, Sardinia	30.35	9.65	4.13	4.32	5.17	1.04	11.1	8.70	19.5	(Garau et al. 2011)

### Acid treatment (neutralization or activation)

Commonly three mineral acids (HCl, HNO<sub>3</sub>, and H<sub>2</sub>SO<sub>4</sub>) are used for neutralization. This treatment eliminates alkali metals, impurities (inorganic or organic), and provokes neo-formed surfaces (Apak et al. 1998; Kirwan et al. 2013). The treatment of red mud with acid can be carried out by two ways: (i) refluxing of red mud sample with solution of acid (0.1–1.0 M) followed by cooling at room temperature and addition of liquor ammonia till complete precipitation. Then, the precipitates were washed with deionized water and dried at 110 °C (Genç-Fuhrman et al. 2004a; Pradhan et al. 1998) and (ii) red mud sample treatment with solution of mineral acid (0.1–1.0 M), washing of residue with deionized water and drying at 100 °C. The reflux time varies from 1 to 2 h in both cases (Altundoğan et al. 2002; Altundoğan and Tümen 2003; Apak et al. 1998). Treatment of red mud with concentrated solutions of acids (0.5 M) (hydrochloric, nitric, and sulfuric acid) caused the dissolution of sodalite and cancrinite, which increased the availability of metal oxide/hydroxide sites. In addition, it also transformed the surface site ≡SOH/≡SO<sup>-</sup> to ≡SOH<sup>+</sup><sub>2</sub> of oxide/hydroxide component of red mud due to protonation. However, sudden changes in pH should be controlled to avoid dissolution of iron and aluminum oxide/hydroxide sites (Liang et al. 2014). The time taken to attain equilibrium pH depends on the degree of dissolution of solid-phase alkalinity (calcium hydroxides, carbonates, and aluminates, such as tricalcium aluminate- (Ca<sub>3</sub>Al<sub>2</sub>(OH)<sub>12</sub>) and the quantity of acid added. For example, the equilibrium reaction

of 5 g of RM slurry (40% solid by weigh) with continuous addition of acid (0.02 N HCl) with 5 min interval to attain a pH of 8 took approximately 50 days and higher acid neutralization capacity (ANC) of 1.8 mEq/g RM under slow titration compared to rapid neutralization of total time 60 min and ANC of 1.2 mEq/g RM. Larger ANC value suggests that the solid dissolution occurs with time and so rapid titration did not capture all of ANC of RM (Khaitan et al. 2009). This is a relatively expensive treatment since large volumes of reagents are required to fully neutralize the red mud and it can increase the amount of impurities to the process water stream (e.g., sulfate in the case of sulfuric acid, chloride in the case of hydrochloric acid). Therefore, reuse of any water from the residue deposits to the production process will be unacceptable without treatment (Apak et al. 1998; Kirwan et al. 2013).

### Thermal activation

Red mud is thoroughly washed with deionized water and heated at various temperatures such as 200, 500, 600, 700, 800, 900, and 1000 °C in an electrical furnace for different time durations (1–3 h). Thermal treatment destroys organic and unstable compounds and excludes water from mineral phases (Altundoğan et al. 2002; Li et al. 2006; Smiljanić et al. 2011). The main crystalline phase in XRD analysis was found to be hematite (Fe<sub>2</sub>O<sub>3</sub>), whereas gibbsite and bayerite (Al(OH)<sub>3</sub>) were identified as Al-bearing minerals. In addition, to the peaks of sodalite (Na<sub>8</sub>Si<sub>6</sub>Al<sub>6</sub>O<sub>24</sub>Cl<sub>2</sub>), calcite (CaCO<sub>3</sub>), and quartz (SiO<sub>2</sub>), TiO<sub>2</sub> was present in the forms of

anatase and rutile. In the investigated temperature range quartz, hematite and rutile were not affected by the heating process. However, improved hematite crystallinity with an increased temperature (i.e., above 600 °C) was clearly observed. An increase in surface area and porosity of red mud due to water exclusion at 500 °C was observed but adsorption efficiency decreased at above 700 °C due to sintering shrinkage of materials (Genç-Fuhrman et al. 2004b; Li et al. 2006; Smiljanić et al. 2011).

### Seawater neutralization

Washing with seawater for neutralization is widely used in recent years. Seawater neutralization significantly facilitates reduction in pH of red mud without altering the acid neutralization capacity of the material. This treatment involves the use of soluble calcium and magnesium ions from seawater to neutralize red mud through the precipitation of hydrotalcite-like compounds and other Mg, Ca, and Al hydroxides and carbonate minerals. An increased use of seawater can reduce pH (8.5–8.8) and improve surface area of red mud to approximately 30–31 m<sup>2</sup>/g (Genç et al. 2003; Hanahan et al. 2004; Palmer et al. 2009; Rai et al. 2013).

### Gypsum neutralization

Red mud can be neutralized using a soluble calcium source such as gypsum. Gypsum addition at the rate of 5% to 8% favored the precipitation of hydroxyl, hydroxoaluminate, and carbonate ions as Ca(OH)<sub>2</sub>, tricalcium aluminate (TCA), hydrocalumite, and CaCO<sub>3</sub>. Red mud pH was reduced consequently to 8.6 (Burke et al. 2013; Gräfe et al. 2011; Kirwan et al. 2013). However, electrical conductivity (EC) increased due to soluble reaction product (like Na<sub>2</sub>SO<sub>4</sub>) but under adequate drainage conditions, salinity can be reduced using water that has lower salinity (Gräfe et al. 2011). Gypsum application demonstrates a positive effect on red mud re-vegetation and can be applied as a self-sustaining re-vegetation technique in the field (Courtney and Timpson 2005; Wong and Ho 1993).

### CO<sub>2</sub> neutralization

The reaction of red mud with CO<sub>2</sub> results in carbonation of the alkaline components of the liquid phase. It involves bubbling of CO<sub>2</sub> through red mud slurry and generates carbonic acid which rapidly reacts with alkaline components of slurry and decreases the pH but it soon rises again due to additional leaching of alkaline material from red mud (Kirwan et al. 2013). The pH of liquid slurry depends on the relative concentration of carbonate species which in turn depends on the partial pressure of CO<sub>2</sub>. At sufficiently low pH under high pCO<sub>2</sub>, solid forms of alkalinity will also react if kept in contact for longer time. Most of the literature regarding carbonation

and reactivity of solid-phase alkalinity has focused on the reactivity of TCA. The reaction of TCA with carbon dioxide leads to the formation of calcite and amorphous aluminum hydroxide and the kinetics of the solid-phase reaction is very slow (Smith et al. 2003). After CO<sub>2</sub> sequestration the intensity of gibbsite was increased prominently and ilmenite (FeTiO<sub>3</sub>) was formed due to dissolution of minerals (Sahu et al. 2010).

### Combined treatments

Combined treatments such as acidification and calcination are frequently used to improve material efficiency for remediation purposes. For example, seawater neutralized red mud (Bauxsol™) was subjected to (i) acidification with HCl, (ii) combined acid-thermal treatment, and then it was treated with ferric sulfate and aluminum sulfate. These treatments enhanced the surface area of material to 130 m<sup>2</sup>/g compared to the initial Bauxsol™ which was 30 m<sup>2</sup>/g (Genç-Fuhrman et al. 2004b). XRD peaks confirm the following mineral phases: hematite (α-Fe<sub>2</sub>O<sub>3</sub>), goethite (α-FeO(OH)), gibbsite (γ-Al(OH)<sub>3</sub>), calcite (CaCO<sub>3</sub>), rutile/anatase (TiO<sub>2</sub>), and quartz (SiO<sub>2</sub>) (Altundoğan et al. 2002; Altundoğan and Tümen 2003; Gupta and Sharma 2002; Sahu et al. 2013).

Further modifications can also be applied to improve the stability and adsorption capacity of red mud including sand coating, granulation and pellet making (Genç-Fuhrman et al. 2007; Han et al. 2002; Zhu et al. 2007). Other reagents used for red mud modification include FeCl<sub>3</sub> and Cetyltrimethyl ammonium bromide (CTAB) (Li et al. 2015; Zhang et al. 2008). Carbonized red mud produced by heating red mud sample from room temperature at a rate of 10 °C/min under a 20 mL/min flow of CH<sub>4</sub> which results in magnetic material of greater surface area (Pulford et al. 2012). H<sub>2</sub>-controlled reduction of red mud at 500–600 °C produces Fe<sup>0</sup>, and thermally stable oxy/hydroxides of Al, Si, and Ti. These oxides support the reactivity of Fe<sup>0</sup> (Costa et al. 2010). Zirconium hydroxide modified red mud porous material (Zr-modified RMPM) was prepared according to the method explained by Lv et al. (2013). Zr(OH)<sub>4</sub> precipitates could coat to the surface of the RMPM and the resulting adsorbent has potential for deflouridation (Lv et al. 2013).

### Microbial neutralization

Few researchers investigated this mode of neutralization despite significant results. This treatment efficiently reduced the pH of red mud (by 2–3 units) and helps to promoting plant growth. For neutralization, bacteria (*Bacillus*, *Lactobacillus*, *Leuconostoc*, *Micricoccus*, *Staphylococcus*, *Pseudomonas*, *Flavobacterium*, and *Endobacter*) and fungi (*Aspergillus tubingensis*) are used (Hamdy and Williams 2001; Krishna et al. 2005). The exact mechanism of microbial neutralization reaction is not fully understood but it is assumed to be a

combination of organic acids released by the microbes and a diffusion of the respiratory gasses into solution (Hamdy and Williams 2001). Microbial neutralization can be considered significant in following aspects:

- (a) Neutralization is continuously controlled by microorganisms.
- (b) Buffering of pH (drops from 13.0 to 6.0–7.0) by microbes is more efficient than buffering chemically controlled as long as nutrients are provided to microbes.
- (c) Presence of microbes improved bulk structure of solid, which improves drainage, nutrient exchange, and the chances for establishing a plant cover.
- (d) Microbes are intrinsic part of functioning rhizospheres of plants covering mine and residue spoils (Gräfe et al. 2011; Hamdy and Williams 2001; Krishna et al. 2005; Vachon et al. 1994).

## Applications of red mud

Red mud has various applications, and the most interesting is in the field of environmental pollution research, i.e., decontamination of wastewater, soil, and sediments.

## Water remediation

Agricultural runoff, industrial, and sewage effluents are the main sources of pollutant discharge in waterways. These pollutants include toxic heavy metals, inorganic anions, metalloids as well as organic compounds such as dyes and phenolic compounds (Bhatnagar et al. 2011). Direct discharge of these pollutants into the environment has toxic effects on humans, animals, and plants. Various techniques are used for water treatment, and among them, adsorption is widely employed due to its cost effectiveness (Wang et al. 2008). Activated carbon has been recognized by US Environmental Protection Agency as one of the best adsorbent for the removal of different pollutants (Derbyshire et al. 2001). However, high cost associated with the production and regeneration of activated carbon has necessitated the search for alternative inexpensive adsorbents (Crini 2006; McKay et al. 1999). In the past decade, researchers have attempted to valorize the use of industrial by-products in pollution treatment. Such as red mud, an industrial by-product has been largely studied as a low cost adsorbent due to its fine granulometry, high porosity, and iron oxide richness. Removal capacities of bauxite residues for various pollutants (trace elements, anions, dyes, and phenolic compounds) present in waste water are discussed in the following section.

## Removal of metal ions

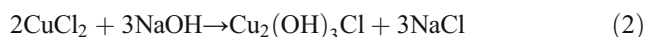
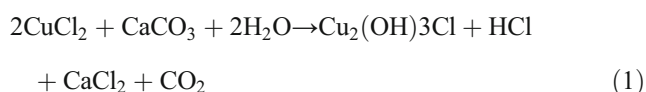
Heavy metal, metalloids, and anionic species are unambiguous in nature and cause harmful effects on humans, animals, and plants (Huang et al. 2010). Mining, metal plating, tanneries, paper and pulp, and petroleum industries are the main sources of water pollution (Wang et al. 2008). Several studies have shown that red mud can be an effective adsorbent for wastewater treatment as it has significant adsorption properties for trace metals. High pH of red mud also facilitates in the adsorption by surface precipitation. General influential factors during adsorption process include pH, adsorbent dosage, contact time, initial concentration of contaminant, and the existence of other ions.

**Nickel (Ni)** Despite the fact that wastewaters contain Ni ions in addition to other cations and anions, only a few researchers investigated the sorption of Ni ions onto red mud. Red mud addition to aqueous synthetic solution of Ni caused precipitation of nickel as insoluble hydroxide with simultaneous adsorption of nickel hydroxide and aiding the flocculation/sedimentation of the resultant fine particulate matter (Zouboulis and Kydros 1993). Red mud treatment with gypsum (8%), washing, acid neutralization (HCl, 0.05–1.0 M), and thermal treatment improved Ni uptake (i.e., 20% higher than inactivated rinsed red mud). The lower amount of Ni uptake was observed in acidic media which is attributed to progressive dissolution of RM components, as well as due to  $H^+$  ion competition with  $Ni^{2+}$  for sorption sites. However, higher  $Ni^{2+}$  removal was observed at pH 4–7 due to the negative surface charge of the adsorbent (López et al. 1998; Smiljanić et al. 2010). The adsorption kinetic was short (< 24 h), and isotherms followed Langmuir model. Low reversibility of adsorption process showed that Ni is tightly bound to treated red mud surface permitting its safe disposal or reuse (Smičiklas et al. 2014; Zouboulis and Kydros 1993). Coexisting divalent cations inhibit the sorption process of Ni in the following order  $Cu > Pb \geq Zn > Cd \gg Ca$  while monovalent cations (Na and K) had no influence. Fluoride ions slightly improve sorption which means that fluoride neither forms sufficiently stable complex with aqueous Ni, nor exhibits sorption affinity for red mud surface higher than Ni. Reduction of the positive surface charge after sorption of negative anions such as  $F^-$  may result in a more attractive surface for Ni sorption. Organic and inorganic anions decreased Ni ions removal in the order of  $EDTA > chromate > acetate > sulfate$ . In addition, the presence of citrate anion decreased the retention of Ni on raw red mud due to its competition for adsorption sites (Smičiklas et al. 2014; Smiljanić et al. 2010; Smiljanić et al. 2011).

**Cadmium (Cd)** The cadmium sorption on red mud is highly pH dependent having optimum removal in the neutral pH (6.5–

7.5) range while cadmium hydroxide precipitation occurs at pH 8.0 (Khan et al. 2015; Vaclavikova et al. 2005). Therefore, it is suspected that precipitation is the removal mechanism instead of sorption at basic pH values (Genç-Fuhrman et al. 2007). In batch studies, satisfactory Cd removal was obtained on non-treated red mud (Ma et al. 2009; Santona et al. 2006; Vaclavikova et al. 2005), while acid treatment decreased the capacity of red mud to adsorb metal ions attributed to the dissolution of cancrinite or other zeolite-type compounds in red mud functioning as adsorption sites (Apak et al. 1998; Santona et al. 2006). However, several studies reported enhanced adsorption rate by acid neutralization or combined treatments such as thermal, gypsum (8%), and formulations (granulation, ball milling, red mud pellets, etc) (Genç-Fuhrman et al. 2007; Gupta and Sharma 2002; Han et al. 2002; Ju et al. 2012; Khan et al. 2015; López et al. 1998; Luo et al. 2011; Zhu et al. 2007). Furthermore, the decrease in adsorption with the increasing temperature shows that adsorption process is exothermic. The optimum temperature for adsorption is the room temperature and the adsorption isotherms were correlated well with Langmuir and Freundlich models (Apak et al. 1998; Gupta and Sharma 2002; Khan et al. 2015; Santona et al. 2006; Vaclavikova et al. 2005; Zhu et al. 2007). Regeneration of spent adsorbent is possible with 1% HNO<sub>3</sub> and saturation of adsorbent in the presence of other cationic pollutants sometimes mobilized the previously retained Cd (Ma et al. 2009).

**Copper (Cu)** Red mud has great retention capacity for Cu compared to other cations (Zn and Cd) due to the formation of atacamite (Cu<sub>2</sub>Cl(OH)<sub>3</sub>) due to NaOH and CaCO<sub>3</sub> content present in red mud (Ma et al. 2009; Vaclavikova et al. 2005).



Favorable removal of Cu can be achieved at pH 5.5 whereas precipitation of Cu at high pH was due to increase in hydroxyl ion in the solution (Agrawal et al. 2004; Apak et al. 1998; Grudić et al. 2013; Han et al. 2002; López et al. 1998; Nadaroglu et al. 2010). There is an approximate ten-fold increase in the removal of Cu by carbonized red mud compared to acidified red mud (Pulford et al. 2012). The adsorption isotherms best fit with Langmuir model (Apak et al. 1998; López et al. 1998; Nadaroglu et al. 2010; Pulford et al. 2012). Red mud loaded with Cu can be treated with cement to form durable concrete mass for its safe disposal (Apak et al. 1998).

**Lead (Pb)** Heterogeneous nature of red mud and combined treatments or formulation makes it an inexpensive choice for

Pb removal from aqueous phase. The zeta potential of adsorbent was found to be 3.1 and the surface has high positive charge density below pH 3.1; the uptake is very low due to electrostatic repulsion. The results suggest that optimum pH for Pb removal is 4.0 because with the increasing pH, the negative charge density on the adsorbent surface increases and thus resulting a sudden change in uptake of Pb (Gupta et al. 2001; Han et al. 2002; Sahu et al. 2013). Carbonization increased removal due to phase transformations and appearance of magnetite, wustite, iron carbide, and iron along with graphite. The Pb adsorption data best fitted with Langmuir model (Apak et al. 1998; Han et al. 2002; Pulford et al. 2012; Santona et al. 2006). Presence of co-existing ions decreased Pb adsorption in the following order: potassium > magnesium > calcium > sodium. The leaching of contaminant was within limits using TCLP test and adsorbent can be easily regenerated under acidic conditions (Sahu et al. 2013; Vaclavikova et al. 2005).

**Zinc (Zn)** Red mud has shown efficient removal capacity for Zn from aqueous media (Ma et al. 2009; Santona et al. 2006; Vaclavikova et al. 2005). Neutralization with acid, gypsum, CO<sub>2</sub>, and heat activation enhanced the retention of Zn was observed at pH 6.0–7.0. High temperature has negative effect on adsorption of Zn (Gupta and Sharma 2002; López et al. 1998; Sahu et al. 2011). Sequential extraction showed that very low amount of Zn is present as water-soluble and exchangeable fraction whereas large fraction of Zn was tightly bound to red mud. It suggests that it is not expected to release readily under natural conditions (Santona et al. 2006). However, saturation of red mud in mixed metal solution (Cu, Cd, Zn) can release previously immobilized Zn in the presence of Cu, which has higher affinity for red mud (Ma et al. 2009).

#### Removal of inorganic anions

**Arsenic (As)** Most common forms of arsenic present in water are inorganic arsenate (As(V)) and arsenite (As(III)). Arsenate oxyanions predominant under oxic conditions (Mohan and Pittman Jr 2007). As(V) removal is favored at highly acidic pH (1.8–3.5) while As(III) is effective in the range of pH 5.8–7.5 (Altundoğan et al. 2000). As(III) is mainly bounded physically and exothermic in nature while As(V) is chemisorbed and endothermic in nature (Altundoğan et al. 2002; Guo et al. 2014). Red mud neutralization with seawater produced a product named Bauxsol™ having pH 8.4–8.8 and a higher surface area. The results indicated that Bauxsol™ had higher affinity for As(V) than As(III) suggests that for a favorable removal, As(III) needs to be oxidized to As(V) (Genç-Fuhrman et al. 2004a; Genç et al. 2003). Bauxsol™ was further subject to combined acid-heat activation and As(V) was 100% adsorbed with or without the presence of competing

ions (phosphates, bicarbonates, sulfates) (Genç-Fuhrman et al. 2004b). Thermally activated seawater neutralized red mud revealed that seawater provokes the precipitation of hydroxalcalites like compounds which in turn facilitates simultaneously the inclusion of arsenate, vanadate, or molybdate anions (Palmer et al. 2009). CO<sub>2</sub> neutralization of RM with thermal activation revealed that the hydroxyl surfaces of Al, Fe, and Ti oxides provides strong adsorption affinity of As (V) by forming inner sphere complexes (Sahu et al. 2010). Addition of acidic waste like phosphogypsum to red mud at an appropriate proportion (RM + 25% phosphogypsum) sorbed 3.5-fold higher arsenic mainly due to presence of Ca<sup>2+</sup> that leads to the formation of ternary complex by altering the charge balance of adsorbent (Lopes et al. 2013). Surface modification with FeCl<sub>3</sub> increased the iron content up to 17.5% and surface area of 192 m<sup>2</sup>/g ultimately improved the adsorption sites for a maximum removal of As(V) (Shuwu and Wenchao 2013; Zhang et al. 2008). Magnetic Fe<sub>3</sub>O<sub>4</sub> nanoparticles were synthesized from red mud to treat As(V) contaminated ground water and the total arsenic concentration from sample could be efficiently reduced up to 99.2% (Akin et al. 2012). Iron-arsenic co-precipitation and arsenic adsorption was obtained by using ferrous based red mud and this treatment was reported to decrease turbidity of water (Li et al. 2010).

In comparison to the Freundlich isotherm model (Akin et al. 2012), the Langmuir isotherm was fitted well with the experimental data (Altundoğan et al. 2002; Genç-Fuhrman et al. 2004a; Genç et al. 2003; Guo et al. 2014; Lopes et al. 2013; Sahu et al. 2010; Zhang et al. 2008). The adsorption of arsenic was increased in the presence of Ca ions as it diminishes the negative charges and forming a metal–arsenate complex or a metal–H<sub>2</sub>O–arsenate complex. The effect of other competitive ions (e.g., bicarbonate and phosphate) had reduced adsorption while nitrate had little effect (Genç-Fuhrman et al. 2004b; Genç et al. 2003; Li et al. 2010; Zhang et al. 2008). The regeneration efficiency of modified red mud was ≈ 92.1% using 0.2 mol/L of NaOH (Zhang et al. 2008).

**Chromium (Cr(VI))** Some researchers have investigated the possibility of using pre-treated red mud for the removal of Cr(VI) from water systems. Only Singh and Singh (2002) used raw red mud in high adsorbent dose (100 g/L) for a complete removal of Cr(VI) from aqueous solution at initial concentration of 10 mg/L at pH 3.0. On the other hand, heat-activated red mud showed better results at pH 2.0 for the same initial concentration of Cr (VI) with 20 g/L of adsorbent dose (Erdem et al. 2004). Acidification, followed by ammonia addition, or heat activation showed that Cr(VI) maximum adsorption was obtained at acidic pH (2.0–3.0) (Gupta et al. 2001; Ma et al. 2014; Pradhan et al. 1999). RM treated with H<sub>2</sub> shown remarkable Cr (VI) reduction in aqueous medium

compared to commercial Fe<sup>0</sup> fine powder (Costa et al. 2010). Recently, cetyltrimethyl ammonium bromide (CTAB) modified red mud also showed favorable results (Li et al. 2015). Moreover, negligible removal was observed at neutral pH and the adsorption process was negatively influenced by increasing temperature while the effect of competing anions (PO<sub>4</sub><sup>3-</sup>, SO<sub>4</sub><sup>2-</sup>, and NO<sub>3</sub><sup>-</sup>) depends on their relative concentration and affinity for the surface. The adsorption of Cr (VI) was found to be exothermic and followed Langmuir isotherm model (Gupta et al. 2001; Li et al. 2015; Ma et al. 2014; Pradhan et al. 1999; Pulford et al. 2012). The Cr(VI)-loaded adsorbent solidification with cement and low leaching of elements confirms the effectiveness of stabilization process and could be used as a building material. Furthermore, the spent red mud can be easily regenerated by simple treatment with H<sub>2</sub> at 600 °C (Costa et al. 2010; Singh and Singh 2002).

**Phosphates** Dephosphatation with chemical is widely accepted technique. Common precipitants used for phosphate removal are lime, aluminum sulfate, and ferric chloride. However, the cost of metal salts and sludge production are the typical draw backs (Altundoğan and Tümen 2003; Zhao et al. 2009). Therefore, dephosphatation potential of various low-cost adsorbents, e.g., fly ash, red mud, natural zeolites, slag, and biochar from wastewater have been widely explored (Chen et al. 2011; Karapınar 2009; Liu et al. 2011; Wang and Wu 2006).

The removal of phosphates on red mud was found to be pH dependent with favorable pH range from 3.2 to 5.5. The mechanism of phosphate adsorption onto red mud was found to be ligand exchange mechanism. Sequential extraction results showed that phosphate retention at pH 4.0 and 7.0 was mainly regulated by two different mechanisms, i.e., chemisorption on RM phases and the formation of metal phosphate precipitates. In contrast, at pH 10.0, it is regulated only by chemisorption (Altundoğan and Tümen 2003; Altundoğan and Tümen 2002; Castaldi et al. 2010; Li et al. 2006; Liu et al. 2007). Acid-treated red mud and Bauxsol<sup>TM</sup> exhibited increased sorption at low initial concentration of phosphate (1 mg/L) (Akhurst et al. 2006; Baraka et al. 2012; Huang et al. 2008). Approximately 80–90% of phosphate removal at constant pH of 5.2 was achieved using precipitated residue having a high specific surface area (249 m<sup>2</sup>/g) obtained after acid activation (Pradhan et al. 1998).

Granulates of red mud, bentonite, and starch (RMGA) were prepared at different mass ratios and sintering temperature. The optimum mixture of RMGA-85% and RMGA-95% showed best result for phosphate adsorption at acidic pH 3.0 (Yue et al. 2010). For the first time, powdered-acid-activated-neutralized red mud (Aan-RM) was employed with hydroxypropyl methylcellulose and powdered straw as the main ingredient for granular Aan-RM production for phosphate removal. X-ray photoelectron spectroscopy (XPS) analysis of P 2p peak

on granular Aan-RM after phosphate adsorption demonstrated that 79.01% of the phosphate was adsorbed through precipitation and ion exchange mechanisms, while the surface deposition mechanism constitutes only 20.99% of the phosphate (Ye et al. 2015). In the presence of bicarbonate ions, adsorption decreased due to competing ion effects while chlorides and sulfates had little effect. Ca and Mg ions increased adsorption due to the increase in positive sites (Akhurst et al. 2006). Regeneration of granulates (RMGA) adsorbent using HCl showed high desorption and low resorption capacities owing to the extraction of effective components from RMGA. In case of NaOH, extractant showed relatively better resorption of phosphate due to OH<sup>-</sup> amelioration of the chemical composition on the surface of RMGA during desorption process (Zhao et al. 2009).

**Nitrates and fluorides** Presence of nitrates in high concentrations in waterways stimulates algal growth and presents a potential risk to public health (Danalewich et al. 1998). Limited researchers used red mud for nitrate removal. Original and modified red mud adsorbents were compared and the adsorption capacity of the acidified red mud was higher than original. The removal mechanism of nitrate was explained due to surface chemical interaction of red mud metal oxides with nitrate ions (Cengeloglu et al. 2006). Approximately 98% removal of nitrates was achieved by mixing acid-activated red mud mixed with Fe<sup>0</sup> in solution. Nitrate was transformed into ammonium indicating that reaction pathway of nitrate removal is associated with reduction. The enhancing effect of activated red mud was assumed to be the result of the scavenging of the reaction precipitate, thereby minimizing passivation of Fe<sup>0</sup> surfaces and formation of additional reactive sites (e.g., green rust) for nitrate reduction (Cho et al. 2011). The rate of nitrate removal decreased at pH above 7 due to stronger competition with hydroxide ions on adsorbent surface (Cengeloglu et al. 2006).

Fluoride is another toxic element present in water which needs to be treated for public health safety. Acid-activated RM has higher fluoride removal potential at pH 5.5 due to its surface charge. Above pH 5.5, the removal efficiency decreased sharply due to competition with OH<sup>-</sup> ions on adsorbent surface. The adsorption of fluorides was also not favored in very acidic pH, which may be due to the formation of weakly ionized hydrofluoric acid. The activated red mud could remove only 77% of 21 mg/L fluoride, leaving 2.7 mg/L fluoride in solution which was still higher than the acceptable levels (Çengelöglü et al. 2002). Best removal efficiency for fluoride was given by H<sub>2</sub>SO<sub>4</sub>-treated red mud because two protons were available to protonate the surface hydroxyl groups (Liang et al. 2014). Thermally activated bauxite (TRB) at 300–450 °C greatly increased its fluoride adsorptive capacity at pH 5.5–6.5 with short equilibrium time (90 min). The adsorption data fitted well with both Langmuir and

Freundlich isotherm models. Uptake of fluoride on TRB was not affected by the presence of common interfering ions. NaOH (0.015 mol/L) was used to get complete desorption of fluoride at pH of 11.1 (Das et al. 2005). Defluoridation capacity of Zr-modified RMPM at 3–4 was 0.6 mg/g. The modified material could be regenerated using NaOH solution at pH 12 with over 90% of recovery ratio (Lv et al. 2013).

Comprehensive summary of adsorption capacity of raw and treated red mud for metal ions and inorganic anions are presented in Table 2 and Table 3, respectively. These tables provide valuable information regarding the effect of treatment on surface area of red mud, initial concentration of various contaminants, optimum pH and temperature range, and the quantities of adsorptions. Adsorption data followed mostly Langmuir isotherm model than Freundlich. The Langmuir model is a simple model that assumes adsorption of molecules on a monolayer on a homogenous surface with a finite number of similar active sites and no interaction occurs between adsorbed species (Langmuir 1918). The well-known expression of the Langmuir model is given in the following Eq. (3):

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m} \quad (3)$$

$C_e$  (mg/L) is the equilibrium concentration,  $q_m$  (mg/g) is the maximum adsorption capacity, and  $K_L$  (L/mg) is the Langmuir constant.

The Freundlich model is an empirical model based on adsorption onto a heterogeneous surface having no equivalent adsorption sites (Freundlich 1906). This model is expressed by the following eq. (4):

$$q_e = K_f C_e^{1/n} \quad (4)$$

where  $K_f$  and  $1/n$  are Freundlich constants related to the adsorption capacity and the adsorption intensity, respectively, and  $C_e$  (mg/L) is the equilibrium concentration. Both of Langmuir and Freundlich isotherms might adequately describe the same set of liquid-solid adsorption data at certain concentration ranges, particularly if the concentration is small and the adsorption capacity of the solid is large enough to make both isotherm equations approach a linear form.

### Removal of organic pollutants

Dyes are widely used in the industries like textile, leather, paper, plastics, printing etc., for imparting color to their products along with consumption of substantial amount of water. As a result, considerable amount of colored effluent is discharged. The presence of dyes in waste streams is the main concern due to their toxic, mutagenic, and carcinogenic properties, and they possess adverse effect on aquatic life and inhibition of light penetration. Other highly carcinogenic



**Table 2** Adsorption capacities of red mud before and after treatment for metal ions

Ions	Red mud and treatments	Initial Conc. (mg/L)	$S_{BET}$ (m <sup>2</sup> /g)	T/°C	pH	Isotherm	Adsorption (mg/g)	Ref
Ni(II)	RM-CaSO <sub>4</sub>	250	58	-	6.9	Langmuir	10.9	(López et al. 1998)
	RM-Rinsed	465	-	-	2.0–3.5	Langmuir	21.8	(Smiljanić et al. 2010)
	RM-heated 600 °C	465	-	-	2.0–3.5	Langmuir	27.54	(Smiljanić et al. 2011)
	RM-0.05 M HCl	465	-	-	5.0	Langmuir	11.11	(Smičiklas et al. 2014)
Cu(II)	RM	3177	14.2	25	6.0	Modified Langmuir	75.2	(Apak et al. 1998)
	RM-HCl	3177	20.7	25	4.5	Modified Langmuir	35.2	(Apak et al. 1998)
	RM-HCl-heated 600 °C	3177	28.0	25	5.7	Modified Langmuir	65.2	(Apak et al. 1998)
	RM-CaSO <sub>4</sub>	250	58	-	5.6–6.2	Langmuir	19.7	(López et al. 1998)
	RM-pellets	20	17.33	25	5.64	Langmuir	6.56	(Han et al. 2002)
	RM-acid	190.62	10–25	30	5.5	Freundlich and Langmuir	5.35	(Nadaroglu et al. 2010)
	RM		10–15	-	11.5	Langmuir	8.9	(Pulford et al. 2012)
	RM-HCl		45–48	-	4.5	Langmuir	3.5	(Pulford et al. 2012)
	RM-carbonized		70	-	8.2	Langmuir	25	(Pulford et al. 2012)
Cd(II)	RM	3934	14.2	25	6.0	Langmuir	66.8	(Apak et al. 1998)
	RM-HCl	3934	20.7	25	4.2	Langmuir	46.9	(Apak et al. 1998)
	RM-HCl-heated 600 °C	3934	28.0	25	5.9	Langmuir	66.8	(Apak et al. 1998)
	RM-CaSO <sub>4</sub>	250	58	-	4.7–6.2	Langmuir	10.57	(López et al. 1998)
	RM-H <sub>2</sub> O <sub>2</sub> -heated 500 °C	100	108	30–50	4.0	Freundlich and Langmuir	11.2–13.0	(Gupta and Sharma 2002)
	RM-pellets	20	17.33	25	6.15	Langmuir	6.62	(Han et al. 2002)
	RM	100	18.38	-	6.0	Langmuir	68	(Vaclavikova et al. 2005)
	RM	337	18.9	-	5.5–5.9	Langmuir	152	(Santona et al. 2006)
	RM-HCl	337	25.2	-	5.5–5.9	Langmuir	102	(Santona et al. 2006)
	RM-granular	400	15.28	20	6.0	Freundlich	38.2	(Zhu et al. 2007)
	RM-granular	400	15.28	30	6.0	Freundlich	43.4	(Zhu et al. 2007)
	RM-granular	400	15.28	40	6.0	Freundlich	52.1	(Zhu et al. 2007)
	RM-2% cement	10	17.42	30	6.5	Langmuir	9.42	(Ju et al. 2012)
	RM-2% cement	10	17.42	40	6.5	Langmuir	10.19	(Ju et al. 2012)
RM-2% cement	10	17.42	50	6.5	Langmuir	10.78	(Ju et al. 2012)	
Zn(II)	RM-CaSO <sub>4</sub>	250	58	-	6.9–7.8	Langmuir	12.59	(López et al. 1998)
	RM-H <sub>2</sub> O <sub>2</sub> -heated 500 °C	120	108	30–50	4.0	Freundlich and Langmuir	11.8–14.5	(Gupta and Sharma 2002)
	RM	100	18.38	-	7.0	Langmuir	133	(Vaclavikova et al. 2005)
	RM	196	18.9	-	5.5–5.9	Langmuir	161.5	(Santona et al. 2006)
	RM-HCl	196	25.2	-	5.5–5.9	Langmuir	104	(Santona et al. 2006)
	RM-CO <sub>2</sub> -heated 500 °C	30	68.22	-	6.0	Langmuir	14.92	(Sahu et al. 2011)
Pb(II)	RM	10,360	14.2	25	6.0	Langmuir	165.8	(Apak et al. 1998)
	RM-HCl	10,360	20.7	25	4.4	Langmuir	117.3	(Apak et al. 1998)
	RM-HCl-heated 600 °C	10,360	28.0	25	5.7	Langmuir	138.8	(Apak et al. 1998)
	RM-H <sub>2</sub> O <sub>2</sub> -heated 500 °C	700	108	30–50	4.0–6.0	Freundlich and Langmuir	66.9–71.3	(Gupta et al. 2001)
	RM-pellets	20	17.33	25	5.68	Langmuir	17.2	(Han et al. 2002)
	RM	621	18.9	-	5.5–5.9	Langmuir	390	(Santona et al. 2006)
	RM-HCl	621	25.2	-	5.5–5.9	Langmuir	160	(Santona et al. 2006)
	RM		10–15	-	11.5	Langmuir	133	(Pulford et al. 2012)
	RM-HCl		45–48	-	4.5	Langmuir	9.0	(Pulford et al. 2012)
	RM-carbonized		70	-	8.2	Langmuir	94	(Pulford et al. 2012)
RM-HCl-heated 500 °C	10	67.10	-	4.0	Langmuir	6.21	(Sahu et al. 2013)	

pollutants are phenols and its derivatives and these pollutants along with dyes need to be removed from effluents before being discharged into water bodies (Wang et al. 2008). In order to widen the applicability of red mud as low-cost adsorbent, its feasibility for organic pollutant removal has been investigated over the past few years for different dyes such as congo red (an anionic dye), acid violet, methylene blue, fast green, rhodamine B, and procion orange. Effects of different initial dye concentrations, agitation time, adsorbent dosage,

and pH were also studied. Quantitative adsorption of congo red, acid violet, and procion orange on red mud was obtained at pH 2.0, 4.1, 2.0, respectively. Maximum removal capacities for congo red and acid violet were 4.05 mg/g and 1.37 mg/g, respectively. The adsorption data obeyed both the Langmuir and Freundlich isotherms. Procion orange adsorption data obeyed Freundlich isotherm model and a maximum removal of 82% of the dye was observed. Desorption studies showed that the adsorption was mainly due to ion exchange

(Namasivayam and Arasi 1997; Namasivayam et al. 2001; Namasivayam et al. 2002). Similarly, acidified RM improved congo red dye removal in short equilibrium time (Tor and Cengeloglu 2006).

Successful removal of rhodamine B, fast green, and methylene blue on H<sub>2</sub>O<sub>2</sub> activated red mud was achieved up to 71.1 to 94.0%. The adsorption was found to be exothermic in nature (Gupta et al. 2004b). It was observed that heating of red mud imparts negative effect on adsorption of methylene blue (basic dye) than acidified red mud, and adsorption was found to be endothermic in nature (Wang et al. 2005). Reactive dyes are used in textile dyeing industries due to their superior fastness to the applied fabric, high photolytic stability, high solubility, and resistance to microbial attack. Adsorption of a reactive dye (Remazol Brilliant Blue (RBB)) on H<sub>2</sub>SO<sub>4</sub>-treated red mud was favored at pH 2.0 to 6.0 and increases with increasing temperature (Ratnamala et al. 2012). Highest percentage of removal was obtained for reactive blue dye 19 with seawater neutralized red mud activated at 400 °C (de Souza et al. 2013). A MgCl<sub>2</sub>/red mud system (MRM) showed 98% of de-colorization at a dosage of 25-g RM/L dye solution. The color removal efficacy was better than the conventional polyaluminum chloride (PAC)/RM and PAC/NaOH systems. The experimental data was best correlated with Langmuir and Freundlich model (Wang et al. 2009). Thermally activated red mud was evaluated to remove reactive blue 19 dye (RB 19). The adsorption of RB 19 was highest when the pH values were lower than the pH<sub>PCZ</sub> (7.0). Thermally activated RM exhibited adsorption capacity of 178.4 mg/g in acidic conditions and obeyed Langmuir model (de Jesus et al. 2015). An anionic surfactant, sodium dodecyl sulfate (SDS), was used to modify the surface of red mud. Adsorption data of Safranin-O dye on SDS modified RM showed good fit to the Langmuir model with a maximum monolayer adsorption capacity of 89.4 mg/g at pH 4.4 and 35 °C temperature. Desorption experiments were carried out by testing several solvents such as water, sulfuric acid, hydrochloric acid, and acetic acid, and the maximum (93.2%) desorption was found using hydrochloric acid (Sahu and Patel 2015).

Phenols and its derivatives represent one of the problematic organic pollutants. Their main sources are petroleum and petrochemical, coal conversion, paints, pesticides, and polymeric resin industries. Phenol presence in drinking water causes unpleasant taste and odor even at low concentrations (Calace et al. 2002). Red mud washed with distilled water used to remove phenol and maximum retention is obtained in the wide pH range of 1.0 to 9.0. The equilibrium was attained in 10 h with maximum adsorption capacity of 4.127 mg/g. The Freundlich model fits well with the measured adsorption data as compared to Langmuir model. The influence of additional ions (chloride, sulfate, and nitrate) on phenol removal depends on their relative concentrations and affinity for the red mud surface. The anions followed the affinity order; sulfate >

nitrate >>> chloride (Tor et al. 2006). Furthermore, neutralized red mud treated with acid showed a two-fold increase in the adsorption capacity (8.156 mg/g) at pH 6. The Langmuir isotherm showed a good fit with the adsorption data. Effect of competing ions on neutralized red mud has shown that presence of chlorides (10 to 50 mg/L) has no significant effect on phenol adsorption, but in the presence of nitrates and sulfate (50 mg/L), phenol adsorption decreased from 66 to 32% and 15%, respectively. Similar effects of anions on the adsorption of phenol by activated red mud can be expected (Tor et al. 2009). HNO<sub>3</sub>-treated RM showed increased removal of phenols in pH range of 3–7, while above neutral, pH it was declined. Adsorption data follow the Freundlich isotherm, whereas kinetic data was well described by a pseudo-second-order kinetic model (Shirzad-Siboni et al. 2013). New RM adsorbent treated with H<sub>2</sub>O<sub>2</sub> and heat (500 °C) removed up to 94–97% of 2,4-dichlorophenol and 4-chlorophenol, while the removal of 2-chlorophenol and phenol was up to 50–81%. The removal took place through particle diffusion mechanism and the order of removal was 2,4-dichlorophenol ≈ 4-chlorophenol > 2-chlorophenol > phenol. The adsorption is endothermic in nature and followed both Langmuir and Freundlich models (Gupta et al. 2004a) (Table 4).

## Red mud application in soil and sediment treatment

Anthropogenic and natural activities increased heavy metal inputs both in soils and sediments. The choice of most appropriate remediation method for soil and sediment depends on the site characteristics, contaminant types and concentration, and the end use of contaminated medium. The potentially available remediation options for contaminated soils and sediments are either in situ or ex situ. In this regards, most frequently used methods include physical, chemical, and thermal treatments. These methods involve physical separation, isolation, sediment/soil washing, extraction, vitrification, and solidification/stabilization (Mulligan et al. 2001). Inexpensive mineral amendments such as apatite, zeolites, clays, beringite, iron bearing materials (e.g., zero-valent-iron, goethite, hematite, ferrihydrite), industrial by-products such as fly ash, and red mud have shown satisfactory performances to reduce metal mobility in multi-contaminated soils and sediments (Kumpiene et al. 2008; Peng et al. 2009). Although red mud may contain traces of metals and metalloids, the bioavailable fraction is low. Therefore, red mud has been investigated by numerous researchers as soil amendment, and recently, it has also been studied for the stabilization of trace elements in contaminated sediments (Liu et al. 2011; Taneez et al. 2015).

**Table 3** Removal capacities of various bauxite residues for inorganic anions

Ions	Red mud and treatments	Initial Conc. (mg/L)	$S_{\text{BET}}$ ( $\text{m}^2/\text{g}$ )	T/ $^{\circ}\text{C}$	pH	Isotherm	Adsorption (mg/g)	Ref	
As (V)	RM	10	-	25	3.2	Langmuir	0.38	(Altundoğan et al. 2000)	
	RM	10	-	25–70	3.5	Langmuir	0.51–0.82	(Altundoğan et al. 2002)	
	RM-HCl	10	-	25–70	3.5	Langmuir	0.94–1.32	(Altundoğan et al. 2002)	
	Bauxsol	0.06–2.4	30	23	6.4	Langmuir	1.08	(Genç et al. 2003)	
	Activated Bauxsol (AB)	2.58–11.39	130	23	7.1	Langmuir	2.99	(Genç-Fuhrman et al. 2004a)	
	Bauxsol-coated sand (BCS)	0.54–20.34	130	23	4.5	Langmuir	3.32	(Genç-Fuhrman et al. 2004b)	
	Bauxsol-coated sand (BCS)	1.16–19.60	7.7	25	7.1	Langmuir	1.64	(Genç-Fuhrman et al. 2005)	
	AB-coated sand (ABCS)	0.54–20.34	47.3	25	7.1	Langmuir	1.07	(Genç-Fuhrman et al. 2005)	
	RM-FeCl <sub>3</sub>	2.0–100	192	20	6.0	Langmuir	68.5	(Zhang et al. 2008)	
	RM-CO <sub>2</sub> - heated 500 °C	10	63	25	4.0	Langmuir	55.5	(Sahu et al. 2010)	
As (III)	75%-RM + 25%-G	7.5–97.4	-	24	5.5	Langmuir	3.333	(Lopes et al. 2013)	
	RM-HCl	0.1–30	89.39	25	7.0	Langmuir	5.16	(Guo et al. 2014)	
	RM	10	-	25	9.5	Langmuir	0.322	(Altundoğan et al. 2000)	
	RM	10	-	25–70	7.2	Langmuir	0.46–0.67	(Altundoğan et al. 2002)	
	RM-HCl	10	-	25–70	7.2	Langmuir	0.34–0.88	(Altundoğan et al. 2002)	
	Activated Bauxsol	0.15–11.8	130	23	6.8	Langmuir	0.54	(Genç-Fuhrman et al. 2004a)	
	RM-HCl	0.1–30	89.39	25	7.0	Langmuir	1.47	(Guo et al. 2014)	
	Cr(VI)	RM-H <sub>2</sub> O <sub>2</sub> -heated 500 °C	300	108	30–50	2.0	Freundlich and Langmuir	21.1–22.7	(Gupta et al. 2001)
		Heated Bauxite	10	86	20–50	2.0	Langmuir	0.403–0.522	(Erdem et al. 2004)
		RM	10–15	-	-	11.5	Langmuir	1.3	(Pulford et al. 2012)
RM-HCl		45–48	-	-	4.5	Langmuir	1.7	(Pulford et al. 2012)	
RM-carbonized		70	-	-	8.2	Langmuir	0.0	(Pulford et al. 2012)	
RM-HCl		0.08	-	30	2.0	Langmuir	0.03	(Ma et al. 2014)	
RM-0.5% CTAB		100	25.7	-	2.0	Langmuir	22.20	(Li et al. 2015)	
Phosphate		RM-HCl	120	294	30	5.2	Freundlich and Langmuir	23.2	(Pradhan et al. 1998)
		Bauxite	10	11	25	4.5	Langmuir	0.67–0.82	(Altundoğan and Tümen 2003)
		Bauxite-HCl-heated 600 °C	10	86	25	4.5	Langmuir	0.98–2.95	(Altundoğan and Tümen 2003)
	RM	155	14.09	25	7.0	Langmuir	113.87	(Li et al. 2006)	
	RM-HCl	155	19.35	25	7.0	Langmuir	161.6	(Li et al. 2006)	
	RM-heated 700 °C	155	9.69	25	7.0	Langmuir	345.5	(Li et al. 2006)	
	RM	155	14.09	25	7.0	Langmuir	95.86	(Liu et al. 2007)	
	RM-HCl-heated 700 °C	155	21.76	25	7.0	Langmuir	202.9	(Liu et al. 2007)	
	RM- heated 700 °C	155	15.69	25	7.0	Langmuir	155.2	(Liu et al. 2007)	
	RM-HCl	1.0	28.48	40	5.5	Freundlich	0.58	(Huang et al. 2008)	
Nitrate	Granular Aan-RM	500	113.54	40	6.0	Freundlich and Langmuir	153.2	(Ye et al. 2015)	
	RM	5–250	14.2	25	6.0	Langmuir	1.859	(Cengeloglu et al. 2006)	
Fluoride	RM-HCl	5–250	20.7	25	6.0	Langmuir	5.858	(Cengeloglu et al. 2006)	
	RM	69.5	14.2	25	5.5	Langmuir	0.164	(Çengelöglü et al. 2002)	
	RM-HCl	69.5	20.7	25	5.5	Langmuir	0.331	(Çengelöglü et al. 2002)	
	Heated Bauxite (TRB-1)	5–40	-	27	6.0	Langmuir	3.70	(Das et al. 2005)	
	Heated Bauxite (TRB-2)	5–40	-	27	6.0	Langmuir	4.13	(Das et al. 2005)	
	Heated Bauxite (TRB-3)	5–40	-	27	6.0	Langmuir	3.91	(Das et al. 2005)	
	Zr-modified RM	10–20	-	15–35	3.0	Langmuir	0.5–0.9	(Lv et al. 2013)	

### Stabilization of trace elements in soil

Chemical stabilization of trace elements (Cd, Cu, Ni, Zn, Pb, As, Cr, V) in soils using red mud has also been assessed. Application of red mud at 2% and 5% rate increased the pH of soil which played dominant role in reducing the metal concentrations in soil pore water and metal fluxes. Red mud converted exchangeable fraction of metals to Fe-oxide fraction, decreased the bioavailability of metals at low pH. The possible fixation mechanism of metals could be specific chemisorption and diffusion of metals into oxide particles (Lee et al. 2011;

Lee et al. 2009; Lombi et al. 2002a; Lombi et al. 2002b). Though the labile fractions of Cd, Zn, and Cu were reduced in amended soil, it is important to investigate the effects of pH changes on the reachability of these elements. Re-acidification of amended soil showed that the leaching was always lower than untreated soils across the range of pH values tested. However, acid leaching of amended soils showed increase in As and Cu mobility compared to untreated soils. Cu is mainly associated to organic matter and addition of alkaline red mud increased the concentration of dissolved organic matter (DOM) in soil pore water and pH variation affected

exchangeable and soluble fraction of Cu. Presence of DOM also decreased the retention of As on goethite (Lombi et al. 2003; Lombi et al. 2004). Field and pot experiments gave similar results as reported by Lombi et al. (2002a), but it increased the concentration of ammonium nitrate-extractable As, Cu, Cr, and V in soil. Despite the increase in Cu mobility, its toxicity appeared to be reduced as indicated by the higher corn biomass production (Friesl et al. 2004; Friesl et al. 2003). Red mud addition in soil can transform 22% of non-specifically adsorbed As to the Fe/Al oxide-bound or specifically adsorbed As fractions (Yan et al. 2013). In further field investigations, it was concluded that if red mud was applied approximately 15 cm below the soils surface, it can reduce ammonium nitrate-extractable Cd, Zn, and Pb up to 99%, but deeper application may be needed to reduce plant metal uptake (Friesl et al. 2006). Finally, it was established that red mud in combination with gravel sludge (a fine-grained waste product of the gravel industry) and metal excluding barley cultivar (*Hordeum distichon ssp. L.*) performed effectively as a stabilizer for the metal-contaminated soil (Friesl-Hanl et al. 2009). Moreover, red mud was reported to be optimal additive for Cd-contaminated agricultural soils due to reduction in water extractable fraction (Feigl et al. 2012; Feng et al. 2013). Combined treatment of limestone and red mud (each applied at 2% rate) decreased sufficiently the  $\text{Ca}(\text{NO}_3)_2$ -extractable fraction of As, Cd, Pb, and Zn by 58%, 98%, 98%, and 99%, respectively. These results suggest that iron-rich industrial by-products could be used for remediation of soils co-contaminated with metals and arsenic (Lee et al. 2011). Long-term application of red mud in sub-acidic mine soils increased soil pH, decrease of total organic carbon, and enhanced water-soluble C, N, and P fraction. Sequential extraction of amended soil samples indicated a decrease of water soluble As, and a remarkable increase of the residual (non-extractable) arsenic fraction (Garau et al. 2011). They further reported increased leachability of As and Pb from mine and chromated copper arsenate (CCA) contaminated soils after amendment addition. This was most likely due to the organic matter degradation and formation of soluble complexes of As and Pb with a low molecular weight organic fractions. On the other hand, the amendment had a more positive response in reducing As and Cu leachability in (CCA) contaminated soil which was probably due to the changes in physical and chemical properties of soil after the addition of sorbents (Silvetti et al. 2014).

Transformed red mud (TRM) was used as a reactive barrier (RB) placed near the anode of an electrokinetic (EK) system for the removal of chromium or arsenic-contaminated clayey soil and favoring entrapment. The outcome of treatment was beneficial in case of Cr(VI) than As (V). Presence of the anodic TRM suppressed formation of an acidic front, thus decreasing the adsorption capacity of the soil for Cr(VI) oxyanions, increasing the rate of electromigration towards the anode, and

limiting Cr(VI) reduction in the soil. Increased mass of TRM in the RB indicates that all mobilized Cr(VI) was trapped before it entered the anolyte, thus preventing contamination of the latter. Conversely, combined treatment was much less effective in case of As-contaminated soil. Low initial As concentration and interference with iron oxides in the soil were likely the reasons underlying low efficiency while attempting As decontamination (Cappai et al. 2012). The efficiency of soil amendments depends on soil conditions, contaminants source, and perhaps most importantly the environmental endpoint considered.

**Trace element uptake by plants and re-vegetation** Red mud treatment not only reduced the labile fraction of trace elements in soil but also significantly increased the soil biomass. Therefore, four crop species (oilseed rap, wheat, pea, and lettuce) were successfully grown in pots (Lombi et al. 2002a; Lombi et al. 2002b). The amendment has positive effect on soil microbial biomass and growth of ryegrass (Lombi et al. 2003; Lombi et al. 2004). Plant uptake was also reduced by 38–87% (Cd), 50–81% (Zn), and 66–87% (Ni) as compared to the control (Friesl et al. 2003). Similar results were found in acidic soil after treatment with red mud and other additives. Particularly, red mud reduced heavy metal uptake of pea and wheat by 60–34% (Pb), 79–80% (Cd), and 93–64% (Zn), respectively (Castaldi et al. 2009). After red mud amended in microcosm (2 years), study reported decrease in Cd and Zn uptake of *Sinapis alba* test plants by 18–29% (Feigl et al. 2012). It was further observed in plant edible part that red mud can stimulate the growth of Pakchoi plant and reduce the accumulation of Cd (Feng et al. 2013). In addition to the reduction in trace element uptake by lettuce (Lee et al. 2011; Lee et al. 2009) and *Festuca rubra* plants, soil microbial activities (soil respiration, urease, and dehydrogenase activity) were significantly increased. Furthermore, a dramatic shift in the culturable bacterial population from Gram-positive to Gram-negative forms in red mud amended soils was also observed (Lee et al. 2011; Lee et al. 2009). Phosphorous application with red mud decreased Pb concentration but not total uptake of Pb in *Festuca rubra* compared to red mud alone (Gray et al. 2006). Despite the high rate of contaminant mobility, most of the soil microbial and biochemical activities were significantly higher in the RM-soil. Bean germination was almost inhibited in RM-soil while wheat growth was similar to that of control (Garau et al. 2014; Garau et al. 2011). The effect of soil amendments was more evident when metal uptake by plants was considered. Trial pot showed that the treatments with seawater neutralized red mud in aerobic condition were able to decrease the plant uptake of As by 34% and 57% in soil 1 (mine contaminated) and by 88% and 87% in soil 2. Uptake of Cu from soil 2 (CCA contaminated) reduced (by 68% and 86%) and of Pb from soil

**Table 4** Removal of organic pollutants

Pollutants	Red mud and treatments	Initial Conc. (mg/L)	$S_{\text{BET}}$ (m <sup>2</sup> /g)	T/°C	pH	Isotherm	Adsorption (mg/g)	Ref
Congo red	RM	10	-	30	7.3	Langmuir	4.05	(Namasivayam and Arasi 1997)
Acid violet	RM	20	-	30	4.1	Langmuir	1.37	(Namasivayam et al. 2001)
Procion orange	RM	10	-	30	2.0	Freundlich	-	(Namasivayam et al. 2002)
Rhodamine B	RM-H <sub>2</sub> O <sub>2</sub> -heated 500 °C	4.8–57.5	108	30	1.0	Langmuir	5.56	(Gupta et al. 2004b)
Fast green	RM-H <sub>2</sub> O <sub>2</sub> -heated 500 °C	7.65–76.9	108	30	7.0	Langmuir	7.56	(Gupta et al. 2004b)
Methylene blue	RM-H <sub>2</sub> O <sub>2</sub> -heated 500 °C	32–352	108	30	8.0	Langmuir	16.72	(Gupta et al. 2004b)
Methylene blue	RM	10	21.0	30	5.2	Langmuir	2.49	(Wang et al. 2005)
Methylene blue	RM-heated 800 °C	10	10.1	30	5.2	Langmuir	0.48	(Wang et al. 2005)
Methylene blue	RM-HNO <sub>3</sub>	10	31.9	30	5.2	Langmuir	1.02	(Wang et al. 2005)
Congo red	RM-HCl	20	20.7	25	7.0	Langmuir	7.08	(Tor and Cengelolu 2006)
Remazol Brilliant Blue	RM-H <sub>2</sub> SO <sub>4</sub> -dired 110 °C	30	27.3	20–40	2.0	Langmuir	25.64–27.8	(Ratnamala et al. 2012)
Reactive Blue dye 19	Seawater neutralized-RM	2000	22.6		4.0	Langmuir	250.0	(de Souza et al. 2013)
	Seawater neutralized RM-heated 400 °C	2000	55.4	25	4.0	Langmuir	416.7	(de Souza et al. 2013)
	Seawater neutralized RM-heated 500 °C	2000	45.4	25	4.0	Langmuir	38.6	(de Souza et al. 2013)
Safranin-O dye	RM-SDS (sodium dodecyl sulfate)	50	67.10	25	4.4	Langmuir	89.4	(Sahu and Patel 2015)
Phenol	RM-water neutralized	25	14.2	35	6.0	Langmuir	4.127	(Tor et al. 2006)
	RM-water neutralized	25	14.2	25	6.0	Freundlich	0.513	(Tor et al. 2006)
	RM-HCl	60	20.7	25	6.0	Langmuir	8.156	(Tor et al. 2006)

1 (by 52% and 34%) as a result of amendment (Silveti et al. 2014).

Besides trace element stabilization in contaminated soils, red mud can also be used for phosphorous retention and re-vegetation after amendment. Bauxite residue (red mud alone and neutralized with gypsum) can increase phosphorous retention in sandy soil catchment (Summers et al. 2001; Summers et al. 1993), improve pasture growth (Summers et al. 1996), increase soil pH, and lower P availability (Snars et al. 2004). A field studied evaluated gypsum as ameliorant at 0, 2, 5, and 8% rate for vegetation on bauxite residue deposits with two grass species. The research showed that gypsum is an effective ameliorant to reduce the pH, electrical conductivity exchangeable sodium percentage (ESP), and significantly enhanced the growth of the two grass species (Wong and Ho 1993). They also used sewage sludge as another ameliorant for re-vegetation of red mud. Sewage sludge gave additional reductions in EC, Na, and ESP. In addition, sewage sludge increased dry weight yield and provided sufficient nutrients for plant growth except K. No heavy metal accumulation was

observed. Sewage sludge can also significantly reduce soil bulk density (25%), particle density (9%), and increase the total porosity of red mud (8%) as well as hydraulic conductivity (from 1.5 to  $23 \times 10^{-5}$  m/s) (Wong and Ho 1994). Similar results were reported that calcium phosphate application into red mud enhanced plant growth and gave the most promising results (Xenidis et al. 2005).

#### Red mud as sediment amendment

Just like soil, similar strategies have also been for remediation of metal-contaminated sediments. Fewer studies reported so far the use of bauxite residue as amendment for contaminants stabilization in sediments. Pot and field experiments were conducted using red mud and other amendments (sludge from drinking-water treatment, lime, bog iron ore, unused steel shot, and steel shot waste) for the immobilization of Cd and Zn in dredged sediment from seaport. The pH and CEC were little influenced by the treatments. In the pot experiments, NH<sub>4</sub>NO<sub>3</sub> extractable amounts of Cd and Zn

in the treated samples were reduced by 50% (DTPA: 20%) while plant uptake was reduced by 20–50%. While in the field trials, Cd and Zn were immobilized in the soil to a certain extent and less effect was observed on the concentrations in plants and soil extracts. Red mud and sludge from drinking water treatment were found to be the effective treatments with regards to metal immobilization. Although the use of red mud is questionable whether it can be applied in practice as it contains high amounts of Cr and Al ions (Müller and Pluquet 1998). Stabilization of multi-contaminated marine dredged sediment was evaluated by using two bauxite residues (bauxaline® and bauxsol) at 5% rate. The results revealed that after 3 months of treatment, pH of leachate decreased from  $42 \pm 3$  to  $12 \pm 3$  mS/cm and pH remained constant around 8.2, cationic trace elements (Cd, Cu, and Zn) were effectively immobilized, but no significant efficacy was observed for anionic pollutants (As and Mo) (Taneez et al. 2015). Increased leaching of anionic pollutants could be limited by addition of higher quantities of amendments. Further investigation by applying neutralized bauxaline® (bauxaline® treated with 5.88% of gypsum) at the rate of 5% and 20% showed relatively better results in case of anionic pollutants. The available fraction of contaminants in the case of 5% neutralized bauxaline® was as follows: Cu (26.5%), Cd (24%), Zn (35%), As (9.6%), Cr (19.1%), and Mo (2.2%). In contrast, with 20% neutralized bauxaline®, Cu (40%), Cd (55%), and Zn (71.2%) were predominantly stabilized as compared to leaching from control sediment whereas Mo (11.7%) and As (5.2%) were less immobilized. pH was around 8.2, and EC was reduced from  $44 \pm 2$  to  $12 \pm 4$  mS/cm in the leachates collected during 3 months of experiments (Taneez et al. 2016). Bauxaline® and steel slag and their composite mixture (50:50) were applied as cap layer of 1–1.5 cm onto spiked sediment in aquariums, and a kinetic model was developed which showed that the release of pollutants was 7 days. The amendments efficiently blocked Cd, Zn, and As release from sediment to water whereas steel slag was the only additive able to capture efficiently Cr. Steel slag is highly alkaline material, and considering the pH, EC variations, the stress on benthic organism, the use of bauxaline/steel slag composite could represent the best compromise between trapping efficiency and environmental conditions (Taneez et al. 2018).

### Leaching and ecotoxicological studies of red mud

US EPA developed a protocol called Standard Toxicity Characteristics Leaching Procedure (TCLP) designated to determine the mobility of both organic and inorganic

analytes present in liquid, solid, and multi-phase wastes. The intent of this leaching procedure is to simulate the conditions that may be present in a landfill where water may pass through waste and travel into the groundwater carrying the soluble materials with it. Standard Toxicity Characteristics Leaching Procedure (TCLP) has been used by many researchers to assess the leaching behavior of trace elements from red mud. Leachability of Cr and Fe from reacted waste using TCLP was determined and waste was treated with Portland cement which minimized further leaching of Cr and Fe (Singh and Singh 2002). Spent adsorbent (Bauxsol and Activated Bauxsol (AB)) were also subjected to TCLP test and the leached concentration of arsenate was very small and below the threshold limit (Genç-Fuhrman et al. 2004a; Genç et al. 2003). Similar results were reported in case of multi metal loaded RM making it environmentally compatible material that could be used for the wastewater treatment (Vaclavikova et al. 2005). Environmental compatibility of Bauxsol™ using three different eco-toxicological tests (Microtox™, ASTM microalgae toxicity, and sea urchin embryo toxicity test) showed no toxic effects. The treated Bauxsol™ showed high metal retention capacity and low leachability at pH 5 of As, Cd, and Cu (<6%) while Mn and Zn were more labile (10–30%) (Brunori et al. 2005). Acute toxic effect of metal-loaded Bauxsol™ reagent (MLBR) containing more than 6450 mg/kg of bound metals, on the earthworm *Eiseniafetida*, was investigated. The results showed good motility and no mortality of *E. fetida* due to low bioavailable fraction of metals as well as the bioaccumulation of metals in the worms and bioaccumulation factors (BAFs) were below than the reported toxicity thresholds to cause mortality (Maddocks et al. 2005). Red mud addition to soil polluted with heavy metals (Castaldi et al. 2009; Garau et al. 2007; Lombi et al. 2002a) and As (Garau et al. 2011; Lee et al. 2011) showed encouraging results in terms of enhanced plant growth, improve biochemical properties of soils, and increased microbial biomass. However, Pagano et al. (2002) reported toxic effects of red sludge and other solid residues from bauxite manufacturing plant (Turkey, France, Greece, and Italy) on sea urchin. These effects were attributed to high concentration of Al and alkaline pH. The variable results in toxicities are attributed to striking variability in ore composition and manufacturing process of by-products. Fluvial sediments collected from a catchment, western Hungary after accidental spill of red mud appeared to induce an increase in the density of aerobic and facultative anaerobic bacterial communities in sediments as compared to unaffected sediments and reference sites while *Lemma minor* appears to be a particularly sensitive test

**Table 5** Ecotoxicological results (Dauvin 2010)

Bioassay	Substrate	1997	1999	2002	2007
Microtox	Organic extract	N	–	–	–
	Interstitial water sample	–	N	–	–
	Lixiviated sample	N	N	N	N
	Sediment contact	–	P	N	N
Larval development (sea urchin/mussel/oyster)	Sediment contact	P <sup>a</sup>	N	N	N
	Lixiviated sample	P <sup>b</sup>	N	N	N
Ames test	Lixiviated sample	N	–	–	–
	Organic extract	N	–	–	–
Acute toxicity	Sediment contact	N	N	–	–
	Elutriated sample	N	–	–	–

N negative, P positive, “–” not measured

<sup>a</sup> Maximum larvae anomaly (38.9%)

<sup>b</sup> Maximal larvae anomaly = 20.1%

organism to the effects of red mud deposition (Klebercz et al. 2012). A more recent study showed that soluble vanadium from red mud spill causes genotoxic and cytotoxic effects in higher plants (Mišik et al. 2014). Moreover, proper ratio of RM addition is an important factor to decrease the toxicities. It was reported that 5% of bauxaline® and bauxsol were not sufficient to lower toxicity of the marine dredged sediment leachates against marine rotifers (Taneez et al. 2015). When the amendment rate was increased (i.e., 20%), the rate of rotifers mortality decreased up to 36% (Taneez et al. 2016). Similarly, decrease in toxicity towards *Aliivibrio fischeri* was also observed at the end of the experiment when 20% of amendment rate was applied compared to the first day of experiment. The results revealed that higher quantity of RM provides more sites for metal adsorptions and the aging help to convert available fraction to other forms (Hurel et al. 2017).

Alteo, the Gardanne alumina refinery (France), is the first site in the world where alumina was manufactured by Bayer industrial process. They formulated a scientific committee in response to the State's regulations to ensure an independent evaluation of bauxite residue discharge on the structure and functioning of bathyal ecosystem in the Cassidaigne canyon (north-western Mediterranean Sea). The committee summarizes the main results obtained during sea campaigns from 1999 to 2007. Variation in the test response depends on the variable composition of the bauxite ore, and manufacturing process as mentioned above (Pagano et al. 2002). No accumulation of trace elements (Al, Cr, Cu, Fe, Pb, Mn, V, and Zn) was found in dominant fish species and no potential health risk due to its consumption. No relationship was also found between measured concentration of toxic metals and the pipe's proximity that reinforces the idea of low potential

danger from the red mud disposal in this area. Nevertheless, the scientific committee has proposed feasible approaches to valorize Bauxaline® because Alteo is compelled to stop discharge at the end of 2015 due to Barcelona Convention for the Protection of the Mediterranean (1976) and the creation of the Calanques National Park (2012). They also recommended that the refinery should conduct a long-term eco-toxicological survey of sediment collected in at least six sampling sites during the next campaign in 2012 (Dauvin 2010) (Table 5). In September 2012, foraminiferal communities (Eukaryota, Rhizaria) were samples from 14 stations at various points and depths from pipe outlet. The gradual change in foraminiferal communities was associated to decrease in sediment organic debris at varying water depths and ecological constrains determined by bottom currents. The study reported no obvious impacts on benthic foraminiferal due to bauxite dispersal suggesting that future studies are required strictly focusing on Cassidaigne Canyon axis near to pipeline outlet to fully understand the spatial hydro sedimentary pollution (Fontanier et al. 2015).

The review of all the afore-mentioned studies revealed that red mud has many environmental but neutralization of red mud is crucial to limit its toxic impacts. The spent RM exhibits low leaching of its components and can be treated further with cement to make it more stable for bricks production or disposed in nonhazardous landfills without causing significant environmental toxicity.

## Conclusions

Red mud is an iron-rich material produced during alumina extraction from bauxite ore. In the past years, red

mud has been widely used as an alternative to expensive adsorbents for environmental cleanup due to its composition. Combined acid and thermal treatment were generally used for improving physico-chemical properties. Large volume of acid is required for a large-scale application which adds cost to the product. Among neutralization methods, the most suitable method which not only improves surface area but also provokes the formation of neo-formed surface without losing acid neutralization capacity of red mud is seawater neutralization. It is evident from the literature that red mud works better after neutralization, i.e., improved stabilization of pollutants in soil/sediments as well as increased retention of metal ions, anions, and organic pollutants from wastewater. Chemical stabilization along with revegetation is an innovative remediation technology. It focuses on reducing the mobility of elements in soil by converting the fraction of elements in non-water extractable forms rather than removing them from medium. On the basis of leaching test, it was confirmed that spent red mud pose no serious secondary contamination and eco-toxicological studies demonstrate that red mud is not toxic to many species test. However, variation in test response depends on different factors such as high pH and Al content, variation in bauxite ore composition, and manufacturing process.

Though the efficacy of treatment depends upon quantity of amendment, media type (soil/sediment) and contaminants to be addressed but large volume of red mud can be consumed. Long-term effectiveness of stabilization process in field experiments should be investigated in future studies focusing on adequate monitoring of the potentially problematic oxyanions (As, Cr, V etc.). Seawater or acid neutralization combined with other treatments can be tested to enhance the adsorption of anionic trace elements. More detailed ecotoxicological investigations of red mud can help to assess its potential ecological and public health impacts and in order to comply with legislative requirements.

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