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A review on bauxite residue usage in air pollution control



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Abstract

Exhausts or emission from industries/automobiles/indoor appliances is one of the most prominent sources of air pollution. Innumerable noxious gases have been identified and been recurrently treated through various technologies from past many decades. Cumulative studies suggest that air pollutants affect the respiratory and cardiovascular systems along with the central nervous system, may it be directly or indirectly. In particular, acquaintances to such air pollutants in early life can lead to developmental delays and may stunt neurological development. This review presents the recent technologies that have been tested at the laboratory level as well as in situ utilizing one of the abundantly available industrial wastes, i.e. red mud. Unlike the conventional expensive catalysts, red mud provides a cheaper alternative in the treatment of toxic exhaust gases from various sources. Furthermore, the review identifies the gap through which experts from other disciplines can explore the employment of red mud in the comprehensive spectrum of pollution control.

Keywords Red mud, Adsorbent, Catalyst, Bauxite residue, Emission control

1 Introduction

Any material, either solid, liquid, gas or a mixture of these, discharged or left as residue from any industry can be categorized under industrial waste. Such waste can be hazardous, non-hazardous, reusable or non-reusable (Taneez & Hurel, 2019). Despite the precautions and several waste management regulations, an enormous amount of waste accumulation is happening. Therefore, industrial waste usage has become one of the major topics for active research and is attracting faculties from different disciplines. Of late, some of the industrial solid wastes are being used as an alternative to commercially available catalysts/adsorbents, thus paving a way for solid waste management. This has also become an important area to explore further.

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Industrial waste is contemplated as problematic due to the increase in industrialization worldwide (Li et al., 2021, Shuai et al., 2021). In this review, we will cover the use of the solid type of industrial waste principally red mud which is obtained from aluminium industries. The review discusses the works related to the application of red mud mainly towards environmental purposes (Bhatnagar et al., 2011, Li et al., 2022, Khairul et al., 2019, Shi et. al., 2020). Bauxite residue has been revealed as a very good industrial waste for adsorption and catalytic processes involving cleansing of gaseous pollutants released from emission/exhausts of different systems (Mishra et al., 2021). This review includes a critical analysis of the red mud production, its usage in the removal of various gases and disadvantages post its usage, thus summarizing the red mud-based adsorption/catalysis process. The literature survey mainly comprises those works where actual emission/exhaust was treated either at lab or in situ by red mud or its components. A peripheral reference has, however, been made about other practical applications of red mud. The review begins with a brief note on the bauxite reserves, bauxite processing



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and properties of bauxite residue with respect to the global and Indian context so that the reader will be able to understand the abundant reserves of this solid waste. The review ends up with a note about the possible future applications of red mud.

2 A note about bauxite and its residue

It is worth mentioning at this juncture the origin of red mud briefly. Aluminium accounts for approximately 7% by mass and is available in the crust of the earth abundantly (Atun et al., 2021; Wang et al., 2019; Zinoveev et al., 2021). The commercial manufacturing of aluminium initially started in the year 1854. It is the most usable metal globally after steel (Evans et al., 2012; Kirwan et al., 2013). Also, owing to its several advantages such as flexibility, impermeability, light weight and corrosion resistant, the demand for aluminium is increasing every year. However, naturally, aluminium is observed as clay [silicates] and as oxides in combination with numerous mixtures of silica, titania and other impurities in small quantities. Production of alumina is a chemical augmentation progression in which alumina is isolated from undesirable ingredients such as oxides of calcium, vanadium, manganese and silicon from bauxite ore (Evans, 2016). During the manufacturing of alumina, two products namely primary and secondary aluminium are obtained. The primary one is molten metal and obtained from bauxite through two processes, the Bayer process and Hall-Heroult process. The secondary aluminium is just a finished or usable part (Thakor et al., 2019). At high temperature and pressure, reaction with NaOH yields red mud as a derivate from bauxite ore (Sutar et al., 2014). It has been estimated that for every 2-3 tons of bauxite utilized during the process about 1-2.5 tons of red mud is obtained. According to the predicted data, approximately 70 million tons of red mud is produced globally where India itself produces about 9 million tons annually (Liu & Wu, 2012; Rai et al., 2012). Being a solid waste, usually, red mud is either dispensed in mud lakes as slurry or dumped off in solid form in the nearby areas. As an abundant quantity of metals is present in red mud, it poses certain environmental threats such as soil contamination and groundwater effluence (Renforth et al., 2012; Wanchao et al., 2014). From the last few decades, substantial work has been reported in the field of utilizing red mud which includes the preparation of boilers/furnace liners, the removal of various metals, fluorides, phosphates and dyes; catalyst preparation; recovery of trace metals; composing of cements; etc. (Liu & Wu, 2012; Kalkan et al., 2006) but a large part of its application still remains an area of research for the scientific and engineering fraternity.

Table 1 Global production of bauxite

Countries	Production [in 1000 tonnes]		
	2019	2020	
Australia	105,000	110,000	
Guinea	67,000	82,000	
China	70,000	60,000	
Brazil	34,000	35,000	
Indonesia	17,000	23,000	
India	23,000	22,000	
Jamaica	9020	7700	
Russia	5570	6100	
Kazakhstan	5800	5800	
Vietnam	4000	4000	
Saudi Arabia	4050	4000	
Other countries	12,000	11,000	

Table 2 Distribution of bauxite in India

State	Percentage
Odisha	52%
Andhra Pradesh	18%
Gujarat	7%
Chhattisgarh	5%
Maharashtra	5%
Others	13%

The alumina source, i.e. bauxite, is a rock-like structure obtained from laterite soil. The soil is sternly leached in a sub-tropical climate and it was diagnosed to consist of aluminium (Liu et al., 2009; Mukiza et al., 2019). Although bauxite does not have any specific constitution, it contains clay minerals, aluminium oxides and hydroxides, etc. It has a specific gravity of 2.6 to 3.5 as is observed in the pink colour due to the presence of iron in it. Bauxite resources are assessed to be 55 billion to 75 billion tons with a breakup of contribution from different countries. The list of countries by production of bauxite as latest reported by the US Geological Survey, Mineral Commodity Summary, January 2021, has been depicted in Table 1.

In India, Odisha itself is responsible for approximately 52% of the country's possessions of bauxite followed by other states (Borra et al., 2016; Rai et al., 2017). The distribution of the bauxite resources has been given in Table 2. India ranks 6th place globally contributing 3.19% to the world's total reserves. Odisha and Andhra Pradesh subsidize for >90% of the country's resources (Lee et al., 2017; Lima et al., 2017).

The abstraction of alumina [Al₂O₃] through the Bayer process is an economic way compared to other processes using bauxite residue, which may result in a relatively small proportion of alumina (Evans, 2016; Rai et al., 2020). The bauxite is crumpled, grinded and then assorted with caustic soda solution and impelled in claves (Samal et al., 2013). Thereafter, under 1-6 bars and at 110-270°C, the liquification of alumina to sodium aluminate takes place. The silica in the form of sodiumaluminium-silicate precipitates out. However, other impurities such as titanium oxides remain unaffected. The by-product obtained is red mud or bauxite residue. It is then washed to recover caustic soda and then dumped off (Reid et al., 2017; Samal et al., 2013). A schematic representation of the Bayer process has been depicted in Fig. 1. The next section briefly presents the properties of bauxite residue which may help subsequently in understanding the chemistry while discussing the applications of the same.

In general, the overall behaviour of a material is intrinsically governed by its particle size and its physical properties. The information obtained from particle size distribution includes a section of particle sizes along with the ascendency of a particular size section (Botelho Junior et al., 2021). As reported, the size of red mud particles ranges between 5 and 10 μ m, i.e. coarse to sub-micron (Tanvar & Mishra, 2021). Some studies have suggested that red mud contains more than 50% of the clay size fraction, which may be attributed to the grinding and crushing process. However, in the Bayer process, grinding is not substantial and can only discharge not less than 10 µm. Newson et al. stated a decrease in particle size due to the washing in acidic solution which has resulted in fine particles getting separated (Newson et al., 2006). Pradhan et al. stated dissimilarities in particle segments in the range 0.01 to 200 μ m due to the variance of the raw bauxite ore and the method adapted for separation (Oprčkal et al., 2020). Wang and Liu stated that particle sizes of red mud are smaller as obtained from the Bayer process in contrast to that obtained from the sintering procedure (Ye et al., 2018). Grinding of the red mud also disturbs certain physical parameters namely angular outlines and resistance due to friction. In addition, the angular outlines influence Young's modulus of particles and improve the friction between the particles, thereby improving the shear force (Deihimi et al., 2018; Vigneshwaran et al., 2019). Angularity is required when red mud is employed in various geochemical applications (Huang et al., 2016; Kirwan et al., 2013). Many researchers have emphasized about the enhancement of the subsiding characteristics of particles as a result of different aqueous environments. However, the occurrence of finer particles, chiefly comprising of minerals such as goethite and sodalite, influences the settling features in the case of red mud (Liu et al., 2017). After the disposal of red mud, segregation of particles starts; hence, understanding the features of the distribution of particle size is significant in recognizing the behaviour of material which will further support in storing of red mud (Chun et al., 2014).

In addition to the physical properties, the mineralogical and chemical compositions of red mud are also vital. The sandy portion of red mud may contain quartz. According to a study (Chun et al., 2017), red mud is composed of Al-goethite, cancrinite, sodalite, haematite, silica, calcium aluminate, calcite, boehmite, anatase, muscovite, perovskite, magnetite, kaolinite, gibbsite and diaspore. The major chemical compositions of red mud are ferric oxide, silicon dioxide, aluminium oxide, titanium dioxide, calcium oxide and sodium oxide. The major and minor mineral forms of bauxite residue have been depicted in Table 3 (Zhu et al., 2012). The XRD studies have shown that the main composition of Bayer red mud depicts the highest percentage of perovskite and sodium aluminate, whereas sintering red mud consists of dicalcium silicate, calcite, perovskite and magnetite. Furthermore, the ICP-MS studies have proved the presence of trace elements in the red mud (Wang & Liu, 2012; Rathod et al., 2013; Liu et al., 2016; Liu & Li, 2015; Zhang et al., 2010; Atun & Hisarli, 2000; Zhang et al., 2018). Chemical compositions of red mud produced by alumina refineries are summarized in Table 4. Quite the reverse, certain measurement errors were seen in red mud from different countries



Table 3 Red mud composition: mineral and chemical

Existing element	Mineral	Chemical composition
Fe	Haematite	a-Fe ₂ O ₃
	Goethite	a-FeOOH
	Magnetite	Fe ₃ O ₄
	Ilmenite	FeO·TiO ₂
	Ferryhydrite	Fe ₂ O ₃ ·0.5H ₂ O
	Maghemite	γ-Fe ₂ O ₃
AI	Gibbsite	α-Al ₂ O ₃ ·3H ₂ O
	Boehmite	α -Al ₂ O ₃ ·H ₂ O
	Diaspore	β -Al ₂ O ₃ ·H ₂ O
Ті	Anatase	TiO ₂
	Rutile	TiO ₂
	Perovskite	CaTiO ₃
	Ilmenite	FeO•TiO ₂
Si, Al, Na, Ca	Quartz	SiO ₂
	Kaolinite	$Al_2Si_2O_5(OH)_4$
	Sillimanite	Al ₂ SiO ₅
	Halloysite	$Al_2Si_2O_5(OH)_4$
	Sodalite	$Na_8(Al_6Si_6O_{24})Cl_2$
	Cancrinite	Na ₆ Ca ₂ [(CO ₃) ₂ Al ₆ Si ₆ O ₂₄] ·2H ₂ O

Table 4 Red mud chemical composition

Composition	Percentage
Fe ₂ O ₃	19%
Al ₂ O ₃	42%
SiO ₂	8%
TiO ₂	11%
Na ₂ O	5%
CaO	3%
Others	12%

(Reddy & Rao, 2018, Aleixandre-Tudó et al., 2019., Dali-Youcef & Queneudec, 2011). Additionally, it is evident that red mud has in abundance oxides of iron which will enable one to make a rational assumption that the nature and behaviour of red mud may be largely influenced by these oxides.

3 Applications of bauxite residue in pollution control technologies

3.1 Bauxite residue as a catalyst for actual exhaust treatment

Using waste material as a possible catalyst supplements value to the waste. Bauxite residue has received a substantial consideration in this respect. Sushil and Batra (2008) studied the removal of highly toxic exhaust gas, i.e. CO, through red mud. They found that acid-treated red mud displayed higher activity towards CO oxidation compared to the original ones. The increased activity of the acid-treated red mud was discovered to be the preservation of hydroxylated iron oxide along with increased surface area. The reason attributed to the increased activity of FeOOH over Fe_2O_3 is the ease with which the oxygen is lost. However, the original red mud was also found to be active towards CO oxidation and the component affecting the catalyzing property was discovered to be Fe_2O_3 . It was also reported that the activity of red mud was more desirable than commercially available red iron oxide.

Mohapatro and Rajanikanth (2012) studied red mud as a catalyst for abatement of NO_x from an actual diesel exhaust engine. The catalyst was operated at a temperature of 400° C. It was reported that the metallic iron was preferable compared to its oxide for the breakdown of NO to NO_2 . NO reduction through CO over Fe_2O_3 takes place as

$$12\text{CO} + 4\text{Fe}_2\text{O}_3 \rightarrow 12\text{CO}_2 + 8\text{Fe} \tag{1}$$

$$8Fe + 12NO \rightarrow 6N_2 + 4Fe_2O_3 \tag{2}$$

$$\rm CO + NO \rightarrow \rm CO_2 + 1/2N_2$$
 (3)

For the NO₂ removal, the possible pathway was stated as follows (Liu et al., 2009):

$$8Fe + 6NO_2 \rightarrow 3N_2 + 4Fe_2O_3 \tag{4}$$

It was also stated that Al_2O_3 present in red mud supports the reduction of NO_x , in the company of formaldehyde which is also a part of diesel exhausts. The possible reaction was as stated,

$$CH_3O + NO \rightarrow CH_3ONO$$
 (5)

$$CH_3O + NO_2 \rightarrow CH_3ONO_2$$
 (6)

It was also reported that the exclusion competence of NO_x augmented with temperature and the maximum efficiency was achieved at 400° C. As observed during the course of the reaction, red mud was also efficient for CO conversion. Hence, the study claimed that red mud can be more economical in the mitigation of carbon and nitrogen oxides from stationary diesel exhausts (Mohapatro & Rajanikanth, 2012).

Kim et al. (2015) studied red mud as a catalyst for the complete oxidation of volatile organic compounds (VOCs). VOCs are one of the most toxic groups of gases generated by several biomass as well as vehicular emissions. They compared Pt-supported catalysts on γ -Al₂O₃ (Pt/Al) with platinum-loaded acid-treated red mud catalyst (Pt/HRM). It was reported that acid treatment tends to increase the

BET surface area of the red mud correspondingly upgrading its catalytic activity. Also, the increase in temperature from 400 to 600°C resulted in a decrement in the catalytic activity, whereas an increase in the platinum loading on acid-treated red mud led to an augmentation in toluene conversion because of improved redox properties. It was also reported that the catalytic activity of Pt/HRM (400°C) was preferable compared to Pt/Al catalysts. However, the study did not target the real-time actual emissions of VOCs which otherwise would have given a clear picture of the catalytic activity of red mud.

Liu et al. (2022) reported the simultaneous elimination of SO_2 and NO_r by a combination of yellow phosphorous emulsions with red mud from coal-fired flue gas. At optimized conditions, the removal efficiency of NO_r and SO_2 was reported to be 97.9% and 100% respectively. Examining the sample before and after the reaction indicated that the gypsum (CaSO₄·2H₂O) is the main product responsible for desulphurization and denitrification. It was demonstrated that O₃ played a significant role in the oxidation of NO to NO₂, NO₃ and N₂O₅, further increasing the amount of acid formation which thereby improvises the denitration efficacy of the system (depicted in Eqs. 7 to 13). The red mud contribution in the removal of NO_r is to offer an environment which is alkaline. It also provides a platform as a pH buffer. An upsurge in the SO₂ removal during the study may be attributed to the decomposition of ferrous in bauxite residue along with the ozone present in the prevailing environment, both of which possess strong oxidation characteristics. This in turn causes the suspension of SO_2 in water, further generating HSO_3^- and the catalytic oxidation of SO_3^{2-} to generate SO_4^{2-} by re-electrolysis (Eqs. 14–16). However, the reaction reduces ferric to ferrous which in turn gets oxidized to ferric again (Eq. 17). Moreover, it was summarized that for red mud concentration greater than 30 g/L, there will be stability in the removal of NO_x and SO₂.

$$P_4 \xrightarrow{O_2} P_2 O_5 + O \xrightarrow{O_2} O_3 \tag{7}$$

$$P_2O_{10} + 6H_2O \rightarrow 4PO_4^{3-}$$
 (8)

$$O_3 + NO \rightarrow NO_2 + O_2 \tag{9}$$

$$O_3 + NO_2 \rightarrow NO_3 + O_2 \tag{10}$$

$$2NO_2 + H_2O \to NO_2^- + NO_3^- + 2H^+$$
(11)

$$NO + NO_2 \rightarrow N_2O_3 \xrightarrow{H_2O} 2NO_2^- + 2H^+$$
(12)

$$NO_3 + NO_2 \rightarrow N_2O_5 \xrightarrow{H_2O} 2NO_3^- + 2H^+$$
(13)

$$SO_2 + H_2 \rightarrow H_2SO_3 \rightarrow HSO_3^- + H^+ \rightarrow SO_3^{2-} + H^+$$
(14)

$$O_3 + SO_3^{2-} \to SO_4^{2-} + O_2$$
 (15)

$$SO_2 + 2Fe^{3+} + 2H_2O \rightarrow SO_4^{2-} + 4H^+ + 2Fe^{2+}$$
(16)

$$2Fe^{2+} + SO_2 + O_2 \rightarrow 2Fe^{3+} + SO_4^{2-}$$
 (17)

Apart from the above, red mud is extensively used as a catalyst in various reactions. Bauxite residue as a catalyst has been used for coal, biomass, organic compounds and petroleum residues. In the case of coal, iron catalyst, pyrites and bauxite residue, etc., have been already used in the past (Wang et al., 2020, Sun et al., 2021, Rahman et al., 2021, Ahmed et al., 2020). It was also reported that bauxite residue is unassailable to catalytic poisons such as sulphur and hence unable to drop their distinctiveness easily (Rahman et al., 2021). However, due to the minor level of dispersion and surface area, the effectiveness of such catalyst has been stunted (Karimi et al., 2010). The activity of this catalyst can be improved through certain treatments such as reduction in size and sulphidation. Also, unlike other expensive catalysts, this does not have to be recovered after the reaction. Catalysts utilized for hydrodechlorination reaction include precious metals such as platinum (Pt), palladium (Pd) and rhodium (Rd). Nevertheless, these catalysts are too expensive and also more susceptible to poisoning by HCl and other complexes generated during the course of the reaction.

Literature shows another application of red mud as a catalyst in the reduction of SO_2 using CO (Saral & Ranganathan, 2021, Wang et al., 2022, Tao et al, 2019). The reaction takes place as follows:

$$\rm CO + SO_2 \rightarrow \rm CO_2 + SO$$
 (18)

$$CO + SO \rightarrow CO_2 + 1 \setminus 2S_2$$
 (19)

$$Or, SO \to 1 \backslash 4S_2 + {}_2{}^1SO_2 \tag{20}$$

$$2\text{CO} + \text{SO}_2 \rightarrow 1 \backslash 2\text{S}_2 + 2\text{CO}_2 \tag{21}$$

However, it was observed that red bauxite and Surinam red mud showed the highest catalytic activity (approx. 30% at around 640 °C) for the $CO-SO_2$ reaction while Jamaican red mud showed moderate activity (approx. 26% around 500 °C), whereas other resources possessing

low or insignificant iron content exhibited poor activity (Jahromi & Agblevor, 2018; Niu et al., 2021).

Shao et al. (2022) demonstrated the use of red mud as a catalyst in the ketonization of bagasse pyrolysis gas. They also studied the metal oxide loading and loading amount on the production of ketones. According to their report, the yield of ketones over the red mud (420°C) and the red mud annexed with CeO₂ was 18.66% and 27.86% respectively. They also stated that loading of both CeO₂ and MnO₂ simultaneously on red mud reduced its cost as well as improved its ketonization ability. The catalytic application of red mud has been summarized in Table 5.

3.2 Red mud as an adsorbent for actual exhaust treatment

The adsorption potential of red mud has been significantly utilized by many researchers. A compilation of studies related to red mud-based adsorbent established along with their adsorption capacities and the mechanism has been provided. Although it is apparent from the literature survey that red mud has been extensively employed as an adsorbent, yet, investigations on the practical utility of these adsorbents on a commercial scale still remain obscure.

Yang et al. (2018) studied bauxite residue, which was treated with potassium bromide and potassium iodide, for the removal of elemental mercury (Hg^0) from the flue gas. The researchers reported that potassium halides enhanced the activity for the removal of Hg^0 in red mud. Also, KI-amalgamated red mud displayed the highest efficacy for Hg^0 elimination. It was also stated that an increase in loading value, reaction temperature, NO concentration and O₂ concentration accelerated Hg^0 capture, whereas an increase in SO₂ concentration retarded Hg^0 removal. Mercury has been viewed among the most toxic pollutants attributed to its several properties such as high volatility, bioaccumulation, neurological toxicity and prolonged existence in the atmosphere. Mercury obtained from fossil fuel emission first remains as elemental mercury Hg^0 in flue gas; then, a small portion gets transformed into particle-bound mercury (Hg^p) and oxidized mercury (Hg^{2+}) respectively. It was also stated that the Hg^0 capture process of KI-modified and KBr-modified red mud displayed a pseudo-second-order kinetic model.

Nath and Sahoo (2018) employed bauxite residue to decontaminate gas with fluorine generated from the aluminium industry. They concluded that the reaction between iron, aluminium and sodium present in the bauxite residue along with fluorine in gaseous form leads to the production of ferric fluoride, ferrous fluoride, aluminium fluoride and sodium fluoride, thus accomplishing the conversion of fluorine gas.

Tao et al. (2019) studied bauxite residue combined with water to form an adsorbent for SO₂ abatement from flue gas. The ratio between liquid and solid was found to be 20:1, the temperature was 25 °C and SO₂ concentration was 1000 mg/m³. It was also stated that the accumulation of SO_4^{2-} decreases desulphurization efficacy. Li et al. (2020) studied the simultaneous elimination of pollutants such as sulphur oxide and nitrogen oxide flue gas originating from industries by employing O₃ oxidation. The result displayed that the increase in oxidation temperature was unfavourable for NO_x adsorption. Furthermore, the study also stated that a high concentration of SO_2 represses the adsorption of NO_r , whereas a low concentration of SO₂ promotes NO_x adsorption. According to the study, at an oxidation temperature of 130°C, the molar ratio of 1.8, O_3/NO_r , the efficiency of bauxite residue for desulphurization reached 93% and for denitration, it was 87% in the first hour.

Zhang et al. (2020a, b) reported that fresh coal cakes can be used instead of raw coal in pollution abatement technologies. In this experiment, bauxite residue was used as a supplement in coal cakes. It results in a reduction of $PM_{2.5}$, organic carbon and elemental carbon. However, total carbon (TC)/PM_{2.5} continued to be constant between raw coal and briquettes, whereas elemental

Field of application	Cotalutic form	
	Catalytic form	[°C]
Organochlorinated compound hydrodechlorination	Calcinated bauxite residue	300
Hydrogenation of coal	Untreated bauxite residue	400
Liquefaction of coal	Sulphur promoted bauxite residue	450
Hydrogenation of rye straw	Untreated bauxite residue	400
Liquefaction of biomass	Sulphur promoted bauxite residue	400
Hydrogenation of naphthalene	Activated bauxite residue	350
Combustion of methane	Activated bauxite residue	640
Reduction of sulphur oxide	Untreated bauxite residue	650
Oxidation of nitrogen oxide	Cu infused bauxite residue	350

Table 5 Catalytic applications of red mud

carbon/organic carbon was modified significantly ranging from approximately 0.3 to 0.08 for bituminous and around 0.080 to 0.030 for anthracite. This may be attributed to the possible adsorption of EC and OC on the bauxite residue surface. In most part of the China region, cooking and heating were carried out by burning the coal. Hence, briquette-loaded red mud can be an economically effective way to improve the air quality which otherwise gets contaminated due to coal combustion releases. Rushendra Revathy et al, (2021) demonstrated carbonation of bauxite residue with flue gas concentration of carbon dioxide. According to the study, the maximum decrease in CO_2 concentration was 18% in wet phase aqueous carbonation of red mud.

Fan et al. (2005) reported a study for coal gas desulphurization. They organized a fixed bed reactor by means of mixed clay containing red mud sorbent. The sorbent showed better performance in durability and sulphur capacity. Sahu and Patel (2011) employed red mud to adsorb hydrogen sulphide gas. They stated the reactions of Fe, Ca and Na in bauxite residue with hydrogen sulphide resulting in the formation of FeS, FeS₂, CaSO₄·2H₂O and Na₂S, along with other compounds. Zhang et al. (2021) worked with red mud-limestone slurry as a composite absorbent for flue gas desulphurization. These researchers concluded that the process is reliable in the case of desulphurization from calcination.

Interestingly, red mud has also been used as an adsorbent for several wastewater treatments. Li et al. (2017) created iron-aluminium-lanthanum trimetallic hydroxide adsorbent for eradicating F⁻ from water using aluminium and iron discharged from bauxite residue as the principal components. They reported the adsorption capacity around 74 mg with pH lying from 3 to 9. The usage of bauxite residue and pyrolusite for the adsorption of Mn and Ar in water has also been studied (Pietrelli et al., 2019). Apart from the above, numerous red mud adsorbents have proved to be beneficial for the removal of phosphate dissolved in water (Chen et al., 2018). The red mud prepared by the ligand substitution mechanism and precipitation on the surface has been more effective in the removal of phosphate using graphite carbonitride $(g-C_3N_4)$ and red mud and preparing a complex mixture through a one-step thermal polymerization technique. This complex mixture was then used to remove organic pollutants dissolved in water such as tertracycline and chlorotetracycline.

Another study conducted by Silveira et al. (2021) reported that red mud cementitious compound cubes adapted with activated carbon can be utilized in sand filters and in filter pools. It was also shown that in pervious concrete making red mud can be used as a covering substance for an environmentally supportable pollution elimination

strategy so that the lakes and dams constructed with this concrete can be certified to hold rainwater. The study concluded that the adsorptive cubes prove to be effective in adsorbing minerals mainly barium to the extent of about 90% just by replacing 10% of the cement with bauxite residue. This result is significant because barium is extremely noxious and broadly used in various industries. Turk et al. (2021) prepared a nitrocellulose membrane coated with bauxite residue that exhibits larger contact angles with water. The top rough surface provided superior oil rejection efficacy. They concluded that the membrane coated with bauxite residue can definitely be an efficient one for separating the oil fraction in water emulsions.

3.3 Red mud cascaded/blended with discharge plasma for actual exhaust treatment

Mohapatro and Rajanikanth (2012) studied the non-thermal plasma effect on gas cleaning by using a novel method, wherein the plasma was connected in series with an adsorbent reactor which was filled with red mud. They have observed that the DeNOx efficiency with bauxite residue and discharge plasma was found to be 31% and 74% respectively. However, it was amplified to as high as 92% when the discharged plasma was cascaded with bauxite residue which was heated to a temperature of about 400°C. The DeNOx study was carried out with clean diesel exhaust and evaluation was done on the performance of the reactor. It was also stated that due to the enrichment of oxygen in diesel exhaust, an efficient conversion of NO to NO₂ is observed. Equations 22-32 can be assessed for the same.

NO–NO₂ conversion involving O/O₃/NO₃

$$O_2 + e \rightarrow O + O + e$$
 (22)

$$NO + O \rightarrow NO_2$$
 (23)

$$O_2 + O \rightarrow O_3$$
 (24)

$$NO + O_3 \rightarrow NO_2 + O_2 \tag{25}$$

$$NO + NO_3 \rightarrow NO_2 + NO_2$$
 (26)

NO reduction reaction

$$N_2 + e \to N + N + e \tag{27}$$

$$NO + N \rightarrow N_2 + O$$
 (28)

NO₂ conversion,

$$NO_2 + O \rightarrow NO + O_2 \tag{29}$$

$$NO_2 + O_3 \rightarrow NO_3 + O_2 \tag{30}$$

$$NO_2 + NO_3 \rightarrow N_2O_5 \tag{31}$$

$$NO_2 + N \to N_2O + O \tag{32}$$

Bhattacharyya and Rajanikanth (2015) conducted a study using high-frequency AC [HFAC] plasma along with red mud to treat biodiesel exhausts. It was observed that the activity of the red mud as catalyst/adsorbent was enhanced on treatment with the proposed combination. The NO_x removal efficiency was approximately 60-72% at a specific energy of 250 J/L. They also analysed the DeNOx efficiency with two plasma reactors having similar geometries and moderately different annular gaps. The result displayed that the NO_x removal efficiency for the reactor with gap length of 3.11 mm and 2.8 mm was 61% and 72% respectively. The power characteristics of the two reactors were also assessed during the study.

Madhukar & Rajanikanth, (2019b) studied the blend of electric discharge along with adsorbent and catalyst using solid industrial waste. Diesel engine exhaust under dry conditions was introduced to discharge plasma environment and the exhausts treated with discharge plasma were put through catalysis over red mud. The DeNOx efficiency was reported as 70% in the above study. Nishanth and Rajanikanth (2021) discovered red mud packed surface reactor and studied the treatment of NO_r and the total hydrocarbons (THC) released from diesel exhausts using plasma catalysis. During the study, NO_r and THC removal efficiency achieved was 96% and 43% respectively. For the NO_r removal study, the plasma catalysis studies were compared with the results of discharge plasma-based studies and with the results of plasma connected in series with bauxite residue. In plasma catalysis, an additional reaction may happen at the surface level owing to the gaseous pollutants getting adsorbed on the surface of the catalyst. The mechanism which might have attributed to the surface-mediated catalytic activity has been given below.

Langmuir-Hinshelwood (L-H) mechanism:

$$O_3 + * \to O_2 + *O_{ads.} \tag{33}$$

$$*O_{ads.} + *HC_{ads.} \rightarrow CO_x + H_2O + *$$
(34)

Eley–Rideal (E–R) mechanism:

$$*HC_{ads.} + O_3 \rightarrow CO_x + H_2O + *$$
(35)

where $*O_{ads.}$ refers to highly active O_2 species adsorbed on the surface of the catalyst and $*HC_{ads.}$ refers to the absorbed HC and * refers to those sites on the catalysts which are active.

It was also reported that the activation of plasma in catalytic oxides in bauxite residue also plays a significant role during catalysis. Fe_2O_3 has been found to play an important role in the reduction of NO/NO₂ through following reactions involving CO and metallic Fe (Sushil and Batra, 2008).

$$3CO + Fe_2O_3 \rightarrow 3CO_2 + 2Fe \tag{36}$$

$$8Fe + 12NO \rightarrow 6N_2 + 4Fe_2O_3 \tag{37}$$

$$8Fe + 6NO_2 \rightarrow 3N_2 + 4Fe_2O_3 \tag{38}$$

 Al_2O_3 has also been reported as a catalyst in the reactions involving NO_x and methoxy radicals (Madhukar & Rajanikanth, 2019b). The following reaction pathway was suggested for NO_x reduction to CH_3NO_2 and CH_3NO_2 in the presence of Al_2O_3 (Madhukar & Rajanikanth, 2019a).

$$CH_3CHO + O \rightarrow CH_3CO + OH$$
 (39)

$$CH_3CO + O \rightarrow CH_3O + CO$$
 (40)

$$CH_3O + NO \rightarrow CH_3NO_2$$
 (41)

$$CH_3O + NO_2 \rightarrow CHNO_3$$
 (42)

In exhaust gas, the reduction of NO_x can be attributed to hydrocarbons and carbon monoxide, as a result of which NO_x is reduced to N_2 and O_2 . However, CO and hydrocarbons oxidize into CO_2 and H_2O . It has also been reported that the reaction intermediates which are formed during NO_x reduction to NO_2 and N_2 are similar to the ones involved in the oxidation of nitromethane (CH₃NO₂). Also, TiO₂ in bauxite residue has been found to be a potent photocatalyst in the presence of plasma for treating diesel exhausts. Activation of TiO₂ is achieved by adsorbing metastable N_2^* species which is present in the plasma environment. Moreover, the following reactions are suggested (Snigdha & Vidya, 2011).

$$2\text{CO} + 2\text{NO} \rightarrow 2\text{CO}_2 + \text{N}_2 \tag{43}$$

$$NO_2 + N \to O + N_2O \tag{44}$$

$$N_2O + CO \rightarrow CO_2 + N_2 \tag{45}$$

$$CH_3O + NO \rightarrow CH_3NO_2$$
 (46)

$$CH_3O + NO_2 \rightarrow CH_3NO_3$$
 (47)

$$2NO_2 + 8CH_3NO_3 \rightarrow 5N_2 + 8CO_2 + 12H_2O$$
 (48)

$$6NO_2 + 8CH_3NO_2 \rightarrow 7N_2 + 8CO_2 + 12H_2O$$
 (49)

Hence, in diesel exhausts, hydrocarbons play a significant role in the oxidation of nitrogen oxide to nitrogen dioxide during plasma catalysis. It was confirmed from the study (Nishanth & Rajanikanth, 2021) that plasma catalysis outstripped other methods involving plasma treatment at larger loads including higher NO_x concentrations.

3.4 Red mud usage as an additive

Several potential and sustainable utilization of red mud has been proposed by many researchers. Prevailing studies suggest that red mud can replace fly ash to a particular extent in cement-based materials, thereby increasing its mechanical strength and reducing the voids of concrete (Tian et al., 2021, Hou et al., 2021, Li et al., 2021., Tang et al., 2019). Red mud has also been utilized in making ceramics, and the effect of temperature and pressure along with microstructure and preparation procedure has been expansively explored by many scholars (Pontikes et al., 2009, Pérez-Villarejo et al., 2012, He et al., 2012a). Red mud has also found its usage in raw building materials like concrete, cement and structural and subgrade fillers, thus reducing the environmental load caused by red mud waste (Krivenko et al., 2017; Liu & Poon, 2016; Panda et al., 2017). Paraffin and red mud have been concertedly utilized to display high thermal stability and enhanced mechanical quality. However, various disadvantages and apprehensions persist such as low compressive strength, and depreciation in mechanical strength in concrete have been noticed. Moreover, the precautional efficacy of leaching and radiation via red mud remains uncertain.

Besides, red mud has also been engaged in geopolymer formation in combination with various minerals such as rice husk, slag municipal, arsenic sludge, fly ash and coal gangue (Afolabi et al., 2019, Ahmed et al., 2021, Qaidi et al., 2021, Qaidi et al., 2022, Zaid et al., 2022). Wagh and Douse (1991) were probably the first ones to publish an organized study on alkali-activated red mud. Different silicate solutions with SiO₂/Na₂O weight ratios of 2.0-3.2 were chosen as activators next to a solid metasilicate. It was reported that a rise in red mud concentration resulted in increasing the setting time of concrete in geopolymer cement and alkali-activated binders, representing that red mud functioned as a retardant (Lemougna et al., 2017a, b, Bayat et al., 2018). Zhang et al. (2020a, b) and Shaker et al. (2022) reported a reduction in the fluidity of the red mud slag paste as the particle size of red mud enlarged. Lemougna et al. (2017a, b) explored the usage of red mud as a solid precursor for inorganic polymers by introducing sodium-silicate taking SiO₂ and Ni₂O at different proportions. It was also reported that higher inclusion of red mud decreases the strength of the polymer to less than 30 MPa (Lemougna et al., 2017a, b). Hairi et al. (2015) employed 94 wt% red mud as the chief constituent for inorganic polymers. To activate the blend, Na-silicate solution was used. They concluded that silica fume specifically promoted the strength of the products. Several studies have been conducted using red mud and fly ash in the synthesis of geopolymers. He et al. (2012a, b) blended fly ash and red mud in three different ratios for the formation of geopolymers, viz., 80:20, 50:50 and 20:80 using 1.5M sodium trisilicate solution as an activator. Kumar and Kumar (2013) studied the introduction of red mud in 0 to 40 wt% in the fly ash and red mud mixture along with NaOH solution as an activator. Zhang et al. (2016) synthesized a geopolymer using red mud and fly ash in a ratio 4:1. The activator employed in this process included 50 wt% sodium hydroxide, 2M sodium trisilicate and deionized water. Choo et al. (2016) used red mud as an alkali activator in enhancing the compression strength of red mud and fly ash. In this experiment, five different median sizes of fly ash $(D_{50}=12, 21, 22, 15,$ 20) were mixed with red mud ranging from 0 to 60%. Nie et al. (2016) studied the increase in compression properties of geopolymers developed out of red mud and fly ash when it was blended with NaOH solution. Kim et al. (2017) prepared a geopolymer mixing red mud with Ca (OH)₂, Na₂CO₃ and fly ash, thus studying the effect with various proportions of red mud. Recently, Guru et al. (2019) proved that the introduction of red mud as inorganic fillers improved the composition of the plastic matrix, thereby upgrading light-shielding, fire-resistivity and insulation capacity.

4 Challenges and scope for future works

Studies show that a considerable amount of work has been done on red mud utilizing it in the production of different building materials such as cement and bricks. Also, the extraction of metals from red mud has been a prominent research area in the last few decades. However, in the field of pollution control technology, limited work has been conducted particularly in wastewater cleansing and treatment of emission/exhaust and other gases containing sulphur. It is worth mentioning that the research on the abatement of major air pollutants and polluted indoor air is still an undiscovered area and needs a serious concern due to the increase in the concentration of air pollutants day by day. Ambient as well as indoor air pollution is one of the major concerns globally. Indoor air pollution is accountable for more than a million death annually. Some common indoor pollutants such as volatile organic compounds [VOCs] and polycyclic aromatic hydrocarbons [PAHs] pose a major threat to human well-being. The sources of these pollutants are present indoors as well as outdoors. PAHs are classified as carcinogenic owing to their various effects on human organs (Dwivedi et al., 2022). In spite of such deadly outcomes, abatement of air pollutants is still an underdeveloped area of research.

5 Conclusion

Summarizing, the use of red mud for pollution treatment is a characteristic illustration of "use waste to treat waste", with significance for employment of solid waste. The potential utilization of red mud has been demonstrated in the current review. It is quite challenging to attain an exclusively cost-effective and environmentally supportable technique for managing this industrial waste. The usage of industrial waste in the abatement of indoor air pollutants will offer a benchmark to professionals in this field. The presence of photocatalysts in some of the solid industrial waste may offer an economical, promising and environment-friendly technology, thus paving a way for a novel area of research in abatement of prevailing air pollutants such as particulate matter, VOCs and PAHs present in ambient/indoor air.

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Authors' contributions

Samridhi Dwivedi: Data curation, Writing- Original draft preparation, Visualization, Investigation. Farheen Zehra: Revision and Editing. Neha Shukla: Editing. Alfred Lawrence: Conceptualization, Methodology. B.S.Rajanikanth: Supervision. The author(s) read and approved the final manuscript.

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Declarations

Competing interests

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