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Impact of lechate chemicals of red mud waste of Alumina industry: its toxicity, impact on photosynthetic efficiency and production of a crop plant

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ABSTRACT

The leached chemicals of the red mud pond at Damonjodi pollutes the surrounding environment, particularly the crop fields, where green gram is cultivated as a second crop of the year after either rice or ragi. The lethal concentration values deduced were -MAC=0.2%; LC_{10}-1.25% and LC_{50}-2% leachate concentration. Hundred percent mortality or LC_{100} was found to be 2.8% leachate concentration. Browening of roots were marked in lechate exposed seedlings and at higher exposure period root death and decay was seen in exposed seedlings. Petriplate experiments revealed that pigments like chlorophyll-a, b; phaeophytin and carotene content significantly declined in leachate exposed green gram seedling leaves compared to control value. Little increment of chlorophyll pigment at lower concentration of the lechate can be attributed to the triggering affect but not stimulatory affect of the toxicant. Significant depletion in respiration rate was noted in leachate exposed seedling leaves. In case of analysis of photosynthetic rate, an initial increase in the parameter and with the increase in leachate concentration the PR decreased significantly. The GPP of the leachate exposed seedlings depleted with the increase in leachate concentration. Interesting results were obtained at sub-lethal concentration of the leachate, where decrease in parameters were not observed, instead an increase or no significant change was noticed. All care should be taken to dispose the wastes of the industry in the mega environment, where complex interaction patterns are not well known and well understood.

***Key words**: Red mud waste, Lechate, Toxicity, Pigments, NPP, PR, GPP.*

Introduction

The red mud waste discharged from NALCO, Damonjodi contains a significant amount of alumina along with other most toxic chemicals. The pH of red mud waste was significantly high and it was to the tune of 13-14. It was observed that chemicals were leaching from the red mud pond. Significant amount of alumina and other toxic chemicals were leaching as lechate from the red mud pond and this lechate passes as a small stream from the red mud waste dumping site (RMP) and enters into nearby crop fields, where either rice / ragi is cultivated in rainy season followed by green gram or black gram as the second crop. Reports pertaining to impact of red mud waste on toxicity and seed biological studies of crop plants are lacking. Samanatray (2000) reported the effect of red mud waste on the germination, seedling establishment & pigment content of rice grains and rice grains by taking the dried red mud waste directly in pot and petriplate cultures. The same author reported the problem of taking the red mud waste directly, where the soil mixture was getting hardened and air space in soil mixture was getting filled up with fine red mud powder, decreasing the water holding capacity of soil mixture. This influenced badly the physiology of germination, growth and development of the crop seeds. Hence in the present study we selected the leached chemicals leaking from the red mud pond as the test chemical. It was observed in the study reported by Pattanaik *et al.* (2017, 2018a) that the leached chemicals leaking from the red mud pond is more toxic than the laboratory prepared red mud waste extract. Alumina is lesser toxic when compared to mercury and other heavy metals but the presence of huge quantities of alumina might be causing the impact on the surrounding biota. Many workers reported presence of cadmium, copper, lead, Arsenic etc. in the lechate. High pH value of the red mud waste and its lechate caused toxicological problems in the surrounding biota. Pattanaik *et al*., (2018b) studied the synergistic impact of red mud waste extract prepared in the laboratory from dried red mud waste and a pesticide (generally used by the farmers) on the germination and seedling behavior in green gram seeds under laboratory controlled conditions. The present study was aimed to study the impact of red mud waste extract collected from discharge site on the seed biology and seedling behavior of green gram seeds under laboratory controlled conditions.

Location of the industry: NALCO the INDUSTRY

Establishmenet of National Aluminium Co. Limited (NALCO) is a major step towards self sufficiency in good quality of Alumina production. NALCO was set up in 1981, to exploit the large deposit of Bauxite, found in the east coast in1975. Aluminium Pechiny of France provided the technology and basic engineering for Bauxite mine, refinery and smelter. Initially 1987-88 the Alluminium production was 160,000 tones the production rate remarkably increased to 807000 tones in1995-96, in 1996-97; 840,000 MT and in 1997-98, it was 883000 MT and has chartered a course of international confidence in India's industrial capability (Photo-1 & 2). NALCO is producing the best alumina by adopting all modern technologies with a high market value. The mines and refinery complex of NALCO, Damonjodi is situated at Similigude block, under Potangi tahasil in the district of Koraput, Odisha state, India. From the district head quarters Koraput, it is 38 kilometers towards south-east on road, i.e. 27kms towards south in NH-43 up to Similiguda junction and further 11kms towards east on project road. It is 60 kms from Jeypore, the oldest city of Koraput district. Damonjodi is at a height of about 1300 mts. from sea level, located at latitude 18^0-6'—18^0-58' towards North and longitude 82^0.57'- 83^0.04' East (photo-1 and 2). The area enjoys an annual rainfall of 1723-1855 mm. The area enjoys a modest climate with little high rainfall when compared to other areas of Koraput district. Southeast side is covered by Deomali hill range. The slope of the area is towards the northwest. A small river Karandia is flowing near the Refinery complex and the Damanjodi township. It carries almost all the emissions of the plant and township and at it's down stream and joins with the Kolab River at its catchments area of Upper Kolab project near Sunabeda. NALCO produces calcined allumina at refinery complex, Damanjodi, Koraput district, Odisha located at latitude 18^0-6'-18^0-58' towards North and longitude 82^0.57'-83^0.04' East. NALCO produces calcined allumina at refinery complex, Damanjodi, Koraput district, Odisha located at latitude 18^0-6'-18^0-58' towards North and longitude 82^0.57'-83^0.04' East. (Photo-3-5). Chemical properties: Typical = Al_2O_3(%)- 98.7; Na_2O(%)- 0.38 ; Fe_2O_3(%)- 0.01; SiO_2(%)- 0.012; and CaO(%)-0.042. Alumina hydrate: Physical properties: Typical: LOI (110-1000^{o}C)%- 34-36, Moisture-3-6; Granulometry: Typical- 45Micron(%)-3-6. Chemical properties: Typical = Al_2O_3 (%) – 65 ± 0.5, Na_2O (%) Total-0.23-0.30, Na_2O (%) Soluble- 0.015-0.025, SiO_2(%)-0.007-0.010, Fe_2O_3(%)-0.006-0.008 and Hydrate Content-99.0% (Samantray, 2000). The red mud waste is dumped in a pond nearby. The leakage of the waste was marked on the earthen bandha (earthen dyke) side. The area enjoys an annual rainfall of 1723 mm in 1998. The relative humidity of area ranges from a minimum of 47% and maximum of 88% in 1998. The temperature of the area varied from a minimum of 15 ^{0}C to maximum 35 ^{0}C in 1997-98 and from a minimum of 9 ^{o}C to maximum of 42^0 C in 1998-99. South east side is covered by Deomali hill range. The slope of the area is towards the northwest. A small river Karandia is flowing near by the Refinery complex and the Damanjodi township. It carries almost all the emissions of the plant and township. At its down stream mixed with the Kolab River at its catchment area of Upper Kolab project near Sunabeda. The Red Mud (RM) pond is situated in such a place that the pond water is restricted by high hill ridges at south, ash pond at west separated by Orissa dam-3. But at its north seepage is marked at a natural nalaha at its down stream about 100mts away from Orissa Dam-2 of RMP. This seepage might be due to the storage of huge quantity of effluent at a high level. From the original point of leaching, the lechate gradually flow down mixed with natural nalaha and ultimately enters into the crop field. This lechate from RMP flowed down in its slope towards the river Karandi in the North West direction and finally mixes with the river Kolab near Sunabeda. As a result cultivators of villages, Sukuriguda, Janiguda, Denga janiguda, Kharaguda, Khajuriguda, Kalapadar and other village in the valley, depending on the water source for their agricultural purpose are being harassed. The contaminated water in the catchments area of Upper Kolab project is being lifted for Sunabeda as well as Damanjodi Township for all domestic use and human consumption. Ultimately this polluted water flows down along the river and being used by the inhabitants of Koraput and Jeypore townships as well as by all the villager of different villages located near the river bank.

Materials and Methods

Red mud waste lechate**:** The red mud waste lechate was collected from the stream originating from the red mud pond (discharge site, Photo-3,4) at Damonjodi in plastic containers and brought to the laboratory and kept in a fridge. The lechate was serially diluted to prepare different concentrations selected from toxicity testing following the procedure as followed by Pattanaik *et al*., (2017). The lethal concentration values deduced were - MAC=0.2% (Conc.–A); LC_{10}-1.25% (Conc.–B) and LC_{50}-2% (Conc.-C) lechate concentration. LC_{100} was found to be 2.8% lechate concentration. All the inoculations and seed arrangements in the petriplates

Photo 1. Showing the satellite view of NALCO at Damanjodi (Source from Google earth); Photoplate- 2: Showing the NALCO Industry at Damanjodi, Koraput, Odisha.)

Photo 3. Red mud pond; Photo-4: Red mud used for road construction; Photo-5: Fly ash used for field preparation and road construction.

were carried out in the laminar air flow chamber. Twenty five viable seeds (collected from the Nursery, Cereal and Pulses Research station, Ratanpur, Ganjam) were taken in each petriplate of control and toxicant (Red mud waste Lechate) exposed sets. The control set was maintained for comparison. The plant pigments like Chl-a, chl-b, total chlorophyll and total phaeophytin was estimated following the procedure of Vernon (1960) and carotene was estimated following the procedure of Davies (1976). The evolution of oxygen due to photosynthesis and consumption of oxygen and release of carbon dioxide in respiration were measured manometrically with the help of a Photo-Warburg's apparatus (New Paul, India) following the procedure of Hannan and Patouillet (1972). The photosynthetic rate, respiration rate was estimated following the procedure Oser (1965). The GPP value was computed from RR and PR (NPP) and all these parameters were expressed as µl of O_2 evolved/g fresh weight/hour and µl of CO_2 produced/g fresh weight/hour.

Results

The pigment contents like chlorophyll-a, b and total chlorophyll content increased at 0.2% lechate concentration. The chlorophyll-a content increased from 0.56±0.08 mg/g fresh weight to 0.58±0.11 mg/g fresh weight and at higher lechate concentration the pigment depleted from 0.56±0.08 mg/g fresh weight to 0.06±0.03 mg/g fresh weight showing significant inhibition.

The chlorophyll-b content increased from 0.54 ± 0.12 mg/g fresh weight to 0.59 ± 0.06 mg/g fresh weight and at higher lechate concentration the pigment depleted from 0.54 ± 0.12 mg/g fresh weight to 0.02±0.01 mg/g fresh weight showing significant inhibition. The total phaeophytin content and carotene content significantly decreased in lechate exposed seedlings from 0.96±0.06 mg/g fresh weight to 0.08 ± 0.01 mg/g fresh weight and from 0.0146 ± 0.0028 mg/g fresh weight to 0.0008 ± 0.0003 mg/g fresh weight compared to control seedlings, respectively (Fig. 1). The pigment ratio values increased at all tested concentrations of the lechate compared to control seedling leaf pigment ratio values (Fig. 2). The Chl-a, b, total chlorophyll, total phaeophytin and carotene content significantly decreased by 89.3%, 96.3%, 92.4%, 91.7% and 94.5% respectively in lechate exposed green gram seedlings (Fig. 3) indicating poisonous nature of the applied toxicant.

Fig. 1: Changes in the pigment content of green gram control and lechate exposed seedling leaves in different lechate concentrations .

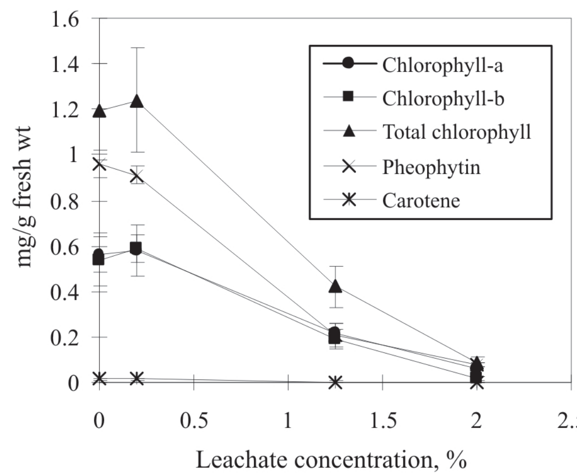
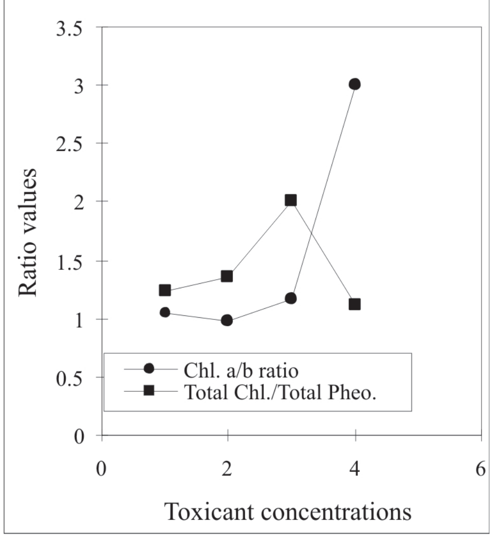
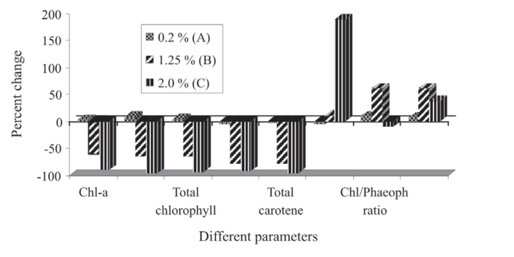


Fig.2: Changes in the pigment ratios in different toxicant concentrrations



The respiration rate decreased from 236.5 ± 28.2 µl of CO_2 evolved /g fresh weight/ hour to 208.4 ± 29.6 µl of CO_2 evolved /g fresh weight/ hour at 0.2% lechate concentration showing 11.9% decrease in respiration rate and at higher lechate concentration the respiration rate depleted from 236.5 ± 28.2 µl of CO_2 evolved /g fresh weight/ hour to 64.5 ± 8.5 µl of CO_2 evolved /g fresh weight/ hour showing 72.7% decrease compared to control value indicating sig-

Fig. 3: Percent change in different pigment contents and ratio values in leachate exposed seedlings at different RMW lechate concentrations, when compared to control values.



nificant inhibition (Fig. 4 and 5). The photosynthetic rate increased from 224.8 ± 26.2 µl of O_2 evolved /g fresh weight/ hour to 246.2 ± 31.3 µl of O_2 evolved / g fresh weight/ hour at 0.2% lechate concentration showing 9.5% increase in photosynthetic rate and at higher lechate concentration the photosynthetic rate depleted from 224.8 ± 26.2 µl of O_2 evolved /g fresh weight/ hour to 74.6 ± 9.4 µl of O_2 evolved /g fresh weight/ hour showing 66.8% decrease compared to control value indicating significant inhibition (Fig. 4 & 5). The gross primary production decreased from 464.3µl of O_2 evolved /g fresh weight/ hour to 454.6µl of O_2 evolved /g fresh weight/ hour at 0.2% lechate concentration showing 1.5% decrease in gross primary production and at higher lechate concentration the gross primary production depleted from 464.3 µl of O_2 evolved /g fresh weight/ hour to 64.5±8.5 µl of O_2 evolved /g fresh weight/ hour showing 71.6% decrease compared to control value

Fig.4: Changes in PR, RR and GPP in control and lechate exposed green gram seedlings after 144hrs of exposure in petriplate culture.

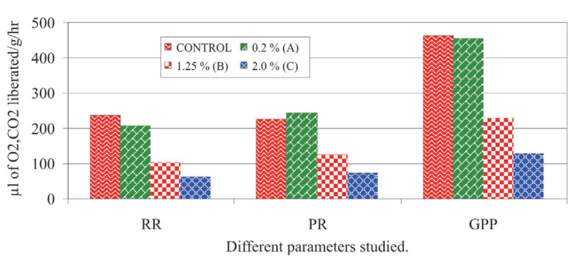
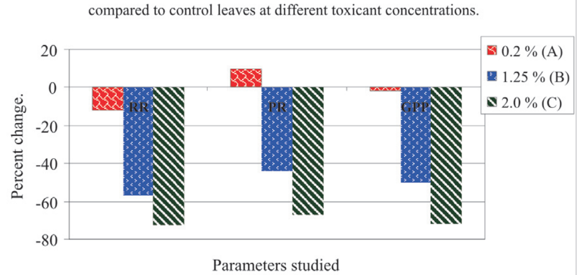


Fig.5: Percent change in PR,RR and GPP in lechate exposed seedling leaves compared to control leaves at different toxicant concentrations.



indicating significant inhibition (Fig. 4 & 5). The data clearly indicated the acute nature of lechate tested. Hence the lechate leaking from the red mud pond is toxic and after joining the water stream the lechate must be affecting the existing flora and fauna in the contaminated area.

Discussion

Due to extremely high demand for Aluminium all over the world, red mud generation by Alumina industries has been reached to more than 150 million tones per year globally (Evans, 2016). Xue *et al.* (2016) reported that "disposal of such huge quantity of wastes includes marine/slurry disposal, dry stacking and dry cake stacking. At present, dry cake stacking is highly adopted as it attempts to produce 65-70% solid cake before disposal which minimizes land acquisition and reduces the risk of environmental contamination". "Improper disposal of poorly treated residue may lead to several environmental problems with its consequent impacts on living beings (Mayes *et al.*, 2016). The red mud waste coming out from the industry at Damonjodi is discharged as slurry into a red mud pond created nearby surrounded by hills from all sides except one opening where the industry owners closed the opening by an earthen dam. The slurry is allowed to dry in the pond. The lechate of the red mud pond have contaminated the surrounding area, where all forms of plant and animal life suffer significantly. In the present investigation, it as observed that the lechate tested is deadly toxic. All most all the parameters like chl-a, chl-b, total chlorophyll, total phaeophytin and total carotene decreased at higher toxicant concentrations and higher exposure period. Pattanaik *et al* (2017, 2018a, b) reported significant effects of lechate and seriously impacting the seed germination, seedling establishment of green gram crop plant. The same author also indicated that little higher values at lower concentration of the toxicant can not be attributable to stimulatory effect of the toxicant. The most important point is dilution factor. To bring the whole red mud waste and dilute 0.2% is practically impossible as this will create a safe disposal problem. The increase in few parameters might be due to the presence of chemicals enlisted under micro and macro nutrients in the red mud waste and red mud waste lechate. The red mud waste should be safely disposed and should not be allowed to enter into natural ecosystems. The leaking of red mud pond should be checked and lechate should be collected and recycled back into the red mud pond. The industry must find out way to dry the red mud waste and carry the waste to safer sites far away from natural water bodies. There is no single well defined technique adopted by the industries. Every industry uses Bayer's protocol for extraction of Aluminium where bauxite ore is treated with hot NaOH (caustic soda) under very high temperature and pressure. Liu *et al.* (2009) reported that "approximately 85-90% of bauxite is converted to alumina followed by Hall-Heroult process for Aluminium production". Xue *et al.* (2016) and Wang *et al*. (2008) indicated that many advanced red mud management protocols like catalytic application processes, metallurgical processes, manufacture of paints and pigments, adsorbents, ceramics, and construction materials. The above options are cost-prohibitive and they are also not eco-friendly and require much polishing and refinement of the wastes before disposal to natural environments. Instead of any type of treatment, the best method of treatment was suggested by Xue *et al.* (2016) pertaining to development of a long lasting and cost effective suitable vegetation cover over red mud dam. Simply this method is not acceptable as the red mud waste is deadly toxic and showed adverse effects on flora and fauna of the area. For this type of method a counterbalanced technique to counter the toxic nature of red mud waste should be adopted first by way of using suitable amendments or by natural ways. The plant over or the vegetation of an area indicates the soil status and condition and any change in the physico-chemical status will alter the vegetation composition and ultimately plant cover. The red mud waste has many nutrients used by plants but an addition to nutrients, the red mud waste contains many toxic chemicals comparatively in huge quantities which can significantly affect plant growth, survival and development.

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