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Chloride Removal from Wastewater by Biosorption with the Plant Biomass

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Abstract:

Chlorides are the natural substances which are found in the water bodies in varying amounts. However, their concentrations are significantly low. However, the industrial, domestic and agricultural wastewaters that are generated from the human society may contain large amount of chlorides, which can cause significant disruption in the ecological balance. Many techniques have been adopted in order to reduce the amount of chlorides in wastewater like demineralization, reverse osmosis, coagulation, precipitation, electrodialysis and so on. However, these techniques are physico – chemical in nature, and are cost consuming capital cost wise as well as maintenance cost wise. Therefore, the following paper makes an effort towards putting forth a biological alternative for the removal of chlorides from wastewater. The present paper studies the suitability of *Parthenium sp.* as a sorbent for chloride removal. Further, variations in the efficiency of biosorption with respect to different pH, concentration and time were studied. The paper concluded that *Parthenium sps.* dried biomass is capable of achieving upto 40% reduction in the chloride content at Lab scale.

Keywords: Biosorption, *Parthenium*, chlorides, wastewater.

1.0 Introduction:

Chloride is a salt compound resulting from the combination of Chlorine gas and a metal. The common chloride salts include Sodium Chloride (NaCl), and Magnesium Chloride ($MgCl_2$). Industrial processes such as battery manufacturing, pulp mills, bullion refining, electroplating, pesticide manufacturing, a large number of small scale processing units etc are the main sources of chlorides in water. In majority of these industries, the main source of chlorides in the effluent is the use of Lime ($Ca(OH)_2$) or Sodium Hydroxide (NaOH) for the neutralization of acidic effluents. At different instances, Acids like Hydrochloric Acid (HCl), or Sodium Hydroxide (NaOH) can be a major part of the industrial processes, where they are used for the initial de-coating of Oil film on the raw material. Naturally, they contribute substantially to the chlorides in wastewater.

The major impact that chlorides impart on the receiving waters is the permanent hardness. They are also known to increase the rate of sedimentation and thereby decreasing the water column depth. When such effluents are disposed on land, chlorides tend to initially percolate some distance, but over a period of time, they cause surface salt formation, thereby causing increased alkalinity of the soil, thereby resulting in loss of soil fertility. In plants, chlorides tend to accumulate in the tissues, especially the leaves. Chloride accumulation in plants is closely related to the chlorine concentration in the external solution and the genotype (Hajrasuliha, 1979). It was also noted that when sodium and chloride, when supplied via landfill leachate irrigation, is accumulated in high concentrations in the tissues of many plants like *Populus* (Zalesny et.al. 2007)

1.1 Properties of Chlorides and Impacts:

Chlorides are widely distributed in nature as salts of sodium (NaCl), potassium (KCl), and Calcium (CaCl2).

Organoleptic Properties: The taste threshold of the chloride anion in water is dependent on the associated cation. Taste thresholds for sodium chloride and calcium chloride in water are in the range 200-300 mg/litre (Zoeteman BCJ., 1980). The taste of coffee is affected if it is made with water containing a chloride concentration of 400 mg/litre as sodium chloride or 530 mg/litre as calcium chloride (Lockhart EE *et al*, 1955).

Environmental fate: Chlorides are leached from various rocks into soil and water by weathering. The chloride ion is highly mobile and is transported to closed basins or oceans.

1.2 Environmental Levels and Human Exposure:

Water: Chloride in surface and groundwater from both natural and anthropogenic sources, such as run-off containing road de-icing salts, the use of inorganic fertilizers, landfill leachates, septic tank effluents, animal feeds, industrial effluents, irrigation drainage, and seawater intrusion in coastal areas (Department of National Health and Welfare, Canada, 1978). Chloride in water may be considerably increased by treatment processes in which chlorine or chloride is used

Food: Chloride occurs naturally in foodstuffs at levels normally less than 0.36 mg/g. An average intake of 100 mg/day has been reported when a salt-free diet is consumed. However, the addition of salt during processing, cooking, or eating can markedly increase the chloride level in food, resulting in an average dietary intake of 6 g/day, which may rise to 12 g/day in some cases.

1.3 Kinetics and Metabolism in Laboratory Animals and Humans:

In humans, 88% of chloride is extracellular and contributes to the osmotic activity of body fluids. The electrolyte balance in the body is maintained by adjusting total dietary intake and by excretion via the kidneys and gastrointestinal tract. Chloride is almost completely absorbed in normal individuals, mostly from the proximal half of the small intestine. Normal fluid loss amounts to about 1.5-2 liters/day, together with about 4 g of chloride per day. Most (90-95%) is excreted in the urine, with minor amounts in faeces (4-8%) and sweat (2%) (Department of National Health and Welfare, Canada, 1978). The oral LD50 values for calcium chloride, sodium chloride, and potassium chloride in the rat have been reported as 1000, 3000, and 2430 mg/Kg of body weight, respectively (WHO report Copenhagen, 1978). The toxicity of chloride salts depends on the cations present; that of chloride itself is unknown. Although excessive intake of drinking-water containing sodium chloride at concentrations above 2.5 g/liter has been reported to produce hypertension (Fadeeva VK., 1971), this effect is believed to be related to the sodium ion concentration.

1.4 Effect of Chlorides

1.4.1 Human Health:

A normal adult human body contains approximately 81.7 g chloride. On the basis of a total obligatory loss of chloride of approximately 530 g/day, a dietary intake for adults of 9 mg of chloride per kg of body weight has been recommended (equivalent to slightly more than 1 g of table salt per person per day). For children up to 18 years of age, a daily dietary intake of 45 mg of chloride should be sufficient (Department of National Health and Welfare, Canada, 1978). A dose of 1 g of sodium chloride per kg of body weight was reported to have been lethal in a 9-week-old child (WHO Report Copenhagen, 1978). Chloride toxicity has not been observed in humans except in the special case of impaired sodium chloride metabolism, e.g. in congestive heart failure (Wesson LG., 1969). Healthy individuals can tolerate the intake of large quantities of chloride provided that there is a concomitant intake of fresh water. Little is known about the effect of prolonged intake of large amounts of chloride in the diet. As in experimental animals, hypertension associated with sodium chloride intake appears to be related to the sodium rather than the chloride ion (Department of National Health and Welfare, Canada, 1978).

1.4.2 Flora:

Chloride tends to accumulate in tissues, particularly leaves, of some plants to toxic levels. Chloride accumulation in plants is closely related to Cl concentration in the external solution and the genotype. (Hajrasuliha, 1979). It was also noted that when Sodium and chloride, when supplied via landfill leachate irrigation is accumulated at high concentrations in tissues of *Populus* (Zalesny J.A et al, 2007). One of the main sources of considerable amounts of chloride to soils is irrigation water. The responses of tobacco (*Nicotiana tabacum* L.) to chloride are varied and inconsistent depending on the tobacco type, variety and methods of fertilization, cultivation and harvesting used. (N.A. Karaivazoglou et al, 2004) The results showed that the adverse influence of chloride in irrigation water on plant height and number of leaves per plant was already substantial above 40 mg L^{-1}, within 30 days after transplanting.

1.4.3 Fauna:

On a positive side, Chloride fluxes play a crucial role in synaptic inhibition, cell pH regulation, as well as in cell volume control. In many neuropathological processes, cell swelling is a pivotal parameter, since cell volume changes and the dimension of the interstitial space critically modulate synchronized neuronal activity as well as the tissue's susceptibility to seizures or spreading depression (M. Müller, 2000). Soluble chloride stimulated catalysis of oxidation of phosphatidylcholine liposomes by the soluble fraction of mackerel muscle. Chloride was determined to be the active component of the salt in this system (Joanne E. Osinchak, 2003)

1.4.4 Microorganisms:

In an incubation experiment that was conducted, Presence of chloride retarded the process of N immobilization; that of NO_3^--N being more affected. Remineralization of immobilized N started within 48 h in case of both NH_4^+- and NO_3^--N and was faster for the latter. Both remineralization and nitrification were significantly delayed in the presence of a chloride; inhibition being more at 4000 mg Chloride per kg^{-1} soil. The inhibitory effect of chloride on remineralization of N was relatively more for NH_4^+-treated soil (F. Azam and M. Ifzal, 2006). The presence of the organism responsive to increased chloride concentration was associated with the highest observed value of chlorination of humic acid, suggesting possible role of this organism in soil chlorine turnover. High chloride concentration in the soil tended to decrease the rate of degradation of trichloroacetic acid (Gryndler M. *et al*, 2007)

1.5 Commercial Technologies Available for the Removal of Chlorides:

1.5.1 Norcure Concrete Chloride Removal System:

Norcure technology is one of the most important techniques which were taken up in order to address the problem of corrosion of the concrete due to the entry of chlorides. The Norcure process is an electrochemical method of removing chloride ions and drawing them out of the concrete. Using this method, concrete could be rejuvenated without the inconvenience and disruption of conventional demotion and repair, resulting in significant savings. The corrosive nature of sodium chloride (salt) is well known. It can bring about rust on automobiles, and wreak havoc on concrete, where corrosive concentrations of chlorides are often found. The chloride ions percolate deep into the concrete structures due the porous nature of concrete, eventually reaching the reinforced steel or rebar. Furthermore, after this, it begins to corrode the structure, and structures such as parking lots, highways and bridges become vulnerable due to its damaging effects. Once chlorides attack a structure, they quickly eat away at the reinforcing steel, causing cracks to appear. If left untreated, these chloride ions can cause concrete spalls, expose steel reinforcement bars and eventually reduce the structural integrity of the structure to dangerous levels.

1.5.2 Chloride/Sulfate Removal System:

A modified gas conditioning system was used in a patent process conducted by Hawks et al in 2001. The liquid cooling spray in the unit was modified to serve the purpose. This modified liquid cooling spray provided for high sulfur dioxide removal efficiency at low molar ratios of alkali to sulfur. (Hawks et al., 2001)

1.5.3 Chloride Removal Using Ion-Exchange Method:

Ion exchange works on the basic principle of charge based transport of ions. In a lab scale study on pulp and paper mill, several resins were tested for chloride removal. The resins were either free base forms or hydroxide base forms. The study concluded that two hydroxide ion based resins named IRN78 and 4400OH achieved approximately 50% and 70% chloride removal at a dose of 10 g / L and were the potential resins that may be used in the reduction in chlorides in Pulp and paper mill effluent. (Giyeon Yun, Ian D. Buchanan, 2006)

1.5.4 Ultra- High Lime With Aluminum (UHLA) Process:

Lime softening serves as the favorite alternative for removing scale forming materials. However, the process does not remove silica, chloride or sulfates. A process named Ultra High Lime Softening was therefore devised, which successfully removed silica, but not sulfur and chlorides. Advanced methods are available for the removal of chlorides and sulfates, viz. reverse osmosis, electrodialysis (Masson and Deans, 1996; Rapp and Pfromm, 1998; and Ericsson and Hallmans, 1996) but lime softening is the cheapest alternative available for recycled cooling water (You et al., 1999). Also, the process like reverse osmosis is not only expensive, but also difficult to maintain. Occurrence of problems like membrane fouling may require frequent cleaning and production of brine in the form of reject creates a problem of effluent disposal. The Ultra High Lime with Aluminum process is an innovative technology which operates in two stages. The high pH and Calcium content in the first stage allows for removal of sulfate by precipitation as Calcium Sulfoaluminate ($Ca_6Al_2(SO_4)_3(OH)_{12}$). Also, these conditions of the first stage allow the precipitation of chlorides as Calcium chloroaluminate ($Ca_4Al_2Cl_2(OH)_{12}$). The cost economics of the process depicted that the capital cost is equivalent to the conventional lime process due to the fact that the same equipment is usable. Operating cost of the UHLA system is slightly higher due to the constant requirement to add aluminum. The sludge that is obtained contains almost 39% aluminum by weight. (Chu, 1999)

1.5.5 Calcined Layered Double Hydroxides (CLDH) Method:

On the basis of an effect known as Memory Effect, it was said that CLDH, within a certain temperature range, has the capacity to regain its original form. Therefore, a study was conducted in order to observe the capacity of CLDH to assimilate chloride ions from aqueous solution. The study concluded that the assimilation of chloride ions by CLDH was consistent with Langmuir and Freundlich models. (Liang Lv. *et al*, 2006).

1.5.6 Electrochemical Method for the removal of chlorides:

Electrochemical Chloride Extraction (ECE) is essentially a simple electrochemical process which consists of the use of the basic principle of ion migration towards oppositely charged poles. The apparatus contained an anode which was inserted in an electrolyte media. The setup was then applied on the concrete surface. The anode and the reinforcing steel were connected to two terminals of a direct current (DC) power supply such that the anode was positively charged. Due to the charge on the anode, the migration of the chloride ions from the concrete to the anode field occurred, thereby reducing the chloride content in the concrete, particularly on and around the reinforced steel end. At the termination of the process, chloride free, highly alkaline concrete is obtained, which results in strong repassivation of the embedded reinforced steel and halting of the corrosion of the same. A study was conducted in order to observe the free chloride content in a concrete block during electrochemical chloride removal. It showed that, due to the free chloride removal, bound chloride is dissolved in order to reestablish the equilibrium between bound and free chloride (Elsener B., Angst U., 2007)

The above literature review clearly indicates the need for research on the application of the biological substances for the chloride removal process. These processes may prove effective solutions for cost economic chloride removal. Therefore, the present paper studies the compatibility of the biosorption phenomena for chloride reduction.

2.0 Materials and Methods:

The materials used in the experiments are:

2.1 Wastewater Sample with Chloride Concentration 3976 ppm: The preliminary experiments were done with this sample.

2.2 Parthenium sps. plant dried powder (containing leaves and stem)

Congress grass / Gajar ghas / *Parthenium sps.* belongs to the family asteraceae. The word '*Parthenium*' has been derived from the Latin word 'Parthenice', meaning reputed medicinal merits. It has been speculated by scientists that the unique properties of this weed can be exploited for different purposes like activated carbon making, biomass generation, pesticidal use etc.

Parthenium sps.

Parthenium is considered to be one of the ten worst weeds in the world. *Parthenium* is a herbaceous annual or ephemeral member of the family Asteraceae. It can reach heights of up to 2 m in good soil, and attain flowering in less than 4 – 6 weeks of germination. Seeds produced per plant can go up to 25000. Dispersion of the seeds occurs through various vectors like water, muddy surfaces, small animals, vehicles, machinery etc. *Parthenium* has a variety of vernacular names, like Congress grass, White top, Star Weed, Carrot Weed, Gajar Ghaas (Hindi), Ramphool, feverfew etc. The pollen and seeds of these plants are known to be a major cause of asthma, and bronchitis. The weed shows the presence of toxins known as Sesquiterpene lactones, parthenin, phenolic acids such as caffeic acid, vanillic acid, anisic acid, panisic acid, and parahydroxy benzoic acid which are known to be lethal to humans as well as animals (Oudhia, 2001).

2.3 Method:

Sample collection was done on the basis of the health of the plant through visual observations. Young plants having a fresh green shoot and sizable stem thickness were selected. On collection, the specimens were washed with tap water and then distilled water. Further, for biomass collection, the specimens were subjected to drying in an oven at 50^0 C for two days. Drying was followed by careful crushing of the specimen, and then sieving the mixture through a 500 micron sieve. The obtained biomass was used for the study. The biomass was added to the test solutions in the ratio of 0.10 g : 100 ml test solution. The pH of the sample was maintained at 7, and the chloride concentration at 100% of the initial wastewater solution. The mixture was then incubated in a rotary shaker incubator at 150 rpm and 30^0 C for 60 minutes. On the termination of contact time, the solution was filtered using an ordinary filter paper. The sample was titrated for chloride content using the argentometric titration method specified in the APHA handbook for water and wastewater analysis. The tests were repeated by carrying out variations in pH, by using different chloride concentration levels, and with variable contact times.

3.0 Results and Discussion:

Chloride content in the water / wastewater has become a major problem in the industrial as well as domestic sector. A variety of techniques have been found to be extremely suitable for the removal of chlorides. Some of these include ion exchange (Giyeon and Buchanan, 2006), reverse osmosis, norcure, etc. However, these techniques, though effective, are not feasible from the cost perspective. Therefore, it is the need of time to come up with newer, low cost treatment methods for these purposes. Biological treatment of waste can be a good option in this regard it suitable amount of work is taken up. The present paper therefore emphasizes the use of a highly resilient weed in order to try and work out a solution to the mentioned problem.

3.1 Influence of pH on Biosorption:

It is a well known fact that the process of Biosorption is governed by the solution pH (Patil, 1999; Patil and Paknikar, 1999). Determination of the optimum pH for the reaction was therefore taken up as the primary procedure. By keeping the contact time and the concentration of the test solution constant, the reaction was carried out at different pH values as depicted in Fig. 1.

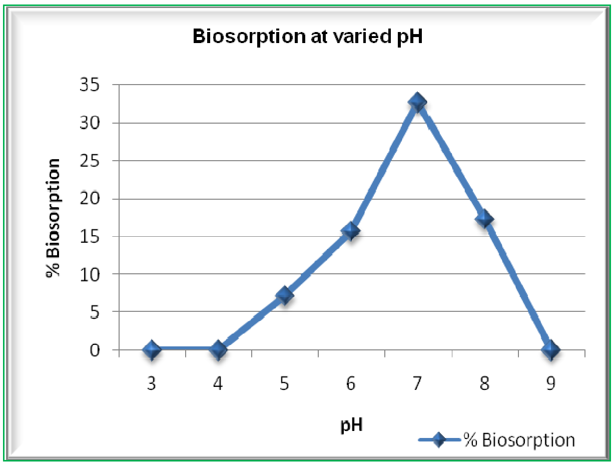

Fig. 1: Biosorption with respect to pH

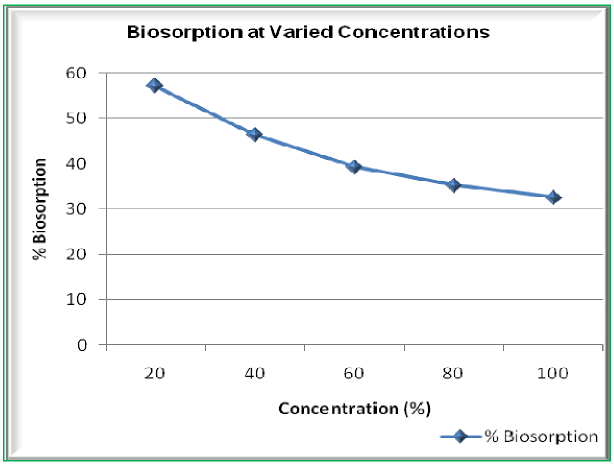

Fig. 2: Biosorption at Varied Concentrations

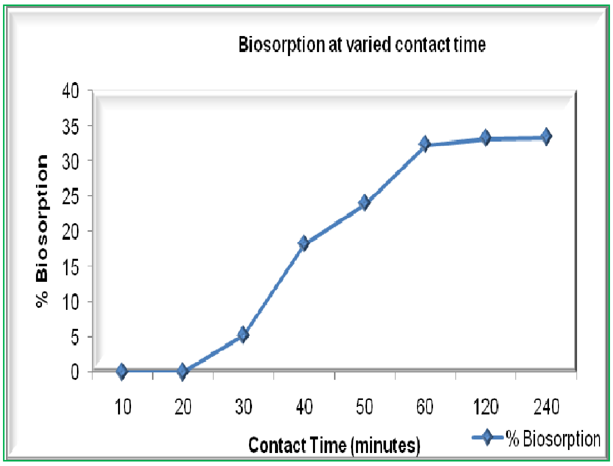

Fig.3: Influence of Contact time on Biosorption

The method of the test was as per the methodology mentioned above. Through this study, it was observed that the optimum pH at which maximum biosorption occurred was in the range of 6.9- 7.4. This is not only helpful in easy monitoring of the further process, but cost economic as well because there is no need of additional pH regulation system.

3.2 Influence of Varied Chloride Concentration on Biosorption:

3.3 It is known facts that increase in strength / concentration of a pollutant, the reaction rate may change. In order to study the impact of chloride concentration on the overall biosorption efficiency, the experiment was carried out at different chloride concentrations as depicted in Fig. 2, while keeping the other parameters constant. At the end of the test, it was noticed that the efficiency decreased with increase in concentration of chlorides, and at a concentration of 100%, the chloride biosorption rate was in the range of 30- 35%.

3.4 Influence of Contact Time on Biosorption:

In the methodology adopted for the experiment, the contact time was kept at 60 minutes. However, as the rate of reaction is time dependant, an experiment was carried out in order to evaluate the reaction rate at variable contact periods as depicted in Fig. 3. The other parameters were maintained constant, while varying the contact time between the biomass and the test solution. As it is clear from the figure, after certain time frame, in the present case 120 minutes / 2 hours, the rate of biosorption remained constant. The experiment that was conducted above was carried out with the sole motive of coming up with a process for the removal of the chlorides from the wastewater stream in order to render it suitable either for disposal, or further, for reuse after suitable treatment. The treatment was successful on the lab scale. However, there are several more aspects that are needed to be assessed before the experiment may be taken up to a pilot scale, such as the regeneration rate, usability limits and biomass production rate. However, this experiment provides a benchmark in regards of the pH, concentration and contact periods, thereby, giving the future researchers a foundation to build on.

4.0 Conclusion:

Chlorides in water / wastewater are a serious concern in the era of water conservation and reuse. There is a need for different methods which are low cost and efficient. The above paper is an effort towards finding such a method. From the above paper, the following conclusions may be drawn.

1. By using plant biomass of Parthenium, chloride removal of 30- 34% can be achieved.
2. The required pH for this process is 7 – 7.5
3. The required contact time is 120 minutes

The biosorption efficiency decreases with increasing concentration of chlorides.

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