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Research Paper

Studying the Stability of Silver ions attached to a Cationic Exchange Resin Under Different Concentrations of Sodium Chloride (Saltwater) Solution

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Abstract: Ion exchange resins (IERS) have a range of applications in the environmental field, especially in water treatment and engineering, such as water softening. Silver ions have been known inhibitors of bacterial growth in literature and have been shown as selective ions for certain IERS. The present study aims to investigate the stability of silver ions adsorbed onto a cationic exchange resin (Indion[®] 220 Na) under different concentrations of sodium chloride (saltwater) solution so as to see whether such a resin could be effective for bactericidal treatment of wastewater over sustained periods of time at an industrial scale. Two batches of 22 cm³ of resin were generated using concentrated hydrochloric acid and then treated with 25% w/v silver nitrate solution. Stock solutions of sodium chloride were made with concentrations of 0 ppm, 30 ppm, 109 ppm, 898 ppm and 6110 ppm and the resin was treated with the same in a ratio of 10 cm³ of solution per gram of dry resin for seven days. Chemical analysis for silver retained on the resin was done using ICP-AES method and this was converted into percentage of silver retained with respect to the original amount of silver ions on the resin. While there was an overall decreasing trend of silver retention with respect to concentration of sodium chloride solution, there were irregularities from concentration to concentration. For the range of concentrations typically obtained in domestic wastewater, silver retention decreased almost linearly with increase in concentration of sodium chloride solution, indicating the instability of silver ions on the particular resin.

Keywords: ion exchange resins, silver ions, sodium chloride, stability.

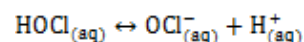
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Introduction

As per the Central Public Health and Environmental Engineering Organisation (CPHEEO), Ministry of Urban Development, Government of India, about 70-80% of total water supplied for domestic use gets generated as wastewater^[1]. It is estimated that by 2050, about 132 billion litres per day of wastewater would be generated^[1]. With a surging population and hence a greater demand for clean, potable water, it is imperative to employ efficient and effective treatment processes in order to recycle domestic water and put lesser pressure on sources of water, having limited supplies.

Wastewater is known to contain a host of pathogenic bacteria including *Campylobacter jejuni*, *Escherichia coli*, *Salmonella typhi* and *Vibrio cholerae*^[2]. These are known agents of diseases such as cholera, typhoid fever and gastroenteritis, the last of which causes around 1.45 million deaths annually, of which 58% are due to inadequate water

treatment^[2]. Current methods to remove such pathogens from the wastewater are mainly biological processes such as Membrane Biological Reactors (MBRs), which use micro or ultrafiltration membranes, or aerobic processes^[2]. Chemical processes also exist of which chlorination is the most common. The dominant form of chlorine that exists when added to water depends on factors such as pH and temperature. It is primarily used in the gaseous form (Cl₂) or as hypochlorite salts to disinfect wastewater, however all forms of chlorine will react with the water to form hypochlorous acid, which in turn quickly dissociates into the hypochlorite ion as per the chemical equation^[3]:



This disinfects by oxidizing the cell wall leading to cell lysis or inactivation of functional sites on the cell's surface in bacteria. However, chlorination causes toxicity to aquatic organisms due to chlorine residues and can also

form organo-chlorinated derivatives that are toxic and bioaccumulative^[3]. Another effective chemical process for disinfection is ozonation. Ozone (O₃) is a highly reactive species with an oxidation potential of 2.07 V^[4]. When ozone decomposes in water, it forms the hydroperoxyl (HO₂) and the hydroxyl (•OH) radicals that have a greater oxidizing capacity than ozone. Ozonation usually kills bacteria because of protoplasmic oxidation leading to cell lysis^[5]. Ozonation is beneficial since it is effective against both bacteria and viruses and can also remove cysts and eggs^[4]. However, ozone is not very soluble in water and any ozone residual quickly dissipates due to its reactive nature – reducing the disinfection capacity of ozone^[3].

The silver ion has been a known antibacterial agent, having activity against a broad range of bacteria. Thus, it has been used in a variety of medical applications including dental work, catheters and healing of burn wounds^[6]. Furr et al reports that an essential mechanism for silver's antibacterial action is its interaction with the thiol groups in enzymes and proteins of bacteria^[7]. It is also believed that silver ions cause the release of K⁺ ions from bacteria and hence the cytoplasmic membrane is a potential target site for silver ions^[6]. Brown and Smith demonstrated that silver ions are deposited in the vacuole and cell wall of target bacteria in the form of granules^[8] leading to significant inhibition of bacterial growth. In fact, Wakshlak et al (2015) have shown the “zombie effect” of silver, wherein silver nanoparticles are accumulated in dead bacterial cells and then leached out to the environment when a living culture of the same species is exposed to the dead bacteria - thus having antibacterial activity via the dead bacteria^[9]. Silver ions, as a result, would be interesting to study as possible antibacterial agents for bactericidal treatment of wastewater.

The removal of an ion from an aqueous solution and its replacement by another ionic species is referred to as “ion exchange”. Ion exchange resins (IERS) are synthetic materials that have been especially designed to enable ion exchange operations on an extremely high performance level. Among their many applications, they are used for water softening, purification and decontamination^[10]. Ion exchange, which is a unit process in chemical engineering, results in no permanent change in the structure of the solid due to its reversible nature. Hence IERS are not consumed during ordinary usage but must be regenerated when they are exhausted^[11] that is when most of its original ions have been exchanged for another ion from the surrounding solution.

IERS consist of a synthetic polymer matrix to which is attached a functional group, giving the resin its specific properties^[11]. These functional groups can interact with water-soluble species, including ions^[10]. This is because each functional group has a fixed electric charge and an associated mobile counter ion of opposite charge^[11]. The interaction between the functional group and the ion is thus

via electrostatic forces that are slightly weak^[10]. The counter ion on the resin is capable of exchanging with an ion of like sign if the latter is present in a solution with which the resin is in contact^[11]. IERS are mostly made of small beads that are insoluble in water or organic solvents^[10] and are usually spherical or in granules^[11]. IERS can be made with porous structures, instead of the solid gel structure, to form macroporous resins. The pores fill up with the solution, allowing the ions in them to come in contact with the active sites on the resin^[11]. A resin having a negatively charged functional group (for example, sulphonic group) has a positive mobile counter-ion and is said to be a cationic exchange resin^[11].

Indion[®] 220 Na is a strongly acidic cationic exchange resin, containing a styrene divinylbenzene copolymer matrix and a sulphonic acid functional group. Its mobile counter-ion is sodium (Na⁺) ions and the resin is supplied as moist golden yellow beads with a solid gel structure. The resin has a total exchange capacity of 1.8 meq/cm³. It is primarily used for water softening and two-stage deionising applications^[12].

The stability study of silver ions by IERS is limited in literature and almost all of these studies involve a weakly acidic cationic exchanger. Roy and Basu (2005) have shown the use of a chelating resin, a thiosemicarbazide incorporated Amberlite IRC-50 (a weakly acidic resin), to trap silver ions^[13]. Chelating resins have an affinity for heavy metal ion such as silver ions due to the behaviour of the functional group as a ligand that participates in complex bonding with the silver ion - not only do they interact via electrostatic forces but also through a coordinate bond between a lone pair on an atom of the functional group and the silver ion^[10].

It is known that the sodium ion is more reactive than the silver ion and hence will displace the latter out of an aqueous solution. Thus, for a resin having an adsorbed silver ion, there would theoretically be no reaction with a solution of sodium chloride, containing the lesser selective Na⁺ ion. However, with different concentrations of sodium chloride solution, it could be possible that the more selective silver ion on the resin is exchanged for the sodium ion in solution, due to the effect of the law of mass action^[10]. Although this effect is weak due to the weak interactions between the less selective ion and the resin's functional group, the effect increases with an increase in the concentration of the solution^[10].

The present study focuses on the stability of silver (Ag⁺) ions on Indion[®] 220 Na ion-exchange resin, a cationic exchange resin, when treated with sodium chloride (salt) solutions of concentrations 0 ppm to 6110 ppm for 7 days. The purpose of the study is to assess if a silver ion coating on available ion exchange resins such as Indion[®] 220 Na would remain on the resin or leach off under different concentrations of wastewater. This in turn would indicate

the efficiency of industrial bactericidal treatment of wastewater on a smaller scale.

Materials and Methods

A 2 liter batch of Indion® 220 Na ion-exchange resin was procured from Pratham Water Solutions. 22 cm³ was suspended in water and packed into a 25 cm³ clean burette serving as a plug flow column reactor. The cation exchange resin had an exchange capacity of 1.8 meq/cm³.

Regeneration of cationic exchange resin

Based on the resin's total exchange capacity, 3.38 cm³ of 37% hydrochloric acid (HCl) was pipetted into the column containing the resin and repeatedly recycled into the column. Presence of H⁺ ions in the solution emerging out of the column was tested using colorimetric pH indicator. Priming was stopped when the pH colour test no longer indicated a red colour complemented by an approximate reduction of 5 cm³ in the volume of the resin was observed. The regenerated resin was then washed with around 1000 cm³ of distilled water to remove any excess H⁺ ions. 2 such batches of primed resin were prepared.

Treatment of regenerated resin with silver nitrate solution

Based on the resin's total exchange capacity, around 6.72g of silver nitrate (AgNO₃) were required plus 25% excess. 25% w/v fresh solution of AgNO₃ was prepared by dissolving 10g of AgNO₃ salt in 40 cm³ of distilled water. The stock solution was gently added to the column containing the primed resin and repeatedly recycled back into the column for complete treatment of resin. Occasionally, a sample of the solution coming out was collected in a 10 cm³ jar and a wooden stick dipped in 37% HCl was immersed into the solution (formation of white silver chloride precipitate indicated presence of Ag⁺ ions and need for further treatment. The process was stopped when the collected solution showed no precipitate upon treatment with HCl and when the pH colour test indicated a deep red colour due to the presence of the displaced H⁺ ions from the resin.

Treatment of silver ion-coated resin with saltwater

Resin treated with silver nitrate solution was collected on filter paper and kept for drying.

Stock salt solutions of concentrations 10 mg/l, 100 mg/l, 1000 mg/l and 10000 mg/l were prepared by dissolving sodium chloride (NaCl) in distilled water. The actual concentrations were determined as 30 ppm, 109 ppm, 898 ppm and 6110 ppm upon running conductivity tests on the solutions.

5g of silver ion-coated resin was weighed and stored in 4 labelled dark bottles each. 50 cm³ of each salt solution was pipetted into the correspondingly labelled bottle. The mixture of resin and salt solution was kept for 7 days and shaken vigorously thrice a day.

Analysis of silver content of resin

After treating the resin with salt solutions for 7 days, the supernatant was filtered off and collected separately. The resin was collected onto filter paper and kept at room conditions for drying. Subsequently the resin samples were analysed for their silver content using inductively coupled plasma atomic emission spectroscopy (ICP-AES) at Exova Metallurgical Services Pvt. Ltd. A blank sample of untreated resin was also analysed for silver content to serve as the control.

Results and Discussion

Table 1 : Concentration and percentage of silver retained on resin after 7 days of treatment with salt solutions of different concentration

Concentration of saltwater/ppm	Concentration of silver on resin/ppm	Silver retained on resin/%
0	6564	100.0%
30	4773	72.7%
109	5005	76.2%
898	464	7.1%
6110	1951	29.7%

As seen in Table 1, there is a clear trend between increasing concentrations of saltwater and the % silver retained on the resin. An increase in the concentration of saltwater from 0.001 ppm to 30 ppm and from 109 ppm to 898 ppm led to a decrease on the percentage of silver retained on the resin. Two anomalies were observed – an increase in % silver retained from 72.7% to 76.2% despite an increase in saltwater concentration from 30 ppm to 109 ppm; a sharper increase in % silver retained from 7.1% to 29.7% despite a sharp increase in saltwater concentration from 898 ppm to 6110 ppm. There is an overall decreasing trend between the concentration of saltwater and the % silver retained on the resin. This trend and its anomalies can be represented through Figure 1 below:

Figure 1: Change in % silver retained on resin with increase in concentration of saltwater

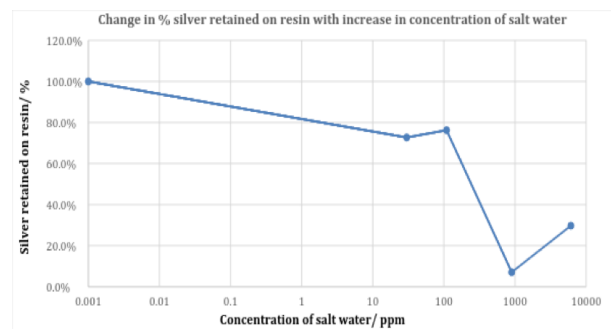
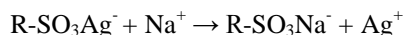


Figure 1 shows how the decrease in % silver retained is gradual for low concentrations of saltwater upto 30 ppm.

However, for higher concentrations of saltwater such as those beyond 100 ppm, the decrease in % silver retained is significantly greater, shown by a sharp decline from 76.2% to 7.1% in Figure 1. Qualitatively, the appearance of the resins after treatment with saltwater was similar for the concentrations 30 ppm, 109 ppm and 898 ppm. The resin had a smooth, amorphous texture and was golden-yellow in colour. The resin sample treated with 6110 ppm saltwater developed a very light pale yellow colour and had clustered into agglomerates. None of the resin samples had retained their gel-type texture.

The results reveal that silver ions on the IER are unstable in the presence of higher concentrations of saltwater. The typical domestic wastewater has a TDS (total dissolved solids) concentration range from 250 ppm to 850 ppm^[14]. Thus, if the corresponding section from Figure 1 is considered, there is a clear negative trend as the % silver retained on resin is shown to decrease with increasing saltwater concentration for the given range.

The silver ion-coated resin has a functional group of AgSO_3^- that interacts with the Na^+ ions from the salt solutions. The IER's functional group then exchanges the Ag^+ ion with the Na^+ ion in the surrounding solution as per the single displacement chemical equation below:



where R is the polymer matrix of the ion exchange resin.

As the concentration of saltwater increases, the concentration of Na^+ ions also increases. According to LeChâtelier's Principle, an increase in the concentration of a mobile reacting ion will shift the equilibrium towards the consumption of that mobile ion. Thus the increase in concentration of mobile Na^+ ions causes the equilibrium system to shift towards consumption of the mobile Na^+ ions by having them attached to the functional group of the IER and in the process displacing the fixed Ag^+ ion into the solution. The greater number of mobile Na^+ groups also means greater number of sites where the Na^+ can displace the Ag^+ ion, thereby leading to a greater leaching of silver ions. The reason why silver ions are unstable on the Indion[®] 220 Na resin in the first place is possibly due to the strongly acidic nature of the resin. The resin lacks a functional group having a lone pair of electrons and thus is unable to form a complex bond with the silver ion that would have given it greater stability due to both electrostatic and coordinate bond interactions.

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