

# A Brief Review on the Removal of Fe<sup>2+</sup> Ions from Water Environment by INDION 220 Na Resin

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**Abstract**— All living organism on this earth chiefly depends on essential and vital elements like carbon, hydrogen, oxygen, nitrogen, phosphorous, sodium, potassium, calcium, magnesium, iron, manganese, and others; for their growth and survival. Water is universally considers as food for all living beings and all waters, whether natural occurring and/or groundwater(GWs) contains significant amounts of Fe<sup>2+</sup>in them This cation is ubiquitous regarding the beneficial and ill-health of human beings and significant amount of Fe<sup>2+</sup> in water pose several potential socio-economic and socio-wellbeing effects to human. So, the modern society seeking GW as source for various consumption purpose (domestic and/or industrial), considerable technological efforts in softening the inevitable hard water. In spite of the availability of plenty of advanced softening techniques, the conventional ion exchangers are still being adopted, of course with the blended version with novel technologies due their public acceptability and demands. Varieties of resins are being made to suit the requirements of diversified consumers. The applicability of ion exchangers-cum-electrochemical methods might be successful in the years to come. The commercial available cation exchange resin INDION 220 Na was properly dried at room temperature, sieved to appropriate sizes, thoroughly washed in distilled water, and later stored in clean glass containers under moist condition .The investigation was done by using fixed bed reactor(FBR) systems under room temperature. Few preliminary investigations were conducted to assess the appropriate size of resin, in FBR system. The fixed-bed studies covered the important experiments such as generation of breakthrough curves (including the effects of initial Fe<sup>2+</sup> concentration, resin size, and flow rate).

**Key words:** Fe<sup>2+</sup> Ions, INDION 220 Na Resin

## I. INTRODUCTION

The impact of continuous population growth, industrial development, and agricultural production in India and other parts of the world, forcing the public to seek groundwater GW as the potential water resource for various purpose (including for drinking purpose). The most common water quality-based associated parameters of GWs are hardness, TDS, Fe<sup>2+</sup>, Mn<sup>2+</sup>, pH, and taste. The secondary predominant cation (i.e; Fe<sup>2+</sup>) gains access into GWs through slow and continuous dissolution of mineral deposits far beneath the ground. Although Fe<sup>2+</sup> is not a hazardous water quality parameter, they pose several deleterious effects within the house and outside. Some of the predominant effects are taste, turbidity, support the growth of 'crenothrix' bacteria, corrosion, and others.

Owing to its potential and diversified effects on human health and other systems, several National and International organisations (including WHO and IS:10500-

1995) have set a maximum permissible limit of 0.3 mg/l for Fe<sup>2+</sup> in a potable water.

In order to satisfy the aforementioned limits in drinking water tremendous efforts have been applied to effectively remove Fe<sup>2+</sup> and Fe<sup>3+</sup> from GWs from past 50 years, conventionally by membrane and ion exchange process in spite of the availability of many techniques. Currently, the blended activated carbon with a mixture of anionic and cationic ion exchange resins or using cross linked  $\beta$ -cyclodextrin polymer are regarded as best chemical abatement technologies, throughout the globe (Charles etal,2016). Moreover several chelating resins are also adopted for the removal of Fe<sup>2+</sup> and/or Fe<sup>3+</sup> from many GWs, in spite of their intrinsic and inevitable drawbacks.

Due to the continuous demand and few public acceptability, several modifications of ion exchangers have been implemented at all the levels. Therefore, combined ion exchanges-cum-electro based processes are being adopted at industrial levels.

Column-type or fixed-bed ion exchanging incorporating polystyrene beads as exchange materials are quite popular at industrial levels in treating very hard waters not only in India, but other parts of the world. On the other hand, to some extent, these materials are being used in smaller capacity exchangers at domestic applications. Even though the ability of sulfonated based polystyrene resins are many times higher than the polystyrene material. Its use had been restricted long back, because of the associated carcinogenic disease produced by it in the softened water. Although the softening potential of INDION 220 Na have been assessed by recent past studies (Shiyamala,2015 and Ruby,2016), appropriate fixed-bed correlation models could not be formulated regarding the removal of Fe<sup>2+</sup> from aqueous phase. Therefore, in this investigation, the fixed-bed performance of INDION 220 Na resin have been assessed particularly with reference to the removal of secondary major metal Fe<sup>2+</sup> from concocted waters.

### A. General

The availability of water for human consumption is highly dwindling year-by-year not only in India, but also in other parts of the world and likewise, available drinking water has been reduced because of the population created naturally and artificially (Low et al, 2008).

All natural waters possess dissolved salts at different concentrations, except rain water may have small amounts of salt due to the impurities in air. Industries also produce salt waters that are not usable for further beneficial use. Among the several water quality parameters, hardness (i.e., presence of multivalent metallic cations like Ca<sup>2+</sup>, Mg<sup>2+</sup>, Ba<sup>2+</sup>, Zn<sup>2+</sup>, Sr<sup>2+</sup>, Fe<sup>2+</sup>, Mn<sup>2+</sup>, Fe<sup>3+</sup>, Mn<sup>2+</sup>, Al<sup>3+</sup>, and others in surface and groundwaters (GWs) is an essential parameter which in excess quantity makes the water

unpalatable and/or nonpotable for human consumption. But, Fe<sup>2+</sup> is also major cations that persist in all GWs.

### B. Iron as cation

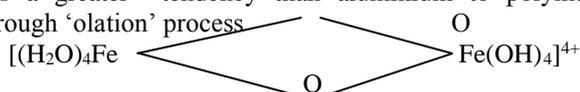
Depending on the focus of interest and the impact of various metals, they can be divided into four major categories like i) toxic heavy metals (Hg, Pb, Cd, and others), ii) strategic metals (Fe, Mn, Al, and others), iii) precious metals (Ag, Au, Pt, and others), and iv) radionuclides (U, Ra, Sr, and others). But, the toxicity and appropriate solution chemistry of metalloids like Cr, As, and Se make them interesting. Iron (i.e; Fe<sup>0</sup>) is one of the major metallic contaminants that is usually found in many source of water. Fe<sup>0</sup> is vitally present in water in two different forms either in soluble ferrous (i.e; Fe<sup>2+</sup>) iron or insoluble ferric (i.e; Fe<sup>3+</sup>) iron. Water containing Fe<sup>0</sup> is clear and colourless, because the Fe<sup>0</sup> is completely dissolved. When exposed to air, the water turns turbid and a reddish brown substance begins to form. This substance is the oxidized or Fe<sup>3+</sup> of Fe<sup>0</sup> that will not dissolve in water. The rate of oxidation is not rapid and Fe<sup>2+</sup> can persist for few minute in aerated water. Moreover it occur when the pH is below 6. In addition, Fe<sup>0</sup> can form stable complexes with humic and tannic substances in water that can be even more resistant to oxidation than the inorganic species alone.

### C. Uses of Iron

Iron is one of the widely used metals in industry especially in steel making and/or its various shapes. On the other hand, there is no industry that exists in the globe, without the use of either cast iron or steel. Moreover it is extending being used in manufacturing metal processing and forming ship building, automobile, tool and die-making industries, infrastructure development, house building, printing-press and others.

### D. Iron in the Environment

Owing to the techno-commercial-social activities, Fe<sup>0</sup> is continuously being released to environment through physical, physico-chemical, biophysical, and biogeochemical processes. Red clayed soils (i.e; especially 'laterite' soils in the Eastern coastal belts of India) are quite rich in Fe content(s). In the aqueous environment, Fe<sup>0</sup> hydrolysis in water with other salts produces series of complexes, such as [Fe(OH)<sub>2</sub>], [Fe(OH)<sub>2</sub>]<sup>+</sup>, [Fe(OH)<sub>3</sub>], [Fe(OH)<sub>4</sub>]<sup>-</sup> and [Fe(OH)<sub>5</sub>]<sup>2-</sup> which are primarily depend on pH of the environment (pH between 3 and 10). Also, in the wastewater coagulation is concerned, Fe<sup>0</sup> 'dimerised' or 'olates' as per Eq.2.1. Further, it has been proved that Fe<sup>0</sup> has a greater tendency than aluminium to polymerize through 'olation' process



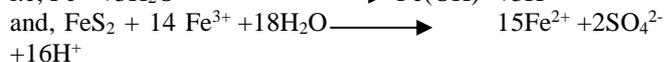
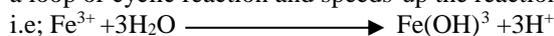
In spite of above, Fe<sup>3+</sup> and SO<sub>4</sub><sup>2-</sup> continuously persist in the vicinity of 'acid-mine drainage' (AMD) fields. AMD is a complex biochemical leaching process, typically occurs in the mining region. The leachate produced from AMD process has typical characteristics like dark-brown to yellow colour highly acidic (pH between 2.5 and 1.5), and high concentrations of Fe<sup>3+</sup> and SO<sub>4</sub><sup>2-</sup>. When FeS<sub>2</sub> (pyrites) is exposed to air and moisture (i.e; during strip or open-cast mining; or from abandoned mining and/or from stacked mined tailings), oxidation of pyrite starts.



This makes the local pH and ips to 2.5, and *thiobacillus ferro-oxidans* (or other *thermophilic Archae* bacteria like *sulpholobus* and *Acidianus*) pyrites oxidize to Fe<sup>2+</sup> and then to Fe<sup>3+</sup>



The Fe<sup>3+</sup> generated through the above Eq.2.3, forms a loop or cyclic reaction and speeds-up the reaction.



Hence, Fe<sup>3+</sup> and SO<sub>4</sub><sup>2-</sup> together : deteriorates the quality of surface and GWs, further dissolves the other metals presents in water like Al<sup>3+</sup>, and greatly affects the fauna and flora of aquatic ecosystem.

### E. Toxicity Biological Effects and Permissible Limits of Fe<sup>2+</sup>

Fe<sup>0</sup> is Iron is commonly present in groundwater worldwide. In India, severe GWs contamination by iron has been reported by several states including Andhra Pradesh, Assam, Chhattisgarh, Karnataka and Orissa. Localized pockets are observed in states including Bihar, Jharkhand, Maharashtra, Kerala, Madhya Pradesh, North Eastern States, Punjab, Rajasthan, Tamilnadu and Uttarpradesh. Also, it is one of the most commonly used metals in the world metal production because of its low price and hardness. Excessive concentrations of Fe<sup>3+</sup>/Fe<sup>2+</sup> in public water supplies cause turbidity, unpleasant taste and odour. It imparts a brownish colour to laundered cloths and stains plumbing fixtures. It also causes difficulties in distribution systems by supporting the growth Fe<sup>0</sup> bacteria, resulting in the clogging of pipes (Onganer and Temur, 1998). Therefore, the presence of Fe<sup>3+</sup>/Fe<sup>2+</sup> is objectionable in certain industries, such as food, textiles and paper (Sag and Kutsal, 1996). While Fe<sup>3+</sup> is found naturally in large concentrations in an insoluble form, it can be converted to soluble forms that often result in water contamination (Indianaraet al., 2009). Even though Fe<sup>0</sup> is an essential mineral helping in the transportation of oxygen in the blood, its presence in ground water above a certain level makes water unusable due to its metallic taste. Moreover excessive Fe<sup>2+</sup>/Fe<sup>3+</sup> in drinking water may cause vomiting, bleeding and circulatory disorders.

In spite of above, Fe<sup>0</sup> do not ultimately yield harmless end products in the metabolism and they are accumulated in the food chain water-plants-animals-humans (Shukla and Pai, 2005) thereby posing the greatest threat to the living organisms. On the other hand, the role played by Fe<sup>3+</sup> in biological systems, it was found that, cells use Fe<sup>0</sup> catalytically in many important and diverse reactions, i.e; electron transport, nitrogen fixation, detoxification and others. Its bioavailability depends on its redox state and the pH, some microorganisms are able to use Fe<sup>3+</sup> as an electron acceptor in anaerobic respiration (Maliki et al., 2006). However, if it is in excess, it can also play an important role in the progression of several types of damage to the human body, so maintaining a balance of Fe<sup>3+</sup>/Fe<sup>2+</sup> in the body is essential to human health. Also when Fe<sup>0</sup> combines with tea, coffee and other beverages, it produces an inky, black appearance and a harsh, unacceptable taste. Vegetables cooked in water containing excessive iron turn dark and look unappealing.

Owing to the diversified effects of Fe<sup>2+</sup>/Fe<sup>3+</sup>, such as physiological bioaccumulation, neurological, and biological effects on human beings the WHO has set a maximum acceptable limits of 0.3mg/l as Fe<sup>0</sup> (i.e; total Fe<sup>0</sup>) in potable water supplies. Based on this several National and International Organization such as USEPA, EUs, UK, Australia, New Zealand and India (i.e; IS:10500,1995) have also fixed an acceptance limits of 0.3mg/l for Fe<sup>0</sup> in drinking water.

#### F. Treatment Techniques for the Removal of Fe<sup>2+</sup>

A wide range of technologies are available for the removal of Fe<sup>2+</sup>/Fe<sup>3+</sup> from industrial wastewaters. Some of them are well-established that have been in practice for decades; others are more recent innovations. While a number of processes simply remove Fe<sup>0</sup> from wastewaters (just the phase transfer from liquid to solid phase) by chemical precipitation and filtration; in recent years, much emphasis is given to recovery and reuse of chromium in the respective industries by adsorption or sorption methods.

##### 1) Physicochemical Methods

Among the several physicochemical methods for removal of metals, chemical precipitation with lime or caustic soda is most conventional and oldest. For Fe<sup>2+</sup> and/or Fe<sup>3+</sup> removals from GW the most commonly used methods like oxidation-precipitation-filtration, lime softening, ion exchange, activated carbon and other filtration materials, adsorption, bioremediation, supercritical fluid extraction, use of aerated granular filter, sub-surface iron removal and membrane processes have been employed (Vaaramma and Lehto, 2003; Munter et al,2005; Aziz et al,2004; Das et al,2007; and Cho,2005). In addition to these methods floatation (Zouboulis et al, 1997), electrolytic recover (canet et al,2002) liquid-liquid extraction (Farajzadeh et al,2009), Solid-phase extraction (Soliman and Ahmed,2009), reverse osmosis (Weng et al,2008) and others, have been tried in the past few years.

Although the above process or operation are significantly efficient in removing Fe<sup>2+</sup>/Fe<sup>3+</sup> from many GWs and industrial wastewaters they are not regarded as effective acceptable techniques because of their couple of intrinsic demerits encounter in the full scale operation. Few critical drawbacks cited in the literature are: exorbitant operational and maintenance costs (Weng et al,2008), huge sludge generation-cum-disposal problems (Suksabye et al,2008), generation of secondary pollutants and narrow application range (oguz 2014) use of expensive solvents and their safe disposal aspects (Subramanian Vasudevan et al,2009) and others. Also, as the concentration of metals in the wastewaters falls within the range of 10 to 100 mg/l, the overall cost of these techniques will be still higher.

##### 2) Sorption and/or Bio sorption Techniques

Owing to the drawbacks of various physicochemical techniques, adsorption or sorption was came to limelight during 1960s, especially in treating metal-bearing wastewaters containing dilute concentrations between 10 to 50 mg/l. The commercially available activated carbons (PAC and GAC) were put to use in sorption process long ago, for removing various metals in the very dilute (5 to 20 mg/l) concentrations. But, the potentials of several artificially prepared activated carbons, inorganic and inert materials, and others in removing Fe<sup>2+</sup>/Fe<sup>3+</sup> from water

environment have been demonstrated (Beenakumari,2009, Aksu and Alperis,2005; and Akpor and Muchie,2010). As per as biosorption of Fe<sup>2+</sup> is concerned, Dhabab (2011) demonstrated the combined removals of Fe<sup>2+</sup>, Cu<sup>2+</sup>, Pb<sup>2+</sup> and Zn<sup>2+</sup> (i.e; each at 50mg/l level of concentration) by 'duckweed' (i.e; an aquatic plant which grows on water surface lives in shallow waters, and is especially distributed in South and Central Iraq). As per the study the selectivity sequence of metal ions by duckweed was Pb<sup>2+</sup> < Zn<sup>2+</sup> < Cu<sup>2+</sup> < Fe<sup>2+</sup>. On the other hand in another study (Yue et al, 2016) infused tea leaves (i.e; Camellia sinensis) was utilised to simultaneously remove Pb<sup>2+</sup>, Fe<sup>2+</sup>, and Cd<sup>2+</sup> from aqueous solution. The authors confirmed that the infused tea leaves could exhibit a selectivity sequence of Pb<sup>2+</sup> > Cd<sup>2+</sup> > Fe<sup>2+</sup> with the respective biosorption capacities of 26.32, 14.29 and 12.38 mg/g (i.e; Langmuire-based isotherm).

##### 3) Ion Exchange Process

Ion exchange or sorption-oriented processes are gaining tremendous scope in pollutant(s) removal from metal polycontaminated surface finishing discharge water. Resins are basically classified as exchange-type or chelating-type polymeric materials. Although in theory many methods could be suitable to finish off the work done during the physicochemical treatment. (i.e; as specified in section 2.6.1), few methods are actually used by small surface finishing plants owing to technical but especially to economic considerations (Barakat, 2011; Fu and Wang, 2011). Also, much effort has recently been focused on various materials based on cyclodextrins (CDs) which are molecules derived from starch.

These substances, and in particular beta-cyclodextrin (β-CD), have the remarkable ability to form inclusion complexes with other molecules through host-guest interactions in solution or in the solid state (Szejtli, 1998; Szejtli, 2004). The specific properties of β-CD combined with its lack of toxicity towards humans have led to its use in numerous applications (i.e; pharmacy, medicine, biotechnology, textile industry, toiletries, cosmetics, food additives, and others.). Recently, Morin-Crini and Crini (2013) showed that β-CDs also deserve particular attention in environmental science in terms of removal of pollutants from water and wastewater using oriented-adsorption processes. Recently Charles et al (2016) utilized them the three different ion exchange resins (i.e; IRA402CI, IR120H, AND TP207) for the removal of Cu, Ni and COD from metal polycontaminated surface-finishing discharge water.

##### 4) Use of INDION 220 Na in Ion Exchange

The INDION 220 Na resin is currently being used to softening of water, both at commercial and individual household levels, throughout India including Tamilnadu state. However this resin was previously used to assess the efficacy of this resin to thoroughly undeveloped influence of combined effects of Ca<sup>2+</sup> and Mg<sup>2+</sup> in softening of concocted waters, at the civil Engg. Dept of C.I.T, Coimbatore-641014(TN) (Ruby 2016 and Shiamala, 2015).

## II. METHODOLOGY

### A. Materials

#### 1) Resin (or Sorbent)

The INDION 220 Na was procured from the Aqua Ion Exchange systems, Coimbatore, Tamil Nadu, India; and

thoroughly washed in distilled water to remove foreign materials and stored in glass beakers under moist condition. Later, it was segregated to different sizes: i) passing through 2.36 mm IS sieve and retaining on 1.18 mm BIS sieve with geometric mean size of 1.67 mm, ii) passing through 1.18 mm IS sieve and retaining on 0.6 mm IS with geometric mean size of 0.84 mm, iii) passing through 0.6 mm IS sieve and retaining on 0.3 mm BIS with geometric mean size of 0.42 mm, and iv) passing through 0.3 mm IS sieve and retaining on 0.15 mm IS with geometric mean size of 0.21 mm.

## 2) Chemicals

All chemicals and reagents used were of AR grade and procured from S.d Fine Chemicals Ltd, Mumbai, India. The distilled water had an average pH of 6.6 and electrical conductivity less than 10 µS/cm.

## 3) Water

All experiments were conducted in tap water (Bhavani water),

## B. Methods

### 1) Analysis of Iron

The analysis of calcium was determined by 1,10-PHENANTHROLINE method, Further, all other analyses which are required for the experiments were analysed as per the Standard Methods for the Examination of Water and Wastewater (APHA *et al.*, 2005). The experimental errors were below 5%.

### 2) Characterization of Resin

The detailed physicochemical characteristics of INDION 220 Na resin. In order to appropriately understand the particle or bead size distribution of INDION 220 Na resin (relation between the amounts of resin retained between the successive sets of sieves), sieve analysis was carried out by using 1 kg<sub>f</sub> of relatively dry resin passing through several BIS sieves, such as 4.75, 4.00, 2.36, 1.18, 0.6, 0.3, 0.15, 0.075 mm, respectively. Later, the amount of resin retained on 4.00, 2.36, 1.18, 0.6, 0.3, 0.15, 0.075 mm sieves were recorded.

### 3) Fixed-bed Studies

Fixed-bed studies were performed for INDION Na 220 resin, using tap water concocted with Fe<sup>2+</sup> ions. A glass column of internal diameter of 3 cm was appropriately packed with INDION Na 220 resin for a required depth necessary for the experiment, by slurry packing method (Keerthinarayana, 1994). Also, the bed was sand-witched between two layers (2 cm on top and bottom) of ordinary cotton, to prevent entrance and exit flow disturbances. The detailed experimental fixed-bed set up is shown in Figs. 3.2, 3.3, 3.4 (multiple ports). The influent and effluent samples were collected periodically and analysed for Fe<sup>2+</sup> concentration.

Experimental breakthrough curves were obtained for: (i) two different sizes of INDION Na 220 resin (0.84 and 0.42mm) (ii) four different initial concentrations of Ca<sup>2+</sup> (i.e., 50, 30, 10 and 5 mg/l), (iii) three different flow rates (i.e., 25, 15, and 5 ml/min). and (iv) five different bed depths (i.e., 30, 24, 18, 12, and 6 cm). In each study, effluent samples were periodically analysed for Fe<sup>2+</sup> concentrations.

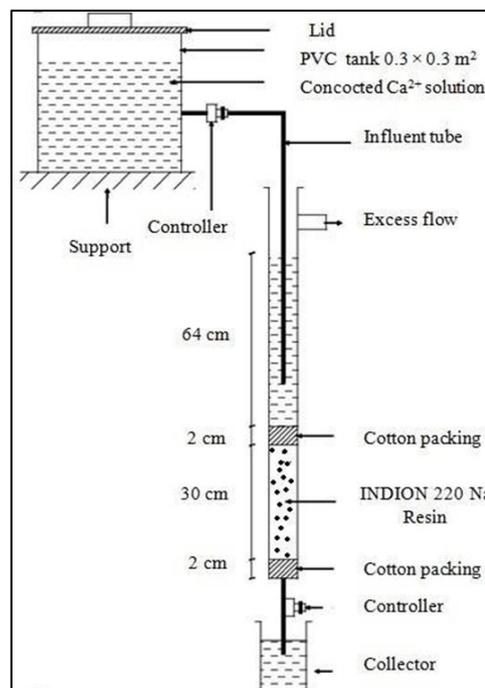


Fig.1: Schematic Sketch showing the Fixed-bed Setup for Fe<sup>2+</sup> Removal.

## III. CONCLUSIONS

This paper outlined and based on the investigation pertaining to the removal of Fe<sup>2+</sup> by INDION 220 Na resin in FBR systems. The INDION 220 Na resin is an effective material in removing Fe<sup>2+</sup> from concocted water and it is highly suitable in FBR systems, in the size range of 0.42 mm to 0.84 mm. The head loss, swelling, and morphological changes of resin beads are insignificant, during the fixed-bed studies.

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