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Magnetic Ion Exchange: Is There Potential for International Development?

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Abstract: Magnetic ion exchange (MIEX®) is an ion exchange resin developed as an additive to existing water treatment plants where additional organic matter is to be removed. The smaller size, magnetic properties and simple regeneration using NaCl distinguishes MIEX® from conventional ion exchange resins and hence its use in international development applications is investigated in this review article. MIEX® has been demonstrated to remove varying levels of dissolved organic matter, inorganic anions such as nitrate and sulphate and micropollutants including non-ionic pesticides. The removal efficiency can also be influenced by temperature, pH and presence of other anions. As MIEX® is unable to disinfect water, the most likely application within international development is as pre-treatment before disinfection or membrane filtration.

Keywords: Magnetic ion exchange, international development, natural organic matter removal, micropollutant removal

1. Introduction

Magnetic ion exchange (MIEX®) is a strong base anion exchange resin with magnetic properties that can be used to adsorb weak organic acidic ions from water [1]. The magnetic properties differentiate it from other ion exchange resins, as it allows for faster resin agglomeration and recovery [2]. The resin was developed with the purpose of removing dissolved organic carbon (DOC) from drinking water supplies [3]. While DOC by itself is relatively harmless, problems can occur when DOC is combined with chlorine, a common drinking water disinfectant, or bromide as they can form disinfection by-products (DBP), which are potential carcinogens [2]. In addition, the removal of DOC from water reduces the need for residual disinfection of bacterial regrowth during distribution, as well as customer complaints relating to taste, odour and colour of the water [4]

The objective of this paper is to review potential applications of this ion exchange resin in international development. One of the main problems facing international development is the provision of safe drinking water, with over 1.1 billion people lacking access to this basic need [5]. Waterborne diseases, associated with pathogenic bacteria, viruses and protozoa, are the most common cause of illness and death related to water and sanitation within developing countries [6]. Therefore, improved microbiological safety through the removal of pathogens is essential for international development. While MIEX® can not be used to disinfect or physically remove bacteria or viruses, it can remove DPB precursors, reduce chlorine demand, and therefore reduce DPB risk [7]. In addition, it can be coupled with disinfection processes such as ozonation or membrane filtration such as ultrafiltration.

This review will describe the principles of MIEX® and focus on its applicability to international development by discussing its ability to remove DOC, as well as a range of inorganic and organic contaminants from water and examine the possibility of MIEX® integration with existing water treatment options. The issue of brine waste disposal options will conclude the paper.

2. Process Principles

2.1. Resin Characteristics

MIEX® is an anionic exchange resin which consists of a magnetic core with a polymer shell (**Error! Reference source not found.**) [8]. The polymer, polyacrylate, is macroporous and contains quaternary amide functional groups, which assist with DOC removal through ion exchange [9]. MIEX® differs from traditional ion exchange resins due to its small size and magnetic properties. These changes were implemented to maximise organic removal and resin reuse. The resin beads have a mean diameter of 150 – 180 µm which is approximately 2 to 5 times smaller than other ion exchange resins [10]. As a result it has an increased surface area to volume ratio compared to other resins, meaning there are more exchange sites which increases exchange kinetics, therefore more DOC can be removed [2, 7]. The magnetic core enables fast agglomeration and settling of resin particles, and this leads to high (up to 99.9%) resin recovery rates [11].

2.2. Adsorption and Desorption

Adsorption and desorption are the chemical reactions that allow the process to function (**Error! Reference source not found.**). The DOC is adsorbed to the resin through ion exchange with the chloride ions at the active sites on the surface. Quaternary amide moieties act as DOC chloride exchange sites [12]. The presence of negatively charged carboxylic groups in DOC enables removal as they are attracted to the active sites [12]. The resin is not limited to the adsorption of DOC. MIEX® also has the ability to adsorb other anions, including nitrate, sulphate, bromide, chromium, arsenic and certain pesticides [13, 14]. The removal efficiency of these compounds will depend on the anion competition for exchange sites.

The resin is regenerated through desorption, which is a reversal of the adsorption process. Desorption is achieved with the assistance of a 10% w/w NaCl brine. Through a reverse of the ion exchange process, the DOC sorbed to the quaternary amide active sites are substituted for chloride ions, and the exchanged DOC goes to the brine [10]. This process occurs due to the high chloride concentration, as the chloride ions have a strong affinity for the exchange sites and force the DOC from the resin [15]. Depending on water quality 2% w/w NaOH can be added to assist regeneration, as the increase in pH increases the solubility of DOC [15]. Conventional ion exchange resins are fouled by organic matter, and thus can not be reused effectively. Therefore, the ability to regenerate is advantageous to application in international development where ease of operation is crucial.

3. Contaminant Removal

3.1. Natural Organic Matter

Natural organic matter (NOM) is a complex mixture of different types of organic molecules including fulvic and humic acids, hydrophilic acids and various low molecular weight compounds [16]. The origins of NOM in water supplies include soil, swamps and plant decomposition, as well as wastewater effluent if present. NOM has colour, taste and odour implications for drinking water, and can also pose a threat to human health when combined with chlorine disinfection as NOM is a DBP precursor [2].

MIEX® was developed for the purpose of removing the dissolved fraction of NOM from water. Previous studies have demonstrated that it effectively removes the ultraviolet absorbing and acidic fractions of DOC over a wider molecular weight range compared to alternative treatment options, such as coagulation [1, 10, 11]. In addition, the resin can also effectively remove both hydrophobic and hydrophilic fractions of DOC [7].

The removal of DOC from raw water using MIEX® is generally around 80% [2, 11]. However, the removal efficiency of DOC can be affected by the quality of the raw water as well as the solution chemistry. Due to the presence of carboxylic groups [12], DOC is in an anionic form from pH 4 - 5. At low pH (<4) it cannot be used to effectively remove DOC, however as most applications are in the pH range of 6.5 – 7.5 it can remove DOC rich in carboxylic groups. However, the removal efficiency would also be greatly reduced if the raw water came from a source rich in tannins. Tannins primarily contain phenolic hydroxyl groups, which are not in an anionic form until approximately pH 8 - 9 [1]. Temperature also has the potential to affect removal. Humbert et al.

[14] found no significant difference in DOC removal between 6 and 26°C, however removal increased slightly as the temperature increased to 36°C. This is because an increase in temperature leads to an augmentation of reaction kinetics.

There are several factors that can impair DOC removal by the resin. Firstly, there is the issue of seasonal variations in the quantity of DOC in raw water. After periods of high rainfall the level of DOC in water supplies can increase [11]. In these situations it may be necessary to alter the dosage of resin, or increase the contact time, to ensure that it can successfully remove DOC. This may make this process vulnerable in international development applications where trained personnel and monitoring may not be easily available. In addition, a high concentration of inorganic anions in the raw water can compete for ion exchange sites, reducing DOC removal [2]. This indicates the studies with specific waters are important before process adaptation.

3.2. Inorganic Matter

MIEX® has the potential remove inorganic anions from water, and the presence of anions such as fluoride or nitrate are common problems in many developing countries. Inorganic anions such as bromide can increase the formation of DBP [3], while trace metal anions such as chromium and arsenic can have serious implications for human health as they are carcinogenic [13]. Several studies have shown that inorganic anion removal is dependant on MIEX® resin concentration [9, 14]. At high resin doses (8 mL/L) as much as 65% of bromide can be removed, while this decreases significantly at lower doses (0.5 mL/L) to 8% removal [14]. The removal efficiency of bromide is further dependant on pH. A study by Singer and Bilyk [7] showed that bromide removal decreased significantly as alkalinity increased. At high pH there is a higher concentration of bicarbonate ions and these compete with bromide for ion exchange sites, reducing the bromide removal.

Removal of sulphate and nitrate has also been studied. The presence of sulphate in the water can cause problems for DOC removal, as it can compete with DOC for exchange sites [3]. Sulphate removal has been shown to be concentration dependant, with 92% removal by MIEX® at 2 mL/L resin concentration, decreasing to 42% removal at 0.5 mL/L concentrations [14]. The resin can contribute significantly to nitrate removal, up to 94% [10, 14].

In addition, the application of MIEX® to removal trace metal anions such as arsenic (As(V)) and chromium (Cr(VI)) has been studied, and showed 37% removal of arsenic and 58% removal of chromium [13]. As arsenic contamination is a problem in some developing countries such as Bangladesh [17] the ability of MIEX® to remove moderate amounts of arsenic is very relevant and promising for international development.

3.3.Micropollutants

Micropollutants, which include pesticides, natural and synthetic hormones and pharmaceutically active products, can be considered ubiquitous in surface and wastewater [18]. Low concentrations of many micropollutants (ng/L to µg/L) can have a significant effect on vertebrate and ecosystem health. Such compounds are of concern where water reuse is practiced intentionally or unintentionally because of polluted waters serving as water supplies downstream. Such sewage-water supply cross-connections are very common in international development due to open sewers, pit latrines and usage streams for disposal and water supply. In developing countries the usage of pesticides that may be banned in developed countries is commonplace and it is likely that this is the most severe micropollutant threat. In addition, many micropollutants are not removed effectively using conventional water treatment, where such treatment schemes exist, and therefore MIEX® may be applied to assist their removal. Within the literature, MIEX® has been applied to remove micropollutants including pesticides atrazine and isoproturon [14, 19] and natural hormones such as estrone [20, 21]. The removal of pesticides from water is particularly applicable to international development due to extensive pesticide use in many developing countries [22].

The removal of atrazine and isoproturon using MIEX® was studied by Humbert et al. [14, 19]. The results demonstrated only 7% of atrazine and 5% of isoproturon could be removed using MIEX® after a contact time of 30 minutes [14]. By increasing the contact time to 24 hours slightly higher (approximately 12%) removal was observed [19]. The poor performance was attributed to the non-ionic nature of the pesticides. However, MIEX® may have greater applicability in pesticide removal when used as a pre-treatment to powdered activated carbon (PAC). Humbert et al. [19] found the use of MIEX® prior to PAC lead to a 20% increase in pesticide removal compared to removal by PAC alone.

The removal of steroidal hormones from drinking water is also of importance. Hormones, such as estradiol and estrone, are naturally excreted by humans, and they are amongst some of the most potent endocrine disrupting chemicals [23]. Mastrup and Schäfer [20] and Schäfer et al. [21] studied estrone removal by MIEX® and found removal was influenced by pH, temperature and ionic strength. The charge of some hormones is affected by pH. For example, estrone changes from a neutral to a negative charge above its acid dissociation constant of 10.4. At pH 11, MIEX® could remove approximately 70% of negatively charged ionic estrone from solution, compared to only 30% when estrone has a neutral charge and is non-ionic [21]. This suggests that while ion exchange interactions are important for estrone removal by MIEX®, estrone must still interact with MIEX® through either specific (e.g. hydrogen bonding) or non-specific (eg van der Waal forces) interactions as 30% is still removed below pH 11.

4. Process Integration

MIEX® can be added to water treatment processes in similar ways to coagulants or PAC. Its magnetic characteristics allow accelerated floc formation and settling. The process, from the input raw water to the output DOC removed water, is shown below in **Error! Reference source not found.** and it can be divided into three key parts, DOC removal, resin recovery and resin regeneration. In addition, MIEX® can be retrofitted to existing treatment plants.

4.1. MIEX Process

The raw water enters a stirred contact, and resin is added. The contractor is stirred to allow the resin to disperse to provide maximum surface area for DOC adsorption [11]. The amount of resin added is typically 5 to 10 mL/L, however this can vary depending on the quality of the raw water [15]. The contact time is typically 30 minutes, however a study by Humbert et al. [14] suggested maximum DOC removal can be reached within 15 minutes using 8 mL/L of MIEX® resin. However, a longer contact time may be required depending on water quality, as it has been suggested by Fearing, *et al.*, [11] that a contact time of 60 minutes is required for optimal DOC removal. In addition, as demonstrated in the case of atrazine and isoproturon, the contact time for optimal removal will vary depending on the contaminant. After detention in the contactor, the resin and water flow under gravity to the separator. Due to its magnetic properties, the resin rapidly agglomerates and forms large particles which settle quickly, allowing fast separation from the supernatant [10]. Only a small amount (<0.1%) is lost during the process, so the rate of resin recovery is greater 99.9% [11], however any resin carryover can increase the turbidity of the treated water [7]. Therefore, an additional water treatment process such as coagulation may be required after to remove any turbidity [3]. Approximately 85 – 90% of the recovered resin is reused in the process, while the remaining resin is regenerated using NaCl brine.

4.2. Pre-treatment

MIEX® cannot be used as a stand alone process to treat drinking water as it does not have the capacity to remove turbidity, particulate matter or pathogens from water. However, it can be coupled with existing water treatment options to produce safe drinking water. Recently research has focused the usage of the resin as a pre-treatment step to coagulation (**Error! Reference source not found.**), ozonation and membrane filtration [1, 2, 11]. Fearing et al. [11] compared DOC removal with MIEX® itself to the resin combined with ferric sulphate coagulation, and found DOC removal increased by as much as 20% in the combined process. In contrast, Boyer and Singer [2] found there was no significant difference in DOC removal between MIEX® itself and for a combined process with alum coagulation. There are several advantages to applying the resin as a pre-treatment. Typically MIEX® removes low to moderate molecular weight fractions of DOC, while coagulation is better suited to remove high molecular weight fractions [24]. Allpike et al. [1] found that the use of MIEX® pre-treatment before alum coagulation lead to a wider molecular weight range of DOC removed compared to the resin or coagulation alone. In addition, pre-treatment with the resin can reduce the coagulation dose required for treatment significantly (up to 85%) [7]. However, as neither MIEX® nor coagulation can disinfect water, even the combined process is not suitable for international development alone, and would need to be coupled with chemical or physical disinfection processes.

Ozonation is a water treatment method that disinfects water without the need for chlorine, however there are some drawbacks which prevents greater ozonation application. Firstly, carcinogenic bromate and bromate DBPs can form when using ozone to disinfect water containing bromide ions [12]. Secondly, energy demand is high, and thirdly, any DOC present in the raw water can increase the ozone demand, which reduces the effectiveness of ozonation [9]. Based on its ability to remove approximately 80% DOC and up to 65% bromide, MIEX® is an attractive pre-treatment option for ozonation. Johnson and Singer [9] found that MIEX® pre-treatment significantly increased the dissolved ozone concentration following ozonation, compared to untreated water. Therefore, with the removal of the majority of DOC the ozone demand could be reduced. MIEX® pre-treatment also has implications for the ozone decay, as Wert et al. [12] demonstrated that MIEX® pre-treatment decreased the ozone decay rate compared to untreated water which can lead to an increase in bacteria and protozoan inactivation. In addition, bromate formation due to ozonation decreased significantly when MIEX® was used for pre-treatment [9]. This is due to the removal of bromide ions, as well as the reduced ozone demand. A hybrid MIEX® - ozonation process could be an option to treat water in developing countries, however the operational and maintenance requirements of ozonation may make it an inappropriate technology option at this stage [6].

Membrane filtration such as ultrafiltration (UF) may be a suitable water treatment option for international development as it disinfects water by physically removing bacteria and viruses, and has a lower chemical requirement compared to conventional treatment [25]. However, organic, biological and particulate fouling which reduces the treated water output and increases costs through high cleaning and maintenance requirements which again may be difficult to achieve in international development. As MIEX® can remove significant amounts of DOC it may prevent some of this membrane fouling. However, studies by Son et al. [26] and Humbert et al. [27] using dead-end filtration configurations found that MIEX® pre-treatment for UF only lead to a minor decrease in membrane fouling compared to no pre-treatment. Son et al. [26] showed that coagulation was a better pre-treatment for UF, suggesting that more fouling was caused by high molecular weight fractions which coagulation can remove, compared to low to moderate fractions MIEX® typically removes. In addition, Schäfer et al. [21] has suggested that MIEX® resin is prone to break up, and this may in fact contribute to membrane fouling. Zhang et al. [28] pre-treated submerged UF membranes with MIEX® and PAC, and MIEX pre-treatment showed no increase in transmembrane pressure, and allowed the process to run for longer, while PAC lead to an increase in transmembrane pressure. Submerged membranes typically require lower pressure and less cleaning than dead-end or cross flow membrane configurations [28], therefore submerged membranes with MIEX® pre-treatment may be more manageable in international development applications.

5. Brine Disposal and Treatment

In the final phase of the MIEX® process the DOC saturated resin is regenerated with 10% w/w NaCl solution [10]. The by-product of regenerate is a waste brine containing NaCl as well as any DOC, inorganics and micropollutants removed from the raw water and recovered from the resin. Such brines are similar in characteristic to reverse osmosis concentrates from desalination or wastewater reuse facilities. As such disposal or treatment can be expensive and have significant environmental impacts it is important to consider brine disposal options suitable for developing countries.

When geographically possible, the majority of such waste brines is disposed to the ocean [29]. This disposal method is applied due to low cost, however disposal can be problematic, as the brine salinity is considerably higher than seawater, disturbing the sea floor [29], while the presence of micropollutants in the brine is likely to have negative implications for aquatic organisms. In situations when ocean disposal is not suitable, such as for inland water treatment, other brine disposal options include solar evaporation, landfill and bore injection [30]. For inland disposal, solar evaporation ponds are the most suitable disposal method in warm or arid developing countries. They are low cost, require little maintenance, and when the ponds are properly sealed there is no contamination of surrounding soil or groundwater [31], unlike the other inland disposal options.

Another option is to treat the brine to separate the organic matter from brine. Using anion exchange brine from a sugar refinery Wadley et al. [32] used nanofiltration to separate NaCl from organic matter. The DOC concentration in brine can be as high as 20 g/L [15], therefore it could be used as a soil supplement, while the NaCl could be reused to regenerate MIEX®. However, due to the higher costs and complexities associated with brine treatment compared to disposal it is unlikely it would be suitable for international development.

6. Integration in Developing Countries

As waterborne diseases are a major cause of mortality in developing countries [33] it is essential to disinfect or physically remove pathogenic bacteria and viruses. As a result MIEX® can not be used alone for international development. However, depending on levels of water turbidity and particulate matter type, MIEX® can be coupled with either chlorine disinfection or submerged ultrafiltration. Some advantages and disadvantages of MIEX® in the context of international development are shown in Table 1. As well as the advantages of removing DBP precursors and reducing chlorine demand, the ability of MIEX® to remove inorganic anions shows great potential for international development in particular where physio-chemical water quality are of concern. While MIEX® can not remove turbidity, and can even increase it, the presence of turbidity does not affect removal of DOC. High turbidity waters are very common in developing countries, particularly during rainy season, hence this is an important characteristic of MIEX® for international development. Finally, waste brine produced by the process can create environmental problems if not properly disposed of, however in arid or warm countries brine can be disposed of with low cost and environmental impact using solar evaporation. Therefore, MIEX can be suitable for international development, provided it is coupled with disinfection or membrane filtration and the waste is dealt with responsibly.

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Table 1: Advantages and disadvantages of MIEX® in international development

ADVANTAGES	DISADVANTAGES
Effective removal of dissolved organic carbon (up to 80%), and hence disinfection by-product precursors	Cannot disinfect water, therefore cannot be used alone for international development applications where microbiology contaminants are significant
Reduced chlorine demand and hence reduce disinfection costs	Cannot remove turbidity or particulate matter, therefore filtration or coagulation is required for turbid raw water
Significant removal of inorganic anions, such as nitrate and sulphate, and certain micropollutants, such as ionic pesticides, pharmaceuticals and hormones	Any resin carryover in the process can increase turbidity of the treated water
Potential to couple MIEX® with other water treatment applications, such as disinfection, coagulation and membrane filtration	Seasonal fluctuations in DOC concentration can require different MIEX® doses or retention times, therefore the process requires monitoring
MIEX® waste brine can be disposed of through solar evaporation at low cost and low environmental impact	MIEX® waste brine requires treatment and disposal
Presence of turbidity and particulate matter do not affect removal of DOC by MIEX, which is good characteristic for international development where surface waters often have extreme turbidity values	

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Figure 1

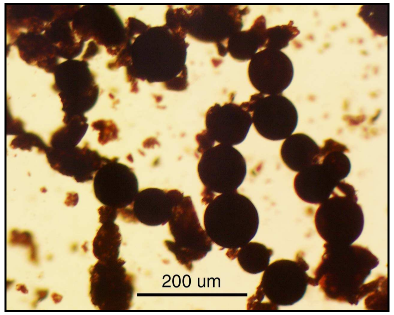

Figure 2

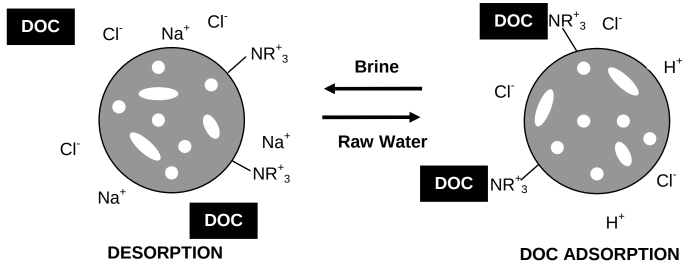

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Figure 3

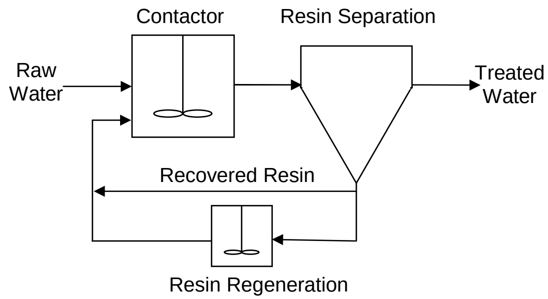

Figure 4