Treatment of Brine Using Nanofiber Materials and Ion Exchange Resiens

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Abstract: Batch sorption experiments were carried out to investigate the sorption properties of PAN, PAN+TiO$_2$ and PAN+ZEOLITE nanofibres for Mg^{2+}, Ca^{2+}, K$^+$ and Na$^+$ ions from brine wastewater. Comparative batch studies using PAN, PAN+TiO$_2$ and PAN+ZEOLITE nanofibres were carried out using Purolite S950 resin as the standard. Parameters which include contact time, effect of temperature, pH, sorbent dose, sorption isotherms were studied in the sorption experiments to understand the sorption phenomena, loading capacity of the sorbents (nanofibres and resin) and the sorption kinetics for Mg^{2+}, Ca^{2+}, K$^+$ and Na$^+$ ions from the simulated brine solutions. The results from the comparative batch studies revealed that the Purolite S950 resin was effective in the removal of the divalent metal ions (Mg^{2+} and Ca^{2+}) over the other metal ions, thereby depicting good selectivity towards Mg^{2+} and Ca^{2+} ions. The removal by the Purolite S950 resin followed the order: Mg^{2+} > Ca^{2+} > K$^+$ > Na$^+$. The binding capacity to the divalent metal ions is influenced by the aminophosphonic acid functional group attached to the resin. Purolite S950 resin had faster kinetics than the nanofibres showing that the sorption equilibrium could be reached within 60 minutes, compared to the sorption equilibrium of 120 minutes by the nanofibres. The order of efficiency and performance of the sorbents can be given as: Purolite S950 resin > PAN+ZEOLITE > PAN+TiO$_2$ > PAN.

Key words: Brine treatment · PAN Nanofibre · PAN+TiO$_2$ · PAN+ZEOLITE · Purolite S950

INTRODUCTION

It is very important here to discuss water scarcity and pollution, brines, the nanofibre materials and properties, their background in use as sorbents as well as their applications. This section is going to present the relevant information on the brine and the use of nanofibre as an alternative sorbent in wastewater treatment such as brines.

Brine: Brine is wastewater saturated with dissolved salts such as potassium, calcium, sodium, sulphates, chlorides and nitrate ions and high total dissolved solids (< 1, 500 mg/kg TDS) [1]. It is formed through water treatment when Tubular Reverse Osmosis (TRO) is employed to treat wastewater. Brine is a concentrated stream that contains a total dissolved solids (TDS) greater than 36 g/L. Brine is water saturated or nearly saturated with salt, while natural brines are waters that contain very high to an extremely high concentration of dissolved constituents such as elements, molecules and ions. It is also considered that brines are those waters more saline, or more concentrated in dissolved materials, than sea water (35 grams of dissolved constituents per kilogram of sea water) [2]. Also, brine can contain concentration of salt more than five times greater than the salt content of average sea water [2]. Brines are basically of commercial interest, especially in the production of table salt. Brines also occur in nature and are found in the earth's interior and also on the earth's surface as a by-product of mining, salt lakes, gas production and oil production. Brine wastewater is a by-product of various water treatment processes such as desalination, power generating stations. There is a need for proper handling when disposed because of its potential to pollute the groundwater and also, cause water pollution which results in levels of salinity in excess of the Department of Water Affairs (DWA)'s limits [3].

Brines from the Desalination Processes: In most arid nations where structural shortage of water is a constant phenomenon, desalination becomes the solution for water scarcity. Countries like Cyprus and Jordan which have exploited their sources of natural water and having no more sources to exploit resort to desalination process as an escape route.

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Desalination is a separation process which is used to reduce the dissolved salt content of saline water to a usable level. Three liquid streams are involved in all desalination processes: the saline feed-water (brackish water or seawater), low-salinity product water and the very saline concentrate (brine or reject water) which must be disposed of.

The volume of concentrate produced from a particular desalination plant is a factor of the recovery rate of the desalination process. However, in the desalination processes, one of the demerits is that seawater reverse osmosis (SWRO) plants can yield a concentrate which is two times more concentrated than the feed waters; on the other hand, the yield concentrate from the distillation process may have salt concentration of only 10% [4; 5]. Brackish water reverse osmosis plants (BWRO) yielded 25% of the total feed water [6], in the case of groundwater reverse osmosis plants (RO), the yield is between 10-25% of the total feed water [7]. The membrane performances which are generally acceptable for water recovery yields fall in the region between 30-60% for Sea Water Reverse Osmosis (SWRO), 60-85% for Brackish Water Reverse Osmosis (BWRO), 85-97% for BWRO with concentrators and 95-99.5% for salt rejection. In spite of energy consumption, the key criterion for implementing the RO technology is the volume of concentrate produced in the process. The volume of concentrate generated is much more critical for inland RO plants situated in areas distant from the ocean [8]. Water quality of RO concentrate from industrial sites however, can be different from the municipal concentrates. For instance, mine-contaminated groundwater treatment sites have a high concentration of calcium (>1000 mg/L), silica (>200 mg/L) and sulfate (>4500 mg/L) in addition to metals [9]. The presence of sparingly soluble salts in RO concentrate from municipal wastewater treatment plants, results in the total organic carbon (TOC) also being high (>30 mg/L) [10] Concentrate generated from the membrane desalination processes has basic characteristics of high TDS and minimal quantity of process-added chemicals. The salinity range 2000 – 5000 mg/L of the brackish waters can be reduced to drinking quality at a cost of approximately $0.75 - $1.00 per 1000 gallons compared to the range of $3.00 - $5.00 per 1000 gallons of seawater desalination costs. Most importantly, the two commercial technologies are based on the membrane and thermal processes. Membrane processes include reverse osmosis (RO), microfiltration (MF), electrodialysis (ED), nanofiltration (NF) and ultrafiltration (UF). While thermal processes include multi-effect distillation (MED), multi- stage flash evaporation (MSF) and vapour compression distillation (VC) [11]. These systems are chosen based on the costs of operation, the effluent stream type and the energy consumption. The multi-stage flash evaporation (MSF) and RO processes have been the most widely adopted for both seawater and brackish water desalination, both making up 84% of the total installed capacity [12]. Also, desalination plants have treated different concentrations of raw water, mostly seawater and brackish water [12].

The Impact of Brine on the Environment: The impact of the desalination process on the environment has been an aspect of desalination that has been ignored. Certain methods are employed in the disposal of brine and each one has merits and demerits and of course, an interplay of factors which include local available resources, cost, impact on the environment and technology. Meanwhile, major environmental issues affecting a desalination plant include brine disposal, energy considerations and the location of the plant. Obviously, plant location becomes an issue in a situation where the selection of site must be determined by considering the energy supply availability and the proximity to feed water intake, site for brine disposal and water end-user. The residues of water-softening chemicals (lime), flocculation (iron and aluminium silicates, sulphates), antiscalants, disinfectants (sodium hypochlorite, chlorine) and antifoaming agents are all contained in the brine reject streams. The primary make-up of reject brine to salinity and high TDS levels in water is the combination of magnesium, sodium, calcium and chloride, which can have harmful effects for livestock and human consumption. Water pollution is the consequence of land disposal which results when concentrated brine is discharged into sources of fresh water and unprotected wells. The composition of brine has a major effect on the environment, as the degree of salinity in soil truncates crop growth, which is shown by the reduction in the growth of plants, leaf colour, darkening and scorching of shoots. The growth of most plants reduces due to the increase in the osmotic pressure as a result of the presence of salts in the soil and soil water. This is because the dissolved salts increase the osmotic potential in the soil water and subsequently increase the energy needed by the plants in the extraction of water from soil. High concentration of solute present in the soil solution is good for favourable physical properties in the soil, while a high concentration of sodium and chloride in clay soil reduces aeration, soil permeability and triggers dispersion of soil particles and could bring about an alteration in the electrical conductivity of soil, invariably changing the sodium sorption ratio (SAR) and subsequently induces specific

ion toxicity [13]. The surface discharge of reject brine from inland desalination plants could have a negative impact on soil and groundwater [14].

The Disposal of Brine: Disposal of brines has been a major problem facing inland desalination plants owing to many factors such as: Environmental regulations aimed at protecting the environment from continued pollution, the increase in the volume of brine rejects being generated and the alarming costs associated with wastewater desalination in an attempt to augment fresh water supplies and the cost of disposal in an environmentally friendly manner. The desalination process produces the highest amount of brine wastewater with about 20-50% of the total feed water flowing as reject brine. The amount of brine produced, as a percentage of the feed water, depends on the choice of the method, initial salinity of feed water and factors affecting the choice of disposal method. The factors that influence the selection of a disposal method were identified by [15] and these include volume of the concentrate, constituent of the concentrate, physical or geographical location of the concentrate discharge point, availability of the receiving site, public acceptance, capital and operating costs and possible facility expansion.

The major methods of brine disposal are: deep well injection, evaporation ponds and solar ponds, they are not however applicable to large volumes of wastewater. There are various other options for the disposal of brine waste water; they are waste minimization, disposal into surface water bodies, disposal into municipal sewers, pumping into specially designed evaporation ponds, thermal evaporation towards the zero liquid discharge (ZLD), concentration into solid salts and irrigation of plants tolerant to high salinity (halophytes). Brine disposal at inland sites is generally limited to three categories namely: deep well injection, evaporation ponds and solar ponds. Water pollution results when hypersaline brine is discharged into the sources of fresh water and unprotected wells as a result of the negative impact of land disposal.

Nanofibres: Electrospinning is a technology that is broadly used for an electrostatic fibre formation which makes use of electrical forces to produce polymer fibres using polymer solutions of both natural and synthetic. This has witnessed a great increase in the research and commercial awareness for the past few decades [16]. The electrospinning process gives capabilities that are unique for the production of novel natural nanofibres and fabrics whose pore structure is controllable. Electrospinning has gained much attention this last

decade for its versatility in spinning a wide range of polymeric fibres and of course, its ability to produce fibres consistently in the submicron range which is difficult to achieve by merely using standard mechanical fibre-spinning technologies. With interesting characteristics like smaller pores and higher surface areas than regular fibres, electrospun nanofibres have been applied successfully in many fields, such as pharmaceutical, biotechnology, optical electronics, tissue engineering scaffolds nanocatalysis, filtration, environmental engineering, protective clothing, defence and security, biomedical and healthcare [17, 18, 19]. Electrospinning is overall, a simple and relatively robust technique in the production of nanofibres from a wide range of polymers. Electrospun nanofibres offer several advantages including, a very high surface-to-volume ratio, malleability and tuneable porosity in order to conform to a wide range of shapes and sizes, also, the ability to control the composition of the nanofibre in order to achieve the desired results from its properties and functionalities. Recently, there is an increasing interest to technologically exploit the increase in the production of nanoscale fibres, especially for the nanofibrous scaffold fabrication from a wide range of synthetic and natural polymers for tissue engineering [20]. In spite of the many advantages offered by the electrospinning process, the rate of production of nanofibres has been a serious factor that limits their application. In order to increase the rate of production of these electrospun nanofibres, a new system has been studied by various research groups which consists of a two-layer electrospinning system, having the lower layer being a ferromagnetic suspension as well as the upper layer being a polymer solution and multiple spinnerets or systems of nozzle which are arranged in a matrix/circle/line and bubble electrospinning (a new bottom-up gas-jet electrospinning) [21, 22, 23]. Since a large quantity of fibres is needed for various applications, the scale-up of nanofibres is not feasible through the use of a single jet. Many researchers have therefore used a porous hollow tube so as to get multiple jets in which case the production rate is enhanced by increasing the number of holes and the tube length [24, 25]. Despite the milestone achieved with the spun nanofibres and the electrospinning method, certain challenges need to be considered. Non-uniform cellular distribution and lack of cellular migration in the scaffold with increasing depth in the normal passive seeding conditions pose a major challenge in the use of electrospun mats and scaffolds in tissue engineering. The case of cellular infiltration into the architecture of the nanofibres is gaining attention owing to its potential in making further applications of

electrospun meshes or scaffolds in various tissue engineering applications stagnant. Nanofibres are obtained in an inexpensive and simple manner through the conventional electrospinning technique, but by this method at times, there is a build-up of meshes with tremendous fibre density. Reports have also shown that decrease in the electrospun fibre diameter leads to an increase in the number of fibre-to-fibre contacts per unit length as the mean pore radius in the mesh decreases [26].

Ion Exchange: Ion exchange is the exchange of ions between two phases [27]. Ion exchange materials can be defined as insoluble substances that contain ions which are loosely held and are capable of being exchanged with other ions in solutions that come in contact with them. These exchanges occur without any damage or physical alteration to the ion exchange material. Ion exchangers are defined as insoluble acids or bases that have salts which are also insoluble, this allows them to exchange either positively charged ions (cation exchangers) or negatively charged ions (anion exchangers). Other natural substances like proteins, cellulose, living cells and soil particles display ion exchange properties that play a vital role in their functions in nature. In the treatment of industrial waste effluents, sorption has been shown to be an effective way of treatment owing to many advantages including cost-effectiveness, availability, efficiency and simple mode of operation. The sorption process is recommended for the removal of low concentrations of metal ions in effluent wastes. In the sorption process, there is a sorbent which binds molecules through the means of physical attractive forces, chemical binding and ion exchange. The sorbent should be regenerable with ease, cheap and must be in large quantities for best result yield. The factors affecting the sorption process of ion exchange include the affinity for sorption of targeted materials and the efficiency of desorption. Sorption efficiency of a target contaminant depends strongly on the sorbent-solute interactions; this can be improved by the attachment of a functional group onto the surface of the sorption site. This process involves two major steps which are sorption and desorption. The ion exchange process is meant to be reversible, in which case the sorbed solutes can be regenerated effectively. But the effectiveness of desorption diminishes for sorbents that are highly selective.

Ion Exchange Resin: Ion exchangers can be divided into two groups, namely organic and inorganic according to their composition.

Organic Ion Exchangers: Most organic resins are made up of a three-dimensional network matrix of macromolecular hydrocarbon chains, which usually consist of a copolymer of styrene and divinylbenzene (DVB), the crosslinking being provided by the DVB. The characteristics of the resin are a function of the ion-exchange groups present on the matrix. Generally speaking, the resin can therefore be categorized into three groups namely: cation exchangers (having strong acid and weak acid groups), anion exchangers (having strong base and weak base groups) and selective chelating groups (specific ion exchangers).

Inorganic Ion Exchangers: Zeolites and clay minerals are characteristic representatives of the group of inorganic materials which are crystalline hydrated aluminosilicates of alkali and alkaline earth cations with an open, infinite and three-dimensional structure. There are two main types of zeolites, synthetic and natural minerals and they can lose and gain water reversibly and also exchange extra framework cations, these are carried out without any alteration to the crystal structure. The components, ion exchange capacity and channel diameter for different clay minerals, synthesized and natural zeolites.

Sorption Isotherms: The relationship existing between the amount sorbed and concentration is known as the sorption isotherm and these are basic requirements for the design of the sorption system used in the removal of pollutants.

Sorption isotherms are mathematical models which describe the distribution of sorbed pollutant (sorbate species) on the sorbent ($q$eq) and the pollutant in solution (Ceq) at a constant temperature, based on a set of assumptions that are related to the homogeneity and heterogeneity of the solid surface, the type of coverage and the possibility of interaction between the sorbate species. The most frequently used two-parameter models in literature describing the non-linear equilibrium are the Langmuir and the Freundlich models.

MATERIAL AND METHODS

Ion Exchange Resin, PAN and Other Materials: The chelating cation exchange resin Purolite S950 and the anion exchange resin PPA500Plus (from The Purolite Company, Bala Cynwyd, USA), PAN polymer, titanium dioxide (TiO_2), Dimethylformamide (DMF) and zeolite Y (from Zeolyst International, Valley Forge, USA), were used in this study. The Purolite S950 is a macroporous aminophosphonic acid chelating resin, designed for the

Table 1: General description and properties of resins

Purolite S950	
Functional group	Aminophosphonic
Matrix	Macroporous polystyrene crosslinked with divinylbenzene
Polymer Structure	Macroporous
Capacity	26 g/l (Calcium)
Specific gravity	1.13
Ionic form	Na^+

removal of cations of toxic metals such as lead, copper and zinc from industrial effluents at low pH. At somewhat higher pH values, calcium, magnesium and barium, as well as the toxic metals cadmium, nickel and cobalt are strongly complexed and may be separated from quite high concentrations of univalent cations. Purolite S950 is highly selective (under appropriate conditions) for a range of both heavy metal and common divalent ions. Therefore, its use can be recommended where it becomes necessary to remove calcium or magnesium in order to avoid possible precipitation, or where its selectivity for a particular range of metals offers advantages. The physicals properties, specifications and general descriptions of Purolite S950 resins as reported by the suppliers are shown in Table 1.

Sampling: The brine wastewater used in this study was a third-stage reverse osmosis effluent. This brine was filtered using a 0.45 im pore membrane filter paper with the aid of a manual pumping device. The filtered brine sample was preserved with 3 drops of concentrated HNO_3 acid for approximately 100 mL of sample. The sample was subsequently preserved at 4°C until analysis for cations using inductively-coupled plasma-optical emission spectroscopy (ICP-OES).

Sorption Experiments: The capacity of sorption of PAN, PAN+TiO_2 and PAN$^+$Zeolite nanofibres toward Ca^{2+}, Mg^{2+}, Na^+ and K^+ ions from metal ion solutions was investigated by batch sorption experiments, with their respective performance compared to the Purolite S950 resin.

In the investigation of the sorption behaviour of these polymers, synthetic solutions were used without the interference of the trace metal ions in the brine waste water. The first set of experiments were carried out with Ca^{2+}, Mg^{2+}, Na^+ and K^+ solutions at the concentration of 100 mg/L in deionized water. The desired pH for each solution was attained by using 0.1 mol/L acetic acid and 0.05 mol/L sodium hydroxide solutions.

Batch Sorption Experiment: The batch sorption experiment for the metal ions ($Ca^{2+,}$ Mg^{2+}, Na^+ and K^+) using a model solution was carried out in a 100 mL plastic bottle using a tray action shaker. Fixed amounts of resin and the nanofibres (0.1 g) were contacted for 8 hours with 50 mL metal ion solution of variable concentration and pH at 25°C. Blank solutions were treated in a similar manner without the adsorbent and the concentrations were recorded as initial concentration at the end of each operation. The residual concentration of the metal ions (Ca^{2+}, Mg^{2+}, Na^+ and K^+) in the solution after the treatment were thereafter measured by ICP-OES. The quantity of metal ion adsorbed (q, mg/g), (q, meq/g), (q, mmol/g) and percent sorption (% A) were calculated.

Effect of Contact Time: The contact time experiments were conducted using a model solution at 25°C in different plastic bottles with covers. The bottles were shaken for different time intervals at constant temperature. Fixed masses of adsorbents (0.1 g each for nanofibres or resins) were contacted with 25 mL of 100 mg/L of the metal ions (Mg^{2+}, Ca^{2+}, Na^+ and K^+) in solution and the phases were separated by filtration after a specified time. The supernatant solution was then collected for analysis by ICP-OES. The experiment was carried out in quadruple under similar conditions.

Sorption Isotherm (Effect of Concentration): The effect of concentration was carried out in a series of 100 mL plastic bottles. The bottles were filled with 25 mL of different initial concentrations that varied from 100 to 500 mg/L while the temperature and adsorbent mass were kept constant. After the equilibration time was reached, the phases were separated by filtration and analysed using the ICP-OES. Blank solutions were also given a similar treatment, but devoid of the adsorbent and concentrations at the end of each operation were recorded as the initial concentration. The data obtained was used to determine the quantity adsorbed at equilibrium (sorption capacity), *qe*, of the adsorbent. The experiment was carried out in quadruple under similar conditions.

Sorption Kinetics: The sorption kinetics experiments were performed by using adsorbent of a fixed mass (0.1 g each for nanofibres and resins) in contact with 25 mL of 100 mg/L of the metal ions (Mg^{2+}, Ca^{2+}, Na^+ and K^+). At different time intervals, the samples were taken and filtered. The subsequent filtrate portions were analysed using the ICP-OES. This experiment was carried out in quadruple under similar conditions.

Effect of Adsorbent Dose: The batch equilibration method was used to measure the metal ion binding capacity by varying the adsorbent mass. Different dry adsorbent amounts (0.1 - 0.5 g for nanofibres and 0.1 - 0.5 g for resins) were contacted with 25 mL of 500 mg/L of the metal ion solutions (Mg^{2+}, Ca^{2+}, Na^+ and K^+) for 8 hours at 25°C with constant shaking. After the completion of the equilibration time, the supernatant solution was analysed by ICP-OES. All test samples were run in quadruples.

Effect of pH: The effect of pH was carried out using the batch technique. 0.1 g each of the sorbents was placed into a series of 100 mL plastic bottles, where 25 mL of 500 ppm of each metal solution had been placed. Prior to the addition of the adsorbents, the metal ions solutions were adjusted to the various pHs in the pH range of 2-7, by carefully adjusting the pH with 0.1 mol/L acetic acid and 0.05 mol/L sodium hydroxide solutions. The mixture was shaken for 8 hours at 25°C. When the equilibration was completed, the supernatant solution was collected and analysed by the ICP-OES. All test samples were run in quadruple. Blank solutions were also treated in a similar manner without the adsorbent and the concentration at the end of the operation was recorded as initial concentration.

Effect of Temperature: The effect of temperature was also studied by the batch equilibration method. This was achieved by placing 0.1 g of the sorbents (the nanofibres and the resin) into the plastic bottles, where 25 mL of 500 ppm of each metal ion solution had been placed, at constant pH. The mixture was shaken for 1 hour at different temperatures (25°C, 35°C, 45°C and 55°C). After the equilibration time was reached, the supernatant solution was analysed by ICP-OES. All the test samples were carried out in quadruple under the same conditions. The data obtained was used to calculate the enthalpy change ($\Delta H°$), entropy change ($\ddot{A}S^?$) and the free energy change ($\Delta G°$).

RESULTS AND DISCUSSION

The Batch Sorption Experiments: Different solutions were synthetically prepared in the range of 100 – 1000 mg/L to imitate the brine effluent generated from the Emalahleni water reclamation plant in the batch sorption experiments for the sorption of Mg^{2+}, Ca^{2+}, K^+ and Na^+. Purolite S950 resin and the nanofibres (PAN, PAN+TiO2 and PAN+ZEOLITE) were employed to carry out the batch sorption experiments. The effect of various parameters such as the temperature, sorbent dosage, pH of the solution, contact time, sorption isotherm and the sorption kinetics were investigated for the sorption of Mg^{2+}, Ca^{2+}, K^+ and Na^+ ions from the solutions.

The Effect of Sorbent Dose: Sorbent dose is an important parameter which influences the extent of metal uptake from the solution by varying the sorption mass. For the various metal ions (Mg^{2+}, Ca^{2+}, K^+ and Na^+), the initial concentration of the aqueous feed solution was 500 mg/L. The experiment was conducted with the metal ion solutions being shaken separately with the various masses of the resin or the nanofibres for 8 hours .

The results of the effect of the Purolite S950 resin dosage on the sorption of Mg^{2+}, Ca^{2+}, K^+ and Na^+ ions from their separate solutions are shown in Table 2 and Figure 1.

The nanofibre mass was also varied from 0.1 to 0.5 g in 25 mL metal ion solutions, the nanofibres include: PAN, PAN+TiO2 and PAN+ZEOLITE. The results shown in Figure 2 reveal a slight increase in the metal ions sorption with an increase in the sorbent dose.

In the case of $PAN+TiO_2$ nanofibres, the results in Figure 3 reveal that as the sorbent dose increased, there was a slight increase in the sorption of metal ions from the solution. From these results, the optimum sorbent amount was found to be 12 g sorbent/L for the sorption of Mg^{2+}, Ca^{2+}, K^+ and Na^+ ions by $PAN+TiO_2$ nanofibres. The subsequent increase in the sorbent dose showed an insignificant increase in the percentage sorption of calcium, magnesium and sodium ions from the solution, this is perhaps due to exchange sites' saturation.

PAN was also doped with zeolite and thereafter, it was used to carry out sorption for the individual metal ion solutions. It can be observed in Figure 4. that there was an increase in the percentage sorption of metal ions generally, compared with the PAN and $PAN+TiO_2$ respectively. PAN+ZEOLITE showed an
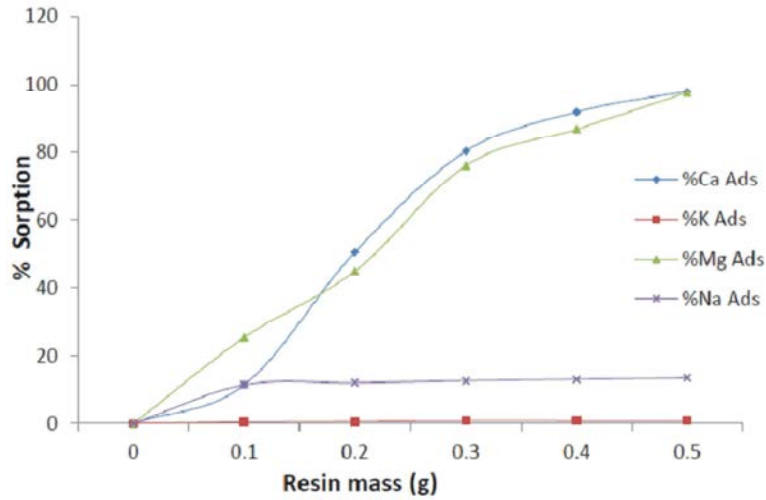
Fig. 1: The effect of resin mass on the sorption of Mg2+, Ca2+, K+ and Na+ by Purolite S950 resin
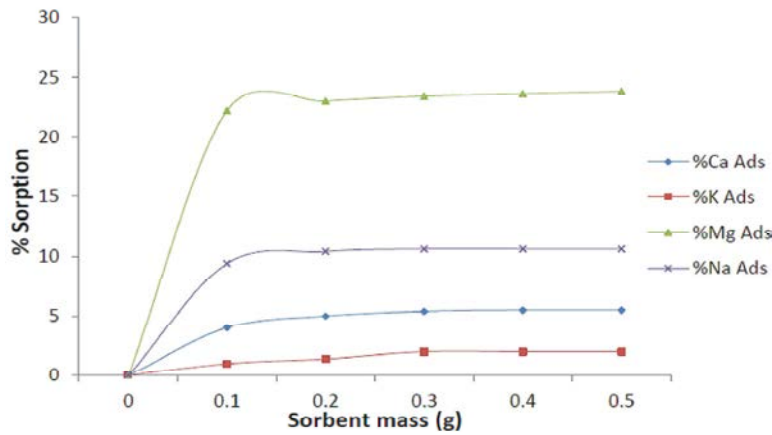(Metal ion concentration, 500 mg/L; Temperature, 25°C; volume, 25 ml; contact time 8 hours

Fig. 2: The percentage sorption of Mg^{2+}, Ca^{2+}, K^+ and Na^+ ions with PAN nanofibres as a function of sorbent mass (Metal ion concentration, 500 mg/L; Temperature, 25°C; volume, 25 mL; contact time 8 hours).
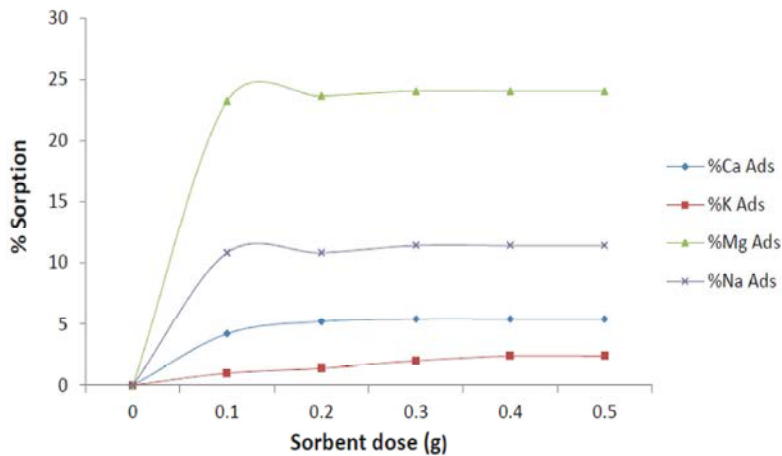

Fig. 3: The percentage sorption of Mg^{2+}, Ca^{2+}, K^+ and Na+ ions with PAN+TiO$_2$ nanofibres as a function of sorbent mass.
(Metal ion concentration, 500 mg/L; Temperature, 25°C; volume, 25 mL; contact time 8 hours)

Fig. 4: The percentage sorption of Mg^{2+}, Ca^{2+}, K^+ and Na^+ ions with PAN+ZEOLITE nanofibres as a function of sorbent mass
(Metal ion concentration, 500 mg/L; Temperature, 25°C; volume, 25 mL; contact time 8 hours).
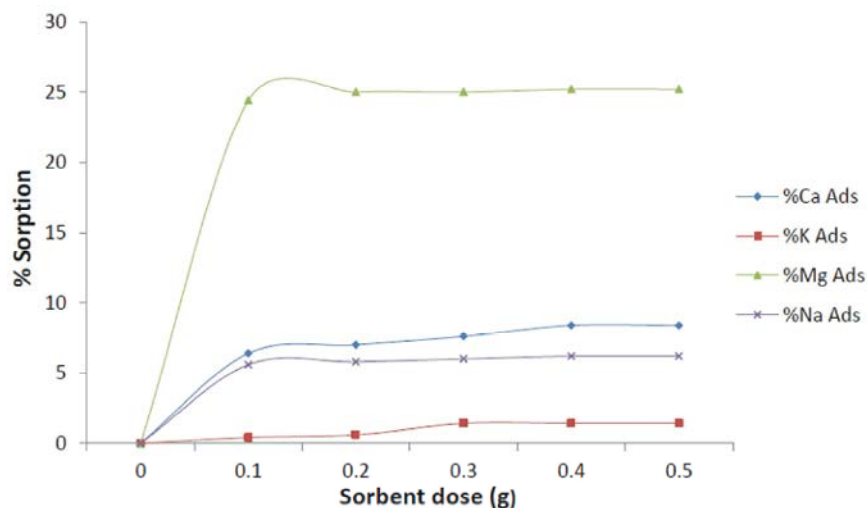
Table 2: Cation exchange capacities of Purolite S950 resin, PAN, PAN+TiO2 and PAN+ZEOLITE obtained in the contact time experiment

SORBENT	Mg^{2+} (meq/g)	Ca^{2+} (meq/g)	K^+(meq/g)	Na^+ (meq/g)
Purolite resin	1.20	1.03	0.11	0.09
PAN	0.12	0.06	0.03	0.02
PAN+TiO$_2$	0.10	0.04	0.05	0.12
PAN+ZEOLITE	0.21	0.09	0.03	0.07

increased percentage sorption for both magnesium and calcium than what was obtained with PAN and PAN+TiO$_2$. The optimum sorbent dose for PAN+ZEOLITE nanofibre was found to be 8 g sorbent/L for the sorption of Mg^{2+}, Ca^{2+}, K^+ and Na^+ ions.

The Effect of Contact Time: The summary of the various exchange capacities of the sorbents is given in Table 2. The Purolite S950 resin achieved the highest capacity owing to the aminophosphonic group attached to it. Its high sorption rate can be attributed to chelation of the ions by the aminophosphonic acid functional groups on the resin. The values for the cation exchange capacities were obtained after 120 minutes for the Purolite resin, 240 minutes for PAN+ZEOLITE, 180 minutes for PAN+TiO2 and 120 for PAN nanofibres respectively. Therefore, the overall order of increasing capacity is PAN < PAN+TiO2 < PAN+ZEOLITE < Purolite S950 resin. The Purolite resin was able to attain the highest capacity within 120 minutes because of the aminophosphonic group attached to its surface, whereby the metal ions were able to bind easily and faster. For the nanofibres, PAN+ZEOLITE achieved the greater capacity within 240 minutes for both magnesium and calcium, 180 minutes

for sodium and 120 minutes for potassium. This increase in time can be attributed to the mild blockage of the binding sites which makes it difficult for the metal ions to exchange into the sorbent rapidly and of course, lack of a ligand to aid in sorption. PAN+ZEOLITE also shows selectivity for calcium and magnesium. PAN+TiO2 nanofibre showed very little improvement compared to PAN itself except for sodium and was able to attain sorption equilibrium at 180 minutes and shows selectivity for sodium probably due to the changes in the physical structure as a result of titanium dioxide incorporation. PAN nanofibre attained sorption equilibrium at 120 minutes for all metal ions; this is due to the accessibility of the metal ions to the available binding sites without any blockage of other inorganic materials.

CONCLUSION

This study has been able to prove that hydrophilic materials like the nanofibres are capable of competing with the Purolite S950 resin in the removal and treatment of major ions (Mg^{2+}, Ca^{2+} K+ and Na^+ ions) from brine effluents, in spite of the fact that no functional groups (ligands) were attached to its structure. The nanofibres

have provided the advantage of their large surface area and many active sites coupled with the incorporation of inorganic materials (titanium dioxide and zeolite) in showing selectivity towards these ions.

The enthalpy change ($\Delta H°$) values for the sorption of Mg^{2+}, Ca^{2+}, K^+ and Na^+ ions onto Purolite S950 resin, PAN nanofibre, PAN+TiO_2 nanofibre and PAN+ZEOLITE nanofibre were positive. Therefore, the sorption processes are endothermic for all the sorbents. This means the sorption of the respective metal ions will be favourable at high temperatures. Consequently, the standard enthalpy change suggests that the sorption of Mg^{2+}, Ca^{2+}, K^+ and Na^+ ions onto Purolite S950 resin, PAN nanofibre, PAN+TiO_2 nanofibre and PAN+ZEOLITE nanofibre is basically governed by physisorption (enthalpy magnitude less than 42 kJ/mol). The free energy change ($\Delta G°$) values for all the sorbents are positive, indicating that the sorption process onto the sorbents was non-spontaneous and thermodynamically unfavourable. The order of efficiency, performance and desired attributes of the sorbents can be given as: Purolite S950 resin > PAN+ZEOLITE > PAN+TiO_2 > PAN.

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