Amberlite IR 120 Cation Exchanger Mixed Matrix Membrane For Iron Removal

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ABSTRACT

Heavy metals have been excessively released into the environment due to rapid industrialization and have created a major global concern. Iron is one of the heavy metal pollutant involves in mining activities, foundries and smelters, steel producing industries, and diffuse sources such as piping, combustion by products, constituents of products and many more. There are many methods have been proposed for the removal of iron ions from wastewater such as chemical precipitation, electrochemical reduction, ion exchange, adsorption, biosorption, membrane filtration, coagulation and flocculation. In the current study, ion exchanger mixed matrix membrane (MMM) was used to adsorb iron from aqueous solution. Several potential cations exchanger resins were screened for the maximum iron removal which are Amberlite IR 120, Amberlyst, Lewatit Monoplus TP 214 and Lewatit CNP 105. The selected resin, Amberlite IR 120 was embedded into the mixture of 15 wt.% and 20 wt.% ethylene vinyl alcohol in dimethylsulfoxide and 1-octanol solution. Conventional casting method was used to prepare the flat sheet MMM. The effect of iron concentration from 50ppm to 500ppm was studied in batch adsorption experiment. At initial iron concentration of 500 ppm, 15% and 20% polymer EVAL loading in MMM showed 298.6 and 196.1 mg Fe/ g MMM binding capacity respectively. The MMM can be regenerated using 10% HCl solution which gives about 86% of iron recovery.

ABSTRAK

Logam berat berlebihan dilepaskan ke dalam alam sekitar akibat perindustrian yang pesat dan telah mencipta kebimbangan utama global. Besi adalah salah satu pencemar logam berat terlibat dalam aktiviti perlombongan, faundri dan pelebur, industri keluli dan sumber-sumber meresap seperti paip, produk dari pembakaran, kandungan produk dan banyak lagi. Terdapat banyak kaedah telah dicadangkan untuk penyingkiran ion besi daripada air sisa seperti pemendakan kimia, pengurangan elektrokimia, pertukaran ion, penjerapan, bio-penjerapan, penapisan membran, pembekuan dan pemberbukuan. Dalam kajian ini, penukar ion bercampur matriks membran (MMM) telah digunakan untuk menjerap besi daripada larutan akueus . Beberapa potensi resin penukar kation telah disaring untuk penyingkiran besi yang maksimum seperti Amberlite IR 120, Amberlyst , Lewatit Monoplus TP 214 dan Lewatit CNP 105. Resin yang terpilih iaitu Amberlite IR 120 telah dienapkan ke dalam campuran 15% dan 20% etilena vinil alcohol (EVAL) dalam dimethylsulfoxide dan 1-oktanol. Kaedah pembentukan konvensional telah digunakan untuk menyediakan kepingan flat MMM. Kesan kepekatan besi daripada 50ppm hingga 500ppm dikaji dalam eksperimen penjerapan secara statik. Pada kepekatan awal besi sebanyak 500 ppm, 15% dan 20% polimer EVAL dalam MMM menunjukkan 298.6 dan 196.1 mg besi / g MMM kapasiti pengikat. Regenerasi dengan menggunakan HCl memberikan peratus pemulihan besi sebanyak 86%.

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AAS	Atomic Absorption Spectroscopy
DMSO	Dimethyl sulfoxide
EVAL	Ethylene vinyl alcohol
MMM	Mixed Matrix Membrane

LIST OF EQUATION

1 INTRODUCTION

1.1 *Motivation and problem statement*

Heavy metals have been excessively released into the environment due to rapid industrialization and have created a major global concern. Cadmium, zinc, copper, nickel, iron, mercury and chromium are often detected in industrial wastewaters, which originate from mining activities, metal plating, battery manufacture and more. Some of these elements (e.g., silver, iron and copper) are precious metals, which can be reused and recycled for a wide range of applications. The treatment of heavy metal is very important because heavy metals are very toxic and can cause serious diseases to humans and animals if the effluent from the industry is not managed properly.

Nowadays, many people and industries are aware about environmental problem. Iron is a chemical element with the symbol Fe and chemical name iron. The amount of iron in industrial wastewater has been increasing and it can cause a serious problem to environment and human health. Iron is non-biodegradable element and can be accumulated in living tissues, causing various disorders and diseases. Human activity has drastically effect the biogeochemical cycles and balance of some metals. The main sources of iron are present and former mining activities, foundries and smelters, steel producing industries, and diffuse sources such as piping, combustion by products, constituents of products and many more. These metals are also known to have adverse effects on the environment and human health and are toxic even at low concentration to human beings and other living beings (Anusha, 2011).

There are many methods have been proposed for removal iron ions from wastewater, including chemical precipitation, electrochemical reduction, ion exchange, adsorption, biosorption, membrane filtration, coagulation and flocculation. In the current study cation exchanger mixed matrix membrane (MMM) will be used for iron removal from wastewater. The preparation concept of MMM, that widely used in gas separation and protein separation application was adopted in this study. Selected cation exchange resin will be embedded at specific percentage in membrane polymer solution and then the mixture will go through casting process to form a membrane.

1.2 Objective of the research

The main objective of this research is to prepare cation exchanger MMM using Amberlite IR 120 as cation exchanger in ethylene vinyl alcohol membrane matrix for iron removal from aqueous solution.

1.3 Scopes of the research

In order to fulfil the research objective, the following scopes were outlined:

i. To screen several potential cation exchange resin that give high binding capacity to iron.

ii. To characterize the binding properties of cation exchanger MMM prepared from ethylene vinyl alcohol (EVAL) based membrane for iron removal

iii. To study the regeneration technique of MMM after binding to the iron using hydrochloric acid and sulphuric acid.

2 LITERATURE REVIEW

2.1 *Source of iron effluents*

Iron is considered as potentially hazard contaminant. Iron ion (Fe (II)) gives water an unpleasant taste and produces black appearance when it combines with tea and coffee. It causes staining on tableware, clothes, fixtures and laundries. Iron is usually found from the effluent released by many industries such as basic steel, alkalis, chlorine, inorganic chemicals, petroleum refining and fertilizers (Prasad et al., 2009). Figure 2.1 shows river polluted by iron effluent.

Iron is one of the vital elements for humans and for other forms of life. Nevertheless, high doses of iron can cause haemorrhagic necrosis, tissue damage to a variety of organs by catalyzing the conversion of H_2O_2 to free radical ions that attack cell membranes, proteins and break the DNA double strands and cause oncogene activation, sloughing of mucosa areas in the stomach (Mahesh et al., 2006). With pathological conditions, it is known that iron metabolism and superoxide metabolism can exacerbate the toxicity of each other. Further iron toxicity leads to related hormonal abnormalities, cardiovascular diseases, and a dysfunctional immune system. Moreover, excess iron may also cause brain damage induced by oxidative stress (Mahesh et al., 2006).

Figure 2-1: River polluted by iron effluent

2.2 Iron removal technologies

There are many technologies has been used to remove iron from wastewater. The technology choose is based on the source of pollutant. Each technologies has their own advantage and disadvantages.

Aeration followed by sand filtration was the method used for the removal of iron (Fe) and manganese (Mn) from Siwa Oasis ground water (Hesham and Naggar, 2010). Figure 2.2 shows the method used to remove iron by aeration followed by sand filtration. The study was carried out on laboratory-scale columns experiments sand filters with variable depths. A traditional method for removal of iron from ground water by using ash has been systematically investigated by Das et al. (2007). Ashes from five different sources were used which are banana rind, banana pseudostem, banana leaf, rice husk and bamboo. The principle applied is enhanced precipitation of iron at high pH caused by ash. The study included laboratory analysis of some relevant chemical parameters of the ashes and the efficiency of the ashes in removing iron from prefabricated water with respect to quantity of ash and corresponding increase in pH of water (Das et. al, 2007).
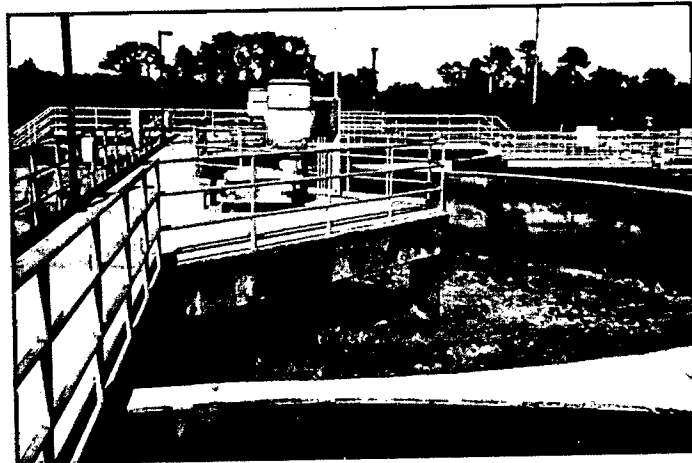
Figure 2-2: Iron removal by aeration and sand filtration

A batch adsorption study has been conducted by Anusha (2011) using activated carbon prepared from Bael fruit shell as adsorben. The removal efficiency was found varied based on various parameters such as dosage, time, pH and concentration. The removal efficiency was found to be more than 60% (Anusha, 2011).

2.3 *Mixed matrix membrane*

Mixed matrix membrane is prepared by the incorporation of a solid dispersed phase into a continuous polymer matrix. These solid can be porous, solid nano particles or catalysts. This concept of MMM has been applied successfully in many separation processes such as gas separation, protein separation and water treatment. Early researchers have created MMM by filling rubbery polymers with fillers and it is used for liquid separation such as reverse osmosis (Solenberger and Withers, 1982), pervaporation, and the separation of submicro particles such as enzymes (Goldberg et al., 1979). Figure 2.3 shows one example of MMM prepared using carbon molecular sieve as solid particle for application in gas separation.
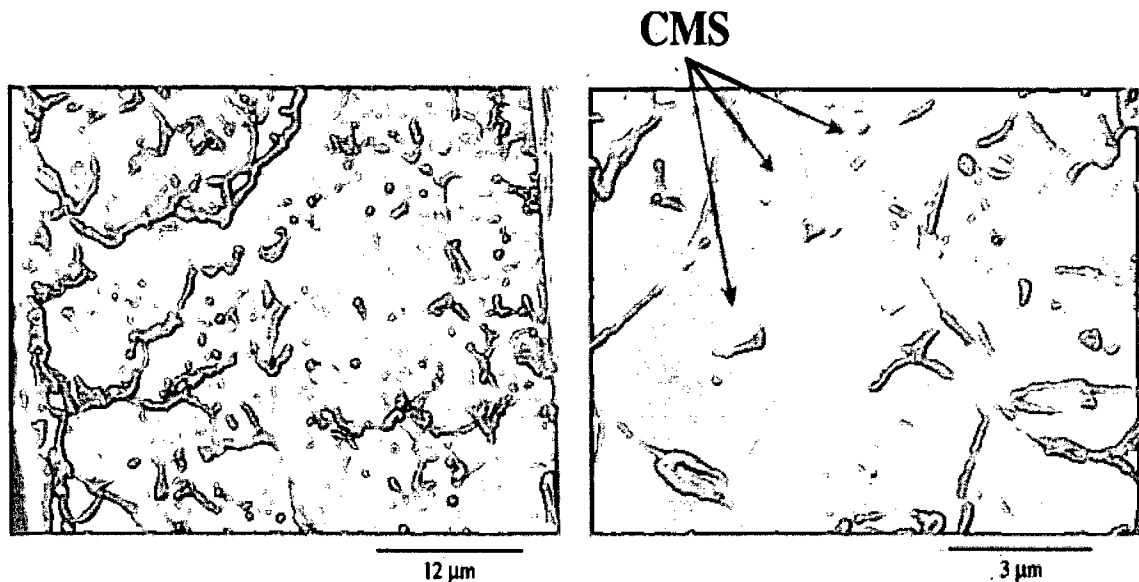
Figure 2-3: MMM prepared using carbon molecular sieve
(Abedini and Nezhadmoghadam, 2010)

Mixed matrix concept combines the processability, flexibility and low capital cost of polymeric materials with intrinsic superior selectivity and permeability of inorganic particles. As a result, membranes of high permeability, selectivity, mechanical strength, and thermal and chemical stability can be achieved. The particle and polymer properties, particle size, particle pore size, particle loading and its distribution can also be adjusted to prepare a more desirable membrane using MMM concept.

The preparation of membrane through mixed matrix membrane concept has several advantages as follows:

I.   Variety of potential adsorbent available in market that can be used to prepare MMM for specific application

II. MMM only involve physical modification

III. The efficiency of MMM is comparable to the adsorbent used in packed bed format

IV. Compare to packed bed configuration, MMM is easy to making as a module and showed less complicated scale up protocol

V.   The MMM has a high separation capabilities, desirable mechanical properties and economical processing capabilities of the polymer.

2.4 Ion exchanger technique

Adsorption of metals using solid resin is a proven technique for the purification and separation of metals from different aqueous solutions. In ion exchanger, undesirable ions are replaced by others which do not contribute to contamination of the environment as shown in Figure 2.4. The method is technologically simple and enables efficient removal of even traces of impurities from solutions. Ion Exchange resins are insoluble granular substances which have in their molecular structure acidic or basic radicals that can be exchanged. Figure 2.5 shows an example of ion exchange resin. The positive or negative ions fixed on these radicals are replaced by ions of the same sign in solution in the liquid in contact with under the name of resins. There are two categories of resins, the resins of the gel type and those of the macroporous or loosely cross-linked type. Their basic structure is identical, the macromolecular structure is obtained in both cases by co-polymerization. The difference between them lies in their porosity.

WATER CONTAINING VARIOUS MINERAL CONTAMINANTS ENTERING HERE

Iron Exchange Material

■ Magnesium Ions
▼ Calcium Ions
⊚ Sodium Ions
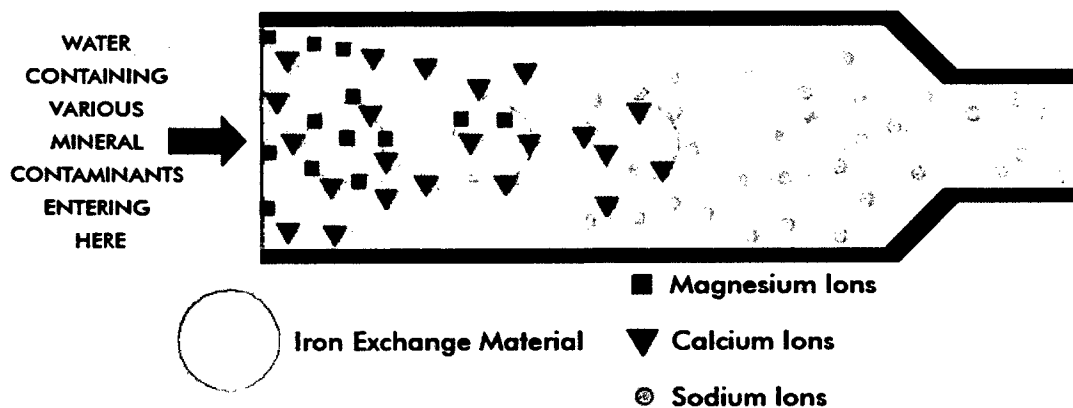
Figure 2-4: Principle of iron exchange
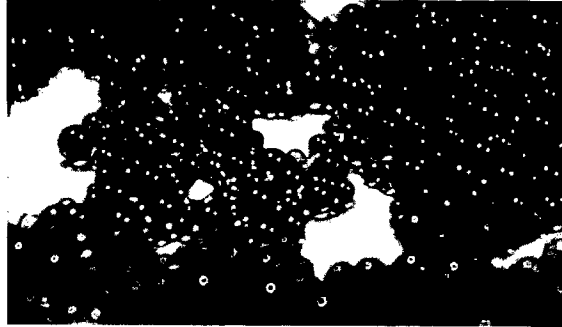
Figure 2-5: Ion exchange resin

A lot of research has been done on the feasibility of using cation exchanger for the removal of heavy metal. Two chelating ion exchange resins Chelex 100 and Amberlite IRC 748 (formerly, IRC 718), both which have iminodiacetic acid (IDA) function group, were used to exchange Cu (II) and Zn (II) from aqueous solutions using batch experiments by Lin and Juang (2004). It was shown that the amount of Cu (II) and Zn (II) exchanged increased with increasing the pH value and temperature. In addition, the amount of metals exchanged using IRC 748 resin was greater than Chelex 100 resin under comparable conditions (Lin and Juang, 2004).

Sorption characteristics of iron (II) on iminodiacetic resin Purolite S930 in various operating conditions such as initial pH, copper concentration, contact time, temperature, ionic form of the resin and resin dose was studied by Bulai and Ciancal (2010). They concluded that the percent of iron (II) removal has a maximum at pH 5.0, and increases with the increasing of resin dose, of the contact time and decreases with increasing initial concentration of solution (Bulai & Cioancal, 2010).

Nowadays, chelating resins are increasingly used in the removal of metal ions due to their high adsorption capacities, selectivity and durability (Zhang et al., 2001; Llosa et al., 2002; Cumbal et al., 2003; Jeon and Holl, 2003; Reddy and Reddy, 2003). The main advantages of ion exchange over other techniques are the improvement of the metals value, high selectivity, lower sludge volume and the ability to meet strict discharge specifications (Gode & Pehlivan, 2006).

2.5 EVAL polymer

Ethylene vinyl alcohol (EVAL) is formed based on polymerization of ethylene and vinyl alcohol monomer as show in Figure 2.6. Combining the excellent gas barrier properties

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and resistance to organic solvents of polyvinyl-alcohol with the thermoforming and water resistance properties of polyethylene, EVAL is a crystalline polymer that widely used in membrane application.

Zhang (2009) incorporated cation exchange resins D061 into EVAL copolymer porous matrix to prepare mixed matrix membrane and used for nitrogen gas separation. Avramescu et al. (2003) prepared MMM based on EVAL matrix using different Lewatit ion-exchange resins to separate two similarly sized proteins, bovine serum albumin (BSA) and bovine haemoglobin (Hb).

In a research done by Saufi and Fee (2009), MMM chromatography was prepared using ethylene vinyl alcohol polymer and lewatit anion exchange resin to form a flat sheet membrane. The membrane was characterized in terms of structure and its static and dynamic binding capacities were measured. The optimum binding for β-Lactoglobulin was found to be at pH 6.0 using 20 mM sodium phosphate buffer. The MMM had a static binding capacity of 120 mg/g membrane (36 mg/mL membrane) and 90 mg/g membrane (27 mg/mL membrane) for β-Lactoglobulin and α-Lactalbumin, respectively.

Borneman and Wessling (2006), reports the use of membrane adsorbers for lysozyme (LZ) capturing and concentration: the membrane adsorbers are prepared by incorporation of ion exchange resins into an EVAL porous matrix. The mixed matrix membrane (MMM) adsorber possesses an open and interconnected porous structure with a large ion exchange surface available for enzyme adsorption

Ethylene   Vinyl ALcohol

$$— (CH_2\text{-}CH_2)m — (CH_2\text{-}CH)n —$$
$$|$$
$$OH$$

Figure 2-6: Structure of EVAL

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2.6 *Adsorption isotherm*

Adsorption is the adhesion of atoms, ions, or molecules from a gas, liquid, or dissolved solid to a surface. This process creates a film of the adsorbate on the surface of the adsorbent. Adsorption is present in many natural physical, biological, and chemical systems, and is widely used in industrial applications such as activated charcoal, capturing and using waste heat to provide cold water for air conditioning and other process requirements (adsorption chillers), synthetic resins, increase storage capacity of carbide-derived carbons, and water purification. Adsorption, ion exchange, and chromatography are sorption processes in which certain adsorbates are selectively transferred from the fluid phase to the surface of insoluble, rigid particles suspended in a vessel or packed in a column.

Langmuir's isotherm describing the adsorption of adsorbate (A) onto the surface of the adsorbent (S) based on the following assumptions:

I.   The surface of the adsorbent is in contact with a solution containing an adsorbate which is strongly attracted to the surface.

II. The surface has a specific number of sites where the solute molecules can be adsorbed.

III. The adsorption involves the attachment of only one layer of molecules to the surface, i. e. monolayer adsorption

The Langmuir Isotherm in linear form was shows in Equation 2.1.

$$\frac{Ce}{q_e} = \frac{1}{q_m K_L} + \frac{Ce}{q_m} \dots\dots\dots \textbf{Equation 2.1}$$

where: q_e= amount of adsorbate adsorbed per amount of adsorbent , Ce= equilibrium concentration , K_L= Langmuir isotherm.((Rengaraj et. al 2007)

The Freundlich adsorption isotherm is often used for heterogeneous surface energy systems. The theory says that the ratio of the amount of solute adsorbed onto a given mass of sorbent to the concentarion of the solute in the solution is not constant at different condition. The freundlich equation may be written as shown in Equation 2.2.

$$\ln q_e = \ln q_f + \frac{1}{n} \ln C_e \ldots\ldots\ldots\text{Equation 2.2}$$

Where: q_e= amount of Fe adsorbed mg Fe/g resin, Ce= equilibrium concentration of Fe mg/L, K_F= Freundlich isotherm. (Kacoba. S, 2007).

3 MATERIALS AND METHODS

3.1 *Materials*

Ethylene vinyl alcohol (EVAL), 1- octanol and dimethyl sulfoxide (DMSO) were used for preparation of polymer dope solution. Several commercial cation resin were purchased from Sigma Aldrich (Malaysia) such as Amberlite IR-120, Amberlyst, Lewatit, and CNP-105 cation. The iron solution was prepared by dissolving an analytical reagent grade iron sulphate ($FeSO_4.7H_2O$) in distilled water. Sulphuric acid was used for the pH adjuststmen if necessary. Most of the chemicals were purchased from Sigma Aldrich (Malaysia).

3.2 *Cation resin screening*

Cation resins were firstly washed by ultra pure water and then dried using freeze drying. Dried resins was ground using ultra centrifugal grinding machine and was passed through a series of sieve tray to get resin particles less than 45 μm. 0.1g cation resin, in centrifuge tube was equilibrated with 10 ml of phosphate buffer pH 7 for 3 hours. The solution was removed by centrifugation at 10 000 rpm for 10 minutes. 30 mL of $FeSO_4.7H_2O$ solution with 500 ppm concentration was added to the tube and was left overnight for binding in rotator. The remaining iron concentration after binding was measured by Atomic Absorption Spectroscopy (AAS). Cation resin with maximum iron removal was selected for the preparation of cation exchanger MMM.
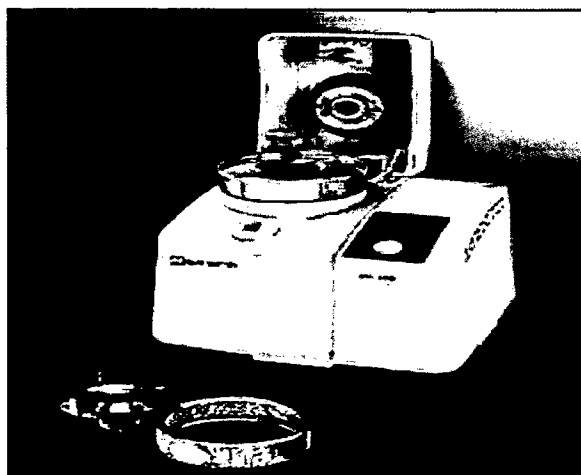
Figure 3-1: Ultra centrifugal eppendorf 5810 R

3.3 Preparation of dope polymer solution

A based polymer solution consisting 5, 10, 15 & 20 wt% of EVAL polymer and 15 wt% of 1-octanol in DMSO was prepared. All the component mixture was continuously stirred at about 60°C for more than 8 hours till all EVAL pellets completely dissolved as shown in Figure 3.3. Selected cation resin from resin screening experiment will be mixed into polymer solution till the mixture is homogenous.
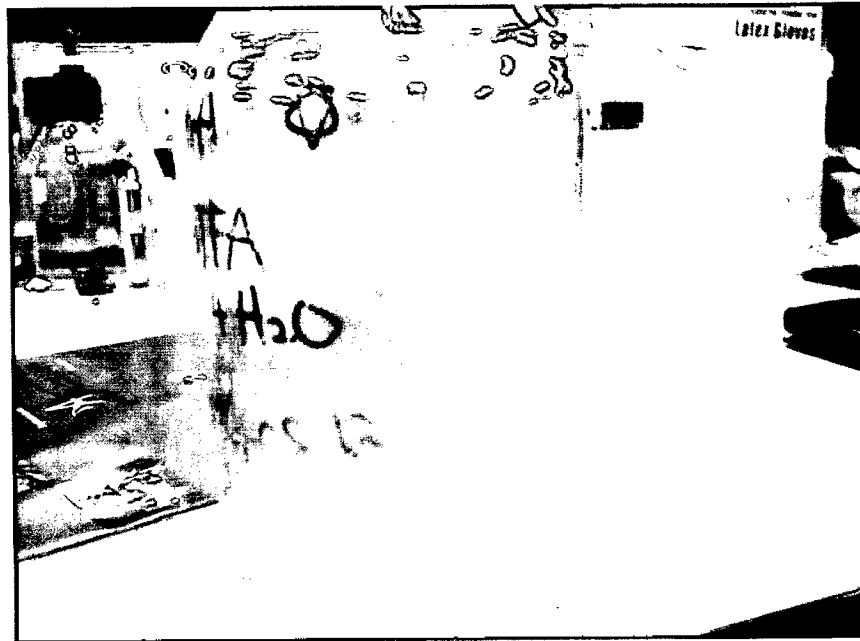
Figure 3-2: Homogenous EVAL polymer solution

3.4 Production of cation exchanger membrane (MMM)

The amount of cation resin loading to be mixed with EVAL polymer solution was calculated by using the Equation 3.1 (Saiful et, al, 2006),

$$\text{Resin loading} = \frac{Wr}{Wp+Wr} \times 100\% \quad \text{.........Equation 3.1}$$

Where,

R = Percentage of resin loading

Wr = amount of cation resins (g)

Wp = amount of EVAL polymer in casting solution (g)

The homogenous casting solution was treated in ultrasonic bath to remove any bubbles in the solution. Conventional casting method was used to prepare flat sheet membrane. The casting solution was pour into a glass plate then spread as thin film using a casting block. The glass plate was immersed into a coagulation water bath until the membrane become solidified and detached from the glass plate as shown in Figure 3.3. Overall production of MMM has been summarized in Figure 3.4.

Figure 3-3: Mixed matrix membrane

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┌──────────────┐                    ┌──────────────┐
│    EVAL      │ ──→  │  ←──        │   Solvent    │
└──────────────┘      ↓            └──────────────┘
              ┌──────────────────────┐
              │  EVAL Polymer Solution │          ┌──────────────────┐
              └──────────────────────┘          │   Cation resin   │
                       │                         └──────────────────┘
                       ↓                                  │
              ┌──────────────────────┐                   │
              │  MMM Casting Solution │ ←─────────────────┘
              └──────────────────────┘
                       │
                       ↓
              ┌──────────────────────┐
              │  Casting on glass plate│
              │     using block       │
              └──────────────────────┘
                       │
                       ↓
              ┌──────────────────────┐
              │  Membrane immersed in  │
              │      water bath       │
              └──────────────────────┘
                       │
                       ↓
              ┌──────────────────────┐
              │ Membrane characterization│
              └──────────────────────┘
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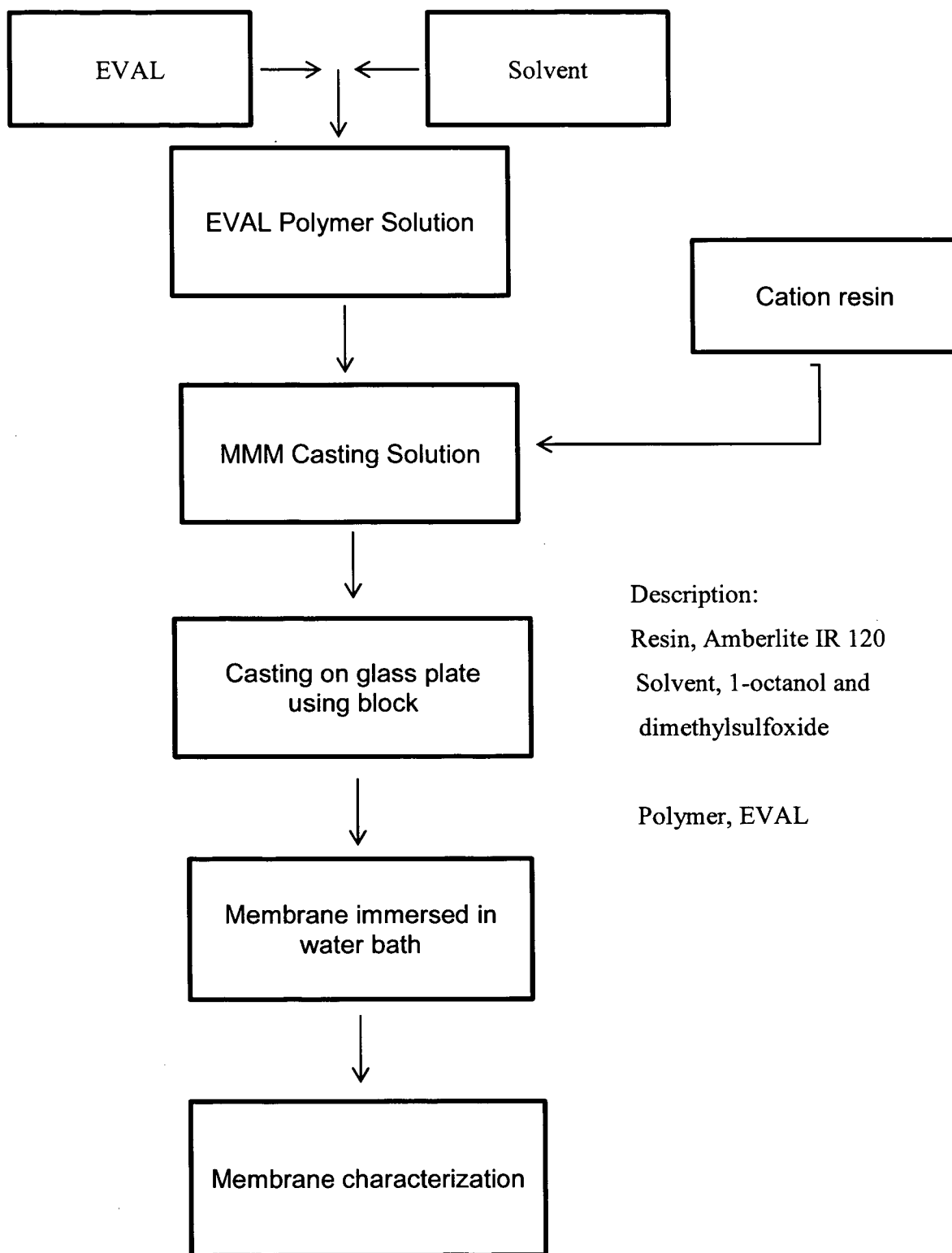
Description:

Resin, Amberlite IR 120

Solvent, 1-octanol and dimethylsulfoxide

Polymer, EVAL

Figure 3-4: Preparation steps in MMM

3.5 *Binding experiment*

Membrane with a dimension of 2cm× 4cm will be used in binding experiment. 15 ml of iron solution with different concentration was added to the membrane in centrifuge tube during binding. The binding was done overnight as shown in Figure 3.5. The remaining concentration of iron after binding was measured by AAS. The binding capacity for catin resins or MMM was calculated using Equation 3.2.

$$q = \frac{v(C-C_e)}{m} \quad \ldots\ldots\ldots\ldots\text{Equation 3.2}$$

Where,

q = dynamic binding capacity, mg Cu/g resin

V = volume of Cu solution, mL

C = initial Cu concentration, mg/L

Ce = equilibrium Cu concentration, mg/L

m = mass of resin, g.

Figure 3-5: Binding of mixed matrix membrane with iron

3.6 *Regeneration of adsorbent*

Cation Resin and MMM were bound with 200 ppm iron ion solution overnight. The remaining copper ion solution was measured to determine the amount of iron bound. The regeneration of bound iron on resin or MMM was tested using 10% of HCL and 5% of H_2SO_4 with a contact time about 20 minutes at room temperature. The concentration of iron ion in regeneration solution was measured by AAS to calculate percentage of recover.

3.7 *Atomic absorption spectroscopy*

To measure the remaining concentration of the iron ion, AAS were used as shown in Figure 3.6.. The standard curve for iron ion solution had been prepared for several concentrations which is 4ppm, 3ppm, 2ppm, and 0.5ppm.

Figure 3-6: Polarized zeeman atomic absorption spectroscopy (Model Z-500 Series)