Dispersion Polymerization of an Unsaturated Polyester Styrene as Ion Exchanger and its Application for Removal of Zn (II), Cu(II), Cd(II), and Pb(II) from Aqueous Solutions.

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ABSTRACT—This work was intended to prepare a very micron-sized ionic exchange resin beads made by dispersion polymerization of unsaturated polyester with styrene monomer units in mass weight of 30% to 40% respectively. The polymerization process involved the use of methyl ethyl ketone peroxide, as a free radical initiator. A couple of factors such as the effect of agitation on resin beads size, and pH on swelling behavior, were studied.

Confirmation of final preparation was made by use of Fourier Transformation Infrared Spectroscopy. The control in diameter of such resin beads within a range of 10 - 150 μm was reached. Thermo-gravimetric technique was also part of the analysis.

The results of this work revealed that such polymeric resin beads were effective in removing Zinc (II), Copper (II), Cadmium (II), and Lead (II) heavy metals from aqueous solutions. During the removal process, batch mode technique was used, and the effects of pH, contact time and heavy metal concentrations on adsorption efficiency were studied. Under the experimental conditions, the removal efficiency of polymeric resin beads in removing such metals were 65%, 73%, 52%, and 80% respectively.

Key words: Unsaturated polyester styrene , Dispersion polymerization, Heavy Metals, Batch mode.

I. INTRODUCTION

Recently, copolymers have become of very importance in industry, because of the feasibility to prepare new contemporary polymers of certain physical and mechanical characteristics by inserting certain composite units in polymer. For instance, there can be a possibility of improving many physical properties such as increasing resistance to radiation, heat, and chemical attacks [1]. The great demand of these very micron-sized particles of polymers was numerously noticed in many modern applications, because of the potentially uniform particles that can be achieved.

Dispersion process is among few developed polymerization processes recognized to produce micron-sized particles with a narrow distribution [2], and to overcome the problems faced by both suspension polymerization famed with the lack of uniformity, and by successive seeded emulsion [3] and two-stages swelling [4] methods which both avoid particle size classifications and are more complicated and time consuming.

In last years, polymers with very micron-sized particles have possessed a wide range of applications in various fields of life. They were potentially requested in preparation of membranes [5] and ion exchange resin beads [6], and used for purification and desalination of water as well as in treatment of chemical and radioactive waste materials.

The presence of heavy metals (HM) such as Zn (II), Cu(II), Cd(II), and Pb(II) in excessive quantities will definitely interfere with many beneficial uses of water, causing serious problems to the environment as well as to human health by means of entering the food chain [6].

Nowadays, many separation methods, involving solvent extraction, ion-exchange, co-precipitation, membrane filtration, bio-sorption and common adsorption, have been developed and used to wipe off HM ions from different aqueous solutions with broad range of concentration. Generally, ion exchange and sorption are mostly preferred for removal of HM ions due to effectiveness and easy handling [7].

Herein this paper, Synthesis of microned-sized resin beads made of an unsaturated polyester styrene (UP-St) as ion exchangers for the removal of Zn (II), Cu(II), Cd(II), and Pb(II) in aqueous solution using batch mode was successfully achieved.

II. EXPERIMENTAL

A. Materials & Method.

Unsaturated Polyester (UP), Styrene monomers (St) by Eurostar Scientific Ltd, England. Polyvinyl alcohol (PVA), and Hydroxypropyl Methylcellulose (HPMC), by Riedel-deHaen AG, Germany.

B. Synthesis of the Copolymer Dispersion

UP-St, copolymer content 30-40% by mass of styrene was emulsified with polyvinyl alcohol solution (PVA), and mixed with cobalt naphthenate (Co NAP) and methyl ethyl ketone peroxide (MEKP) which were respectively used as
an accelerator and initiator. Then, all of the above was mixed with the dispersant matrix made of hydroxypropyl methylcellulose (HPMC). The mixture was heated to 60 °C, and stirred at a rate of 120 rpm. Next, the nitrogen gas was passed through the solution for 20 min to remove oxygen. And finally, agitation was applied continuously till the solid of particles was achieved.

The polymer particles were isolated from the matrix by washing [4, 8]. The standard recipe and the reaction parameter investigated in this study are shown in table (I).

TABLE I: Reaction conditions.

<table>
<thead>
<tr>
<th>Material</th>
<th>weight, (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>UP-St copolymer, (30–40)% St.</td>
<td>50</td>
</tr>
<tr>
<td>Polyvinyl alcohol</td>
<td>2.0</td>
</tr>
<tr>
<td>Cobalt naphthanate solution</td>
<td>0.2</td>
</tr>
<tr>
<td>Methyl Ethyl Ketone Peroxide</td>
<td>1.0</td>
</tr>
<tr>
<td>Hydroxypropyl Methyl Cellulose</td>
<td>45.0</td>
</tr>
</tbody>
</table>

C. Instrumentation

Mechanical stirrer with a semicircular anchor-type blade, model 7813D Type-RW 20, speed ranged from 60 – 2000 rpm model V50-1000., GMBH Co., and Fourier Transform Infrared spectrophotometer were supplied by Tripoli Petroleum Research Center (PRC) Laboratories.

D. Characterization

A Fourier-transform infrared spectro-photometer (FTIR) was used to characterize the functional groups in final product. Figure 1-A & 1-B showed that the spectra of absorption peaks of around 780 cm\(^{-1}\) and 1641 cm\(^{-1}\) indicating the C=C in styrene and unsaturated polyester respectively. However, the absence of an absorption band of such wavelengths for the final product suggested that cross-linking occurred between the styrene and the unsaturated polyester chain at C=C active site of the unsaturated polyester as can be seen in figure 1-C. The absence of these bands is also being observed from the spectra of polymerized material in unsaturated polyester resins [6, 9].

E. Thermo-gravimetric Analysis (TGA)

Prior to thermo-gravimetric analysis, samples of the final product were dried in the oven at 75 °C for 24 hr. Then, after, the analysis of TGA revealed weight stability of the unsaturated polyester styrene polymeric resin beads samples at 209 °C (Figure 2).

III. RESULTS AND DISCUSSION

A. Effect of Agitation Rate

Results from figure (3) showed that agitation was required to ensure a complete mixing of the reaction mixture, and also to prevent sedimentation to the bottom of the vessel as seen in other study [4,8]. The results demonstrated that the control of the size of the resulting particles could be made by adjusting the agitation rate. In general, increasing the rate of agitation corresponds to increasing the shear force, which causes the particle size to decrease. Previous work pointed out to the action of dispersant in this system as a spacer or matrix between particles that inhibits coalescence. Such dispersants would adsorb on the surface of particles, preventing the touching of these particles. It was noticed that the increase of agitation rate, will make the spacing becoming smaller, due to the system being more dynamic. As a result, smaller particles will be obtained [8].

B. Preparation of Cationic Exchange Resins for Removal of Heavy Metals

Typical strongly acidic cation exchange resins are prepared by the sulfonation of the cross-linked polystyrene. Under controlled conditions, one sulphonic acid group is introduced into each aromatic nucleus. The total number of functional groups per unit of resin volume determines the theoretical exchange capacity. Since no other functional groups are present, the exchange is considered as a monofunctional [7].

C. Batch Experiment

Adsorption was performed in batch mode experiment (for the advantage of local equilibrium assumption), where 100 ml of heavy metal solutions was added to 5 g of exchangers in conical flasks and mixed with rotary shaker.

D. The Effect of pH on Swelling

The pH dependence of swelling at ambient temperature. The resin beads shrunk at pH < 3. However, resin beads started to swell as pH started to increase towards neutrality. SW values of batch was observed to 70%.

E. The Effect of pH on Heavy Metal Removal

The effect of pH on Zn (II), Cu(II), Cd(II), and Pb(II) adsorption onto UP-St ion exchangers was studied over a pH range of 3.0 – 9.0 at 25 °C. The procedure followed was with 5 g exchangers and 100 ml of 100 mg/l heavy metal ions concentration. As shown in Fig.(4), it was apparent that the removal efficiency percentage of each (HM) ion increased with increasing pH till reaching 6.5, then started to decrease slightly with increasing pH, with most preferability to pb (II) ions. The main factor effecting pH on the removal efficiency is the species of the those (HM) ions. In low pH, most pb(II) species (and other HM ions) exist as pb\(^{2+}\) ions, and only a small portion of pb(OH)\(^{+}\) ions are also present in case of pH approaching 6. The final equilibrium
pH of the reaction mixture was found to be 2.6, 4.9, and 6.5 for the exchangers, when initial pH was 3.0, 5.5, and 8.0 respectively. And as can be noticed that final pH values were always less than initial pH, indicating that H⁺ ions were released from the surface of the exchangers as (HM) ions were adsorbed, indicating the adsorption of such ions in an ions exchange mechanism. The negative charge on the surface of carbon increased since the functional group became more and more deprotonated with increasing pH. Thus, the electrostatic attraction between the adsorbent and the HM ions increased with increasing pH.

F. The Effect of Contact Time and the Initial Concentration

Figure 5 shows the effect of contact time on the adsorbed amount of studied (HM) ions from their aqueous solutions with different initial concentrations of 50 and 100 mg/l for four of them at 25 °C. It was observed that adsorption of those (HM) ions increased sharply with contact time in the first 20 min and attained equilibrium with removal efficiency percentage values of 65%, 73%, 52%, and 80%, within 35, 30, 40, and 25 min, in respect to Zn(II), Cu(II), Cd(II), and Pb(II). Once again, the variations detected perhaps due to the type of species and their solubilities at different pH values. Yet, it still show rapidity in removal efficiencies for four (HM) ions, which was perhaps due to the participation of specific functional groups on the adsorbent surface [6]. It is also clear from Fig. 4 that the efficiency of adsorption increased reaching their max. values with increase in initial concentration of all HM ions from 50 mg/l to 100 mg/l, indicating the suitability and availability of the active sites in UP-St resin beads.

IV. CONCLUSION

In the present work, ion exchangers made of micron-sized resin beads of unsaturated polyester styrene using suspension polymerization. Such exchangers were efficiently used in a batch mode technique for the removal of Zn(II), Cu(II), Cd(II), and Pb(II) reaching maximum values of 65%, 73%, 52%, and 80% respectively, in a time of 35, 30, 40, and 25 min, respectively.

REFERENCES


Figure 1: FTIR Spectrum of (A) St. monomer, (B) Polyester, (C) Polyester Styrene.
Figure 2: Cross Linked final product TGA

Figure 3: The effect of agitation rate on Resins Size

Figure 4: The effect of pH on heavy metal removal.

Figure 5: Effect of initial concentration and time on heavy metal removal.