MICRON-SIZED POLYMER PARTICLES FROM TANZANIAN CASHEW NUT SHELL LIQUID. PART II: AN ASSESSMENT OF CATION-EXCHANGE CAPABILITY OF THE CARBOXYLATED PARTICLES

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ABSTRACT. Micron sized polymeric particles were prepared from cashew nut shell liquid and subsequently functionalized to produce micron-sized carboxylated cation exchange resin (MCCER). By titrimetry and analytical procedures employing atomic absorption spectrometry, an assessment of the cation exchange capability of the carboxylated particles was made. The total cation exchange capacity of MCCER was found to be 5.4 ± 0.1 meq/g. The apparent acid strength exponent (pK) of the resin was estimated to be 5.6 ± 0.1 at 30 °C. The resin was found to be nonselective toward calcium, magnesium and sodium ions and the affinity of the resin toward competitive exchange of the ions followed the order: $Ca^{2+} > Mg^{2+} > Na^+$. The results indicate that cation exchange capacity of MCCER is comparable to other commercially produced carboxylic cation exchange resins.

KEY WORDS: Carboxylated cation exchange resins, Cation exchange capacity, Cashew nut shell liquid

INTRODUCTION

Petrochemicals and natural products are the principle sources of monomers used in various polymerizations processes. Petrochemicals cannot be sustained due to their high cost and depletion rates that lead to economical and environmental predicaments. On the other hand, natural products, as exemplified by cashew nut shell liquid (CNSL), are renewable and environmentally friendly [1, 2]. Having unsaturated long chain phenolic components [3], CNSL serves as a promising supplement monomer resource for the polymer industry and a number of CNSL based polymer formulations have been reported in literature. These include surface coatings and brake linings [2, 4, 5], CNSL-based spherical polymer particles for adsorption and immobilization [6] processes, formulation of sisal reinforced composites [7], and polyurethane form [1] among others.

Formulation of ion exchange resins, (IERs), from CNSL is another prospective use of the natural monomer [4]. Synthetic ion exchange resins are polymers with electrically charged sites at which ions replacement can occur. The charges (ions) within the resin matrix are fixed, but these are accompanied by mobile counter ions of opposite charges that can be exchanged for other similarly charged ions. The demand for synthetic ion exchange resins is on the rise due to their higher ion exchange capacity as well as superior chemical resistance and mechanical properties compared to natural ion exchangers and versatility [8]. Ion exchange separation processes find interesting applications in the recovery and separation of metallic and rare earth elements, biochemical components, and in trace analysis [9]. Other applications involve water treatment including purification and de-ionization of water, desalination of seawater and industrial wastewater treatment [10].

In ion exchange processes, two or more similar charged ions compete for attachment at active sites in the resin. For acidic cation exchange resin, H^+R^-, in contact with aqueous solution

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containing M^{x+} cations the following equilibrium is established between the solid resin and the aqueous solution [8]:

$$M^{x+}(aq) + x[H^+R^-](s) \rightleftharpoons xH^+(aq) + x[M^{x+}R_x^-](s)$$
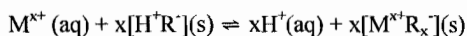
The ion-exchange behavior of a resin is mainly determined by the fixed ionic groups in the matrix. The total exchange capacity is determined by the concentration of the fixed ionic groups and the position and reversibility of the ion-exchange equilibrium, which is influential for the resin performance, is affected by the chemical nature, vis, the acid or base strength of the fixed ionic groups. Therefore characterization of ion exchange resins involves determination of total capacity and acidity or basicity (pK) values of the ionogenic groups. Both quantities can be determined by titrimetric techniques.

In our previous paper [11], the preparation and characterization of micron-sized polymer particles from cashew nut shell liquid and subsequent functionalization of the particles with chloroacetic acid to obtain micron-sized carboxylated cation exchange resin (MCCER) was reported. In this work an assessment of the MCCER for possible applications in ion exchange processes is made.

EXPERIMENTAL

Materials and reagents

Technical CNSL was supplied by TANITA Company Limited based in Dar es Salaam, Tanzania. Reagents and solvents were A.R. grade supplied by BDH Chemicals. 200 ppm stock solutions of Na^+, Ca^{2+} and Mg^{2+} ions, respectively, were prepared by dissolving appropriate amounts of sodium sulphate, calcium sulphate and magnesium sulphate, respectively, in distilled water.

Preparation of MCCER: (surface reaction with monochloroacetic acid)

The micron-sized polymeric particles (MSPP) and the corresponding chemically modified micron-sized carboxylated cation exchange resin (MCCER) were prepared by using the procedures described previously [11]. The MCCER samples were prepared from MSPP obtained from successful recipes EC-02, EC-03, EC-07, EC-08 and EC-16 and the particle sizes of MCCER ranged from 0.1 to 4.4 μm as previously indicated [11].

Determination of the acid strength constant (pK) and the total cation exchange capacity of MCCER

The pH-titration method described by Inczedy [12] was adopted. 15 portions of exactly 0.50 g of the H-form cation exchange resin were each placed into 50-mL titration flasks. 20 mL of 1 M NaCl solution was pipetted into each of these flasks and then, different portions of 1.003 M NaOH standard solution from the burette in increasing amounts from 0 to 15 mL were added. The flasks were shaken for over 12 hours to make sure that equilibrium is attained. The pH values of the solutions were recorded at constant pH readings using RS pH-meter model 610-540 calibrated with standard buffer solutions of pH 7 and pH 4.

Determination of affinity of MCCER

An aqueous solution containing equal concentrations (135.0 ppm) of Na^+, Ca^{2+} and Mg^{2+} was passed through the column packed with H-form MCCER. 50 mL of eluate was collected at a flow rate of 5 mL/min, and the concentrations of the ions were analysed by flame atomic absorption spectroscopy (FAAS) using a Perkin-Elmer spectrophotometer model AA-300. The amount of the each ion adsorbed in the resin was determined from the difference between concentration of the ion in the eluent and the concentration of the same ion in the effluent. The relative affinity of the MCCER for a given cation was calculated as a ratio of the amount exchanged of the given ion to the total amount of all ions (Na^+, Ca^{2+} and Mg^{2+}) exchanged.

Regeneration efficiency of exhausted MCCER

Exhausted MCCER samples were regenerated by flushing with concentrated HCl solutions and the effect of HCl concentration on the regeneration efficiency was evaluated. The exhausted MCCER were packed into three identical ion-exchange columns and HCl solutions of different concentrations (1, 3 and 6 M) were passed through the columns. From each column eluate in portions of 25 mL were collected and then analysed for concentration of Na^+, Ca^{2+} and Mg^{2+}, respectively, by atomic absorption spectrometry. The amount of each ion present in the eluate was compared with the amount of that ion in the exhausted MCCER and the percentage recovery (regeneration) was calculated. Elution rate of 5 mL/min was maintained.

RESULTS AND DISCUSSION

Preparation of micron-sized carboxylated cation exchange resin (MCCER)

The CNSL based MSPP prepared by emulsion polycondensation of CNSL with formaldehyde were largely insoluble to most common solvents and chemical reagents, as previously reported [11]. The presence of surface phenolic OH groups enables activation of the MSPP by alkali to produce strong nucleophiles, phenoxide ions, which are capable of effecting a number of surface nucleophilic reactions. Thus, nucleophilic substitution of the MSPP with monochloroacetic acid to produce the carboxylated cation exchange resin, MCCER, was achievable.

Cation exchange capacity and equilibrium constant of MCCER

The total cation exchange capacity (CEC) of a resin specifies the amount of fixed ionogenic groups in meq/g of dry resin in the H-form that is accessible for exchange process. For any resin the cation exchange capacity thus defined is a constant independent of the experimental conditions. The cation exchange capacity of the prepared MCCER can be obtained from the inflection point of the pH titration curve (as shown in Figure 1). Table 1 summarizes the results for cation exchange capacity of MCCER samples obtained from different polymerization recipes and average CEC value of 5.4 ± 0.1 meq/g is estimated.

In a previous study [11], the MCCER was reported to exchange 86 mg of calcium ions per gram of polymer particles at 30 °C, which is equivalent to 4.3 meq/g resin. That exchange of calcium was less than the CEC obtained in this work by 1.1 meq/g. This is not unexpected since CEC obtained from pH titration gives the total (maximum) capacity of the resin while the absorption of calcium ions into the weakly acidic MCCER should depend on the prevailing experimental conditions, specifically the pH of the aqueous phase and the concentration of the

cation in the aqueous phase. Thus at lower and moderate pH range the 'apparent' capacity for calcium should expectedly be less than the total cation exchange capacity of the resin.
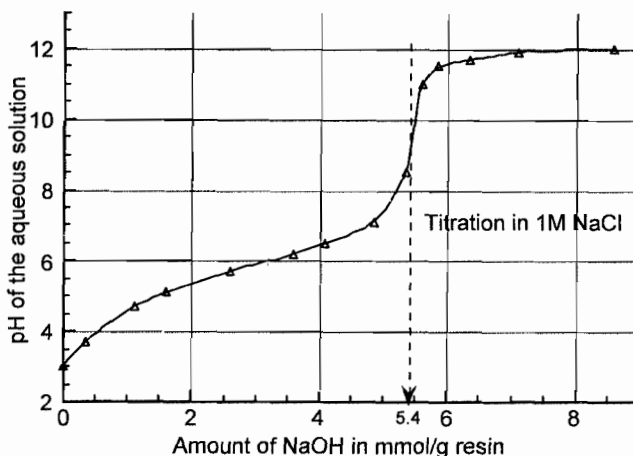

Figure 1. pH titration curve for the determination of cation exchange capacity of the MCCER. Recipe EC-08.

Table 1. Results of cation exchange capacities (CEC) in meq/g for the MCCER samples from different recipes.

Sample	X (CEC)	$\overline{X}- X$	$(\overline{X}- X)^2$	SD
EC 07	5.58	-0.142	0.0202	
EC 03	5.56	-0.122	0.0149	
EC 16	5.31	0.128	0.0164	0.124
EC 02	5.36	0.078	0.0061	
EC 08	5.38	0.058	0.0034	
The average CEC = 5.438 ± 0.124 meq/g				

The pH titration curves can also be used to evaluate apparent acid strength exponent, the pK values, of the resin acid groups. In this case the apparent pK value of MCCER was computed from the conventional titration curve (i.e. pH of the aqueous phase versus amount of the titrant added) by using the Henderson-Hasselbach equation: $pH = pK - log\{(1-\alpha)/\alpha\}$ where α is the degree of dissociation of the resin acid groups with assumptions that the pH in the resin and in the aqueous phase are the same and that half the resin is converted when half the amount of titrant is added to the aqueous phase. Since MCCER particles are non-porous the exchange reaction should largely occur on the surface of the particles and the two assumptions should apply for this cation exchange system.

From Figure 2, the apparent acid strength exponent (pK value) of the MCCER obtained from polymerization recipe EC-08 is evaluated as approximately 5.56 at 30 °C. Table 2 summarizes the pK values for all MCCER samples obtained from different successful recipes and average pK value of 5.6 ± 0.1 is calculated from the data. The estimated literature values of pK$_a$ of most carboxylic acid ion exchange resins lie in the range of 5 to 6. Thus, the acid strength constant of the carboxylated MCCER prepared from Tanzanian CNSL is comparable to the acid constants of most commercially produced carboxylic resins. Likewise, the average CEC of the prepared

MCCER is comparable to the CECs of most commercially produced carboxylic cation exchange resins [8].
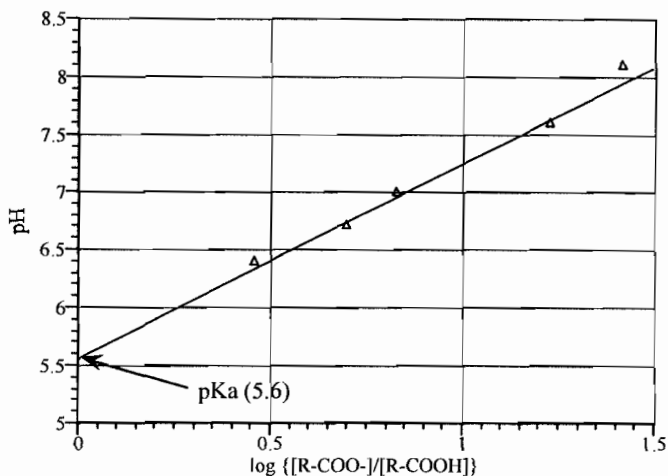

Figure 2. A graph of pH against log ([R-COO⁻]/[R-COOH]) for determination of pK_{H-Na}. Recipe EC-08.

Table 2. Results for the determination of apparent acid strength exponent pK for the MCCER samples from different recipes.

Recipe	X (pKa)	$\overline{X} - X$	$(\overline{X} - X)^2$	SD
EC 07	5.55	0.032	0.0010	
EC 03	5.65	-0.068	0.0046	
EC 16	5.49	0.092	0.0085	0.103
EC 02	5.75	-0.168	0.0282	
EC 08	5.56	0.022	0.0005	
The average pK = 5.582 ± 0.103				

Comparison of cation affinity of MCCER

The results of affinity of the prepared MCCER in exchanging three selected cations, follow the order, $Ca^{2+} > Mg^{2+} > Na^+$, as shown in Figure 3. These results seem to support the observation that cation exchange resins adsorb cations of higher charges more strongly than those of lower charges as reported by various workers [8, 12]. In this case the carboxylic acid resin exhibit a relatively high affinity for alkaline earth metal ions Ca^{2+} and Mg^{2+} than the alkali metal ion Na^+. The relative affinities of cation exchange resins toward metal ions have been explained on the basis of ionic hydration, vis, the ions that have smaller hydrated radii are more strongly bound to the resin matrix because of greater electrostatic attraction to the fixed charges. Since the process of ion exchange is controlled by electrostatic forces, the adsorbability of two competing ions will depend on the relative charge densities, i.e. ionic charges and ionic radii of the two ions competing for the exchange [8].
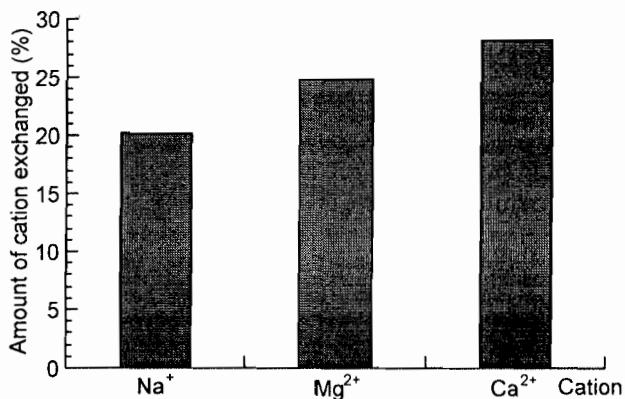
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Figure 3. Relative affinities of exchangeable cations for MCCER in columnar ion exchange operation. Total concentration of cations = 405.0 ppm and eluate flow rate = 5.0 mL/min.

Regeneration efficiency of exhausted MCCER

The factors that affect regeneration efficiency of exhausted MCCER in columnar operations include resin particles size, elution flow rate and concentration of the regenerant. In this study, the eluent flow rate was set constant at 5 mL/min and the particles sizes were predetermined by the conditions of their preparation. The concentration of the regenerant was therefore varied so as to determine the optimum concentration that would effectively regenerate the exhausted MCCER.
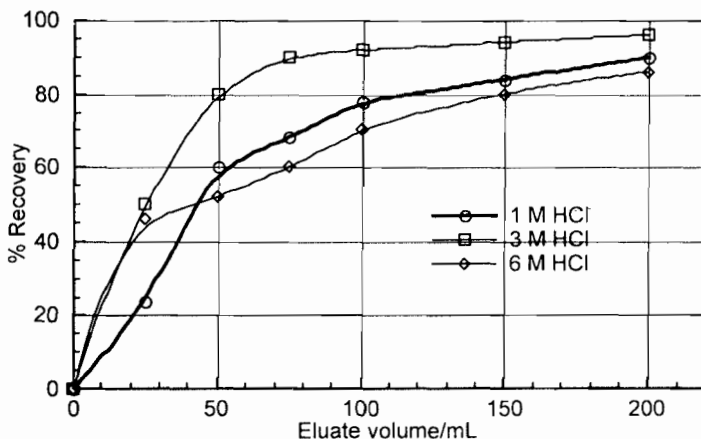

Figure 4. Regeneration of Ca^{2+}-exhausted MCCER by aqueous HCl solutions. Eluate flow rate = 5.0 mL/min.

Concentrated hydrochloric acid was used for regeneration of the resin due to the great affinity of weakly acidic resins for H^+ compared to other cations in acidic conditions. As seen in Figure 4, the regeneration efficiency was found to increase as the concentration of the acid was increased from 1 to 3 M. However, when the concentration of the acid was increased further to 6 M the regeneration efficiency diminished to less than that of 1 M HCl. The lower regeneration efficiency shown by the 6 M HCl solution compared to the 1 M and 3 M solutions can probably be attributed to the increased viscosity of the aqueous phase at high acid concentrations. The increased viscosity of the more concentrated regenerant solution could adversely influence the regeneration efficiency by impairing diffusion of the desorbed ions out of the resin matrix into and through in the liquid phase. Similar results have been reported by Samuelson [13].

CONCLUSION

MCCER with particle sizes ranging from 0.1 to 4.4 µm was successfully prepared through emulsion polycondensation of CNSL and subsequent functionalization of the particles with chloroacetic acid. The cation exchange capacity and the apparent acid strength exponent of the MCCER were evaluated as 5.4 ± 0.1 meq/g and 5.6 ± 0.1, respectively, at 30 °C. The MCCER was found to be nonselective toward calcium, magnesium and sodium ions and the affinity of the resin to exchange the three ions followed the order: $Ca^{2+} > Mg^{2+} > Na^+$. The favorable HCl concentration for regenerating the exhausted MCCER was determined to be 3 M. The results suggest that MCCER is a suitable ion exchange resin with properties similar to those commercially prepared carboxylated cation exchange resins.

ACKNOWLEGEMENT

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