A new optional recycled water pre-treatment system prior to use in the household laundry

Zhuo Chen[a], Huu Hao Ngo[a,*], Wenshan Guo[a], Thi Thu Nga Pham[a], Richard Lim[b], Xiaochang C. Wang[c], Clayton Miechel[d], Kelly O' Halloran[e], Andrzej Listowski[f], Nigel Corby[g]

[a] Centre for Technology in Water and Wastewater, School of Civil and Environmental Engineering, University of Technology Sydney, Sydney, NSW 2007, Australia

[b] School of the Environment, Faculty of Science, University of Technology Sydney, Sydney, NSW 2007, Australia

[c] Key Lab of Northwest Water Resources, Environment and Ecology, Ministry of Education, Xi'an University of Architecture and Technology, Xi'an 710055, China

[d] Port Macquarie-Hastings Council, PO Box 84, Port Macquarie, NSW 2444, Australia

[e] Gold Coast City Council, Gold Coast MC, QLD 9726, Australia

[f] Sydney Olympic Park Authority, 7 Figtree Drive, Sydney, NSW2127, Australia

[g] City West Water, 247-251 St Albans Road, Sunshine, VIC 3020, Australia

* Correspondence author. Tel: +61 2 9514 2745; Fax: + 61 2 9514 2633.
Email address: h.ngo@uts.edu.au

Highlights

• A small pre-treatment unit for recycled water purification was introduced.

• The performance of the zeolite material for reducing water hardness was analysed.

• The operability and cost-effectiveness of the zeolite filter system were discussed.

• The capacity and column service life for a household laundry were calculated.

• Field trial operations and scale-up pilot studies should be further performed.

Abstract

With a constantly growing population, water scarcity becomes the limiting factor for further social and economic growth. To achieve a partial reduction in current freshwater demands and lessen the environmental loadings, an increasing trend in the water market tends to adopt

recycled water for household laundries as a new recycled water application. The installation of a small pre-treatment unit for water purification can not only further improve the recycled water quality, but also be viable to enhance the public confidence and acceptance level on recycled water consumption. Specifically, this paper describes column experiments conducted using a 550 mm length bed of zeolite media as a one-dimensional flow reactor. The results show that the zeolite filter system could be a simple low-cost pre-treatment option which is able to significantly reduce the total hardness level of recycled water via effective ion exchange. Additionally, depending on the quality of recycled water required by end users, a new by-pass controller using a three-level operation switching mechanism is introduced. This approach provides householders sufficient flexibility to respond to different levels of desired recycled water quality and increase the reliability of long-term system operation. These findings could be beneficial to the smooth implementation of new end uses and expansion of the potential recycled water market. The information could also offer sound suggestions for future research on sustainable water management and governance.

Keywords

Recycled water; zeolite filter system; new application; household laundry

1. Introduction

Recycled water for a household laundry has been increasingly regarded as a prospective new end use since significant fresh water savings could be achieved if potable-quality water used for clothes washing is replaced with recycled water (Chen et al., 2012). However, despite that many water authorities have encouraged the new applications of recycled water in dual pipe systems and stipulated corresponding policies, guidelines and regulations, the use in practice of recycled water with relatively close human contact is still quite limited. International research has identified significant community resistance to the use of recycled water in some circumstances, resulting in the abandonment of such projects. These instances include the Toowoomba, Australia, San Diego, USA and Lichi Rijin, the Netherlands (Hurlimann and McKay, 2006). Public concerns on individual health, water clarity, cost and machine durability might be major issues that prevent the society from establishing and promoting the new end use (Pham et al., 2011). Notably, the recent social surveys in three different locations of Australia (i.e., Port Macquarie, Melbourne and Sydney) indicated that the community's confidence on the use of recycled water in a household laundry would be

greatly enhanced with the operation of a small unit for pre-treatment of recycled water prior to use in a washing machine (Chen et al., 2013). Hence, this paper aims to analyse the feasibility and cost-effectiveness of employing a small pre-treatment unit for water purification in the household laundry.

1.1. Recycled water sample

The actual recycled water (Class A) samples from the City West Water (CWW) Western Treatment Plant, Melbourne, Australia, have been considered for experimental analyses. The Western Treatment Plant has been supplying 37 GL per year of recycled water for agriculture and landscape irrigation (e.g., golf club, parks, zoos and wetlands) in the Werribee area, a suburb around 32 km southwest of Melbourne's CBD. The dual pipe recycled water systems have already been installed in front/back yard of 2000 new homes in Wyndham Vale, and Werribee and Class A recycled water will be supplied to local households in December 2013 or early 2014 (City West Water, 2012). Thus, if the pre-treatment unit is demonstrated to be beneficial to ensure the reliability and consistency of recycled water consumption, the system can be widely adopted in real cases. By this means, residents are likely to be more optimistic and confident in establishing and implementing new applications of recycled water. This would further contribute to significant freshwater savings and to achieving water recycling targets toward a sustainable water cycle development.

1.2. Hardness of recycled water

When it comes to water hardness, the majority of the hardness ions are calcium and magnesium, but small amounts of other ions such as iron and manganese can contribute as well. Hard water minerals in recycled water can react with soap anions which might cause difficulty with soap lathering, decreasing the cleaning efficiency. The insoluble precipitates can also induce scaling problems and serious mechanical failures by forming crusty deposits in household appliances, thereby shortening the life of the washing machines and reducing the machine efficiency (City West Water, 2009 and Seo et al., 2010). Other problems not so visible but quite significant are deposits on clothes fabrics, namely soap curd or scum, after they have been washed. Dull whites and colours caused by soap curd might not be easily removed in the rinse cycles. This can also shorten the life of clothes that are washed and worn frequently (Wist et al., 2009).

The Australian Drinking Water Guidelines (ADWG) state that there is no health guideline value for total hardness (referred to as calcium carbonate, $CaCO_3$), but an aesthetic value should not exceed 200 mg/L. Comparatively, the Canadian Guidelines regard the water with total hardness over 200 mg/L as poor quality, and 80–100 mg/L as an acceptable level (ADWG (Australian Drinking Water Guidelines), 2011 and Health Canada, 2003). The average water hardness level in the drinking water supply from CWW at Werribee area, Melbourne, is approximately 30 mg/L, with maximum levels less than 50 mg/L. As the total hardness of CWW recycled water nearly approaches the ADWG guideline upper limit and is significantly higher than that of drinking water in the local community, the pre-treatment unit is primarily designed to mitigate the current hardness level so as to improve the performance of soaps and laundry detergents, and protect the washing machine from scaling during clothes washing activities.

There are many different methods that have been widely adopted as a means of effective water softening, including chemical precipitation, ion exchange process, membrane techniques (e.g., nanofiltration and reverse osmosis) and electromembrane systems (e.g., electrodialysis, electrodialysis reversal, and electro-deionization reversal). However, in the case of chemical precipitation, the choices of additional chemicals are restricted as some of them might be deleterious to human health. With respect to membrane and electromembrane systems, high power consumption and expenses are required for operation and maintenance of the equipment. Besides, when water hardness level is high, calcium deposits will quickly make the membrane less permeable, causing membrane fouling within a short period of time. The affordability and operability of these advanced techniques are likely to present barriers to their actual application at household levels (Gabrielli et al., 2006, Wist et al., 2009 and Seo et al., 2010). Therefore, a cost-effective, simple and low energy consuming approach has been forced on water softening processes.

1.3. Potential application of natural zeolites for water softening

As zeolitic minerals have been discovered in many areas of the world, natural zeolites have found a variety of applications in adsorption, catalysis, building industry, agriculture, soil remediation and energy production. Natural zeolites are crystalline microporous minerals with a well-defined open framework structure, consisting of a three-dimensional network of SiO_2 and Al_3O_4 tetrahedra linked together by common oxygen atoms. The mobile non-

framework cations are located in cavities and wander inside the hexagonal channel walls within the structure and so natural zeolites possess valuable physicochemical properties, such as high cation exchange and sorption capacities (Sivasankar and Ramachandramoorthy, 2011 and Loiola et al., 2012).

Due to their intrinsic properties and significant worldwide occurrence, application of zeolites for water and wastewater treatment has become a promising technique (Wang and Peng, 2010). The effectiveness of applying zeolites on ammonium and heavy metal ion removal from wastewaters has been well documented in the literature (Cooney et al., 1999, Panayotova, 2001 and Sarioglu, 2005). However, information regarding the capacity of zeolites for water softening in the process of ion exchange to remove total hardness from highly treated recycled water, which contains much lower concentrations of ammonium and heavy metal ions but relatively high levels of hardness ions, is still very limited (Cinar and Beler-Baykal, 2005). Consequently, considering the practicality, simplicity and economy of the small treatment unit, natural zeolites have been selected as the filtration material in the laboratory scale analyses. To simulate the real operating situations, the results of continuous flow experiments for zeolite column testing will be presented; these results can provide scale-up information to the design of a commercial scale zeolite pre-treatment system for actual application in local households.

2. Materials and methods

2.1. Feed solution

In this research, recycled water from CWW Western Treatment Plant has been employed as the feed solution. When the recycled water was insufficient, synthetic water was used to simulate the composition of CWW recycled water. The synthetic feed solution was prepared by dissolving 300 mg/L of $CaCl_2 \cdot 2H_2O$ in deionised water. Overall, the feed solution used for all the experiments had a total hardness level between 175 and 200 mg/L as $CaCO_3$, indicating relatively high levels of hardness.

2.2. Pre-conditioning of natural zeolites

The natural zeolites were provided by Castle Mountain Zeolites (Quirindi, New South Wales, Australia) which are clinoptilolite-rich minerals composed of clinoptilolite (around 85% by
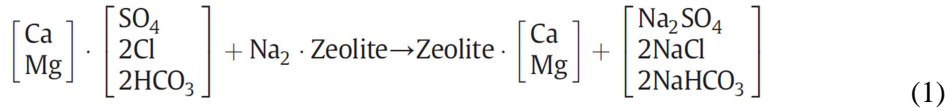
weight) and mordenite (around 15% by weight) with trace amounts of quartz. The nominal mineralogical composition of Castle Mountain Zeolites is listed in Table 1 and the Si/Al molar ratio calculated from the composition data is 5.03 (An et al., 2011 and CMZ (Castle Mountain Zeolites), 2013). The zeolite type FM 16/30 was used in the experiment with a particle size of 0.5–1.5 mm and bulk density of around 1100 kg/m^3 (CMZ, Castle Mountain Zeolites, 2013).

Table 1. Chemical composition of Castle Mountain Zeolites.

Mineral content	Percentage by weight (weight %)
SiO$_2$	71.81
Al$_2$O$_3$	12.10
Fe$_2$O$_3$	1.14
Na$_2$O	2.33
K$_2$O	0.90
CaO	2.60
MgO	0.65
TiO$_2$	0.22
MnO	0.03
P$_2$O$_5$	< 0.01
SrO	0.22
Loss on ignition	7.77

Note: Adapted from An et al. (2011); CMZ (Castle Mountain Zeolites) (2013).

Regarding the pre-treatment and preparation of filtration materials, natural zeolites have been initially washed and cleaned with deionised water so as to remove impurities. As shown in Eq. (1), the main mechanism of zeolites in hardness removal is ion exchange, in which hardness ions such as calcium and magnesium are taken up by the zeolite column and an equivalent amount of more desirable ions such as sodium and potassium are released simultaneously (GE, General Electric, 2012).

$$\begin{bmatrix} Ca \\ Mg \end{bmatrix} \cdot \begin{bmatrix} SO_4 \\ 2Cl \\ 2HCO_3 \end{bmatrix} + Na_2 \cdot Zeolite \rightarrow Zeolite \cdot \begin{bmatrix} Ca \\ Mg \end{bmatrix} + \begin{bmatrix} Na_2SO_4 \\ 2NaCl \\ 2NaHCO_3 \end{bmatrix} \tag{1}$$

Consequently, to attain a high sodium form of the exchangeable surface ions, the cleaned zeolites were then conditioned with a saturated sodium chloride solution (360 g/L) in flasks under a magnetic stirring thermostatic water bath at 50–60 °C for 24 h. By this means, higher adsorption capacity of modified zeolites can be obtained (Inglezakis, 2005, Sivasankar and Ramachandramoorthy, 2011 and Lin et al., 2013). The treated zeolites were finally rewashed three times with deionised water to remove excessive sodium chloride deposited on the

particle surface and then dried at 105 °C for 2 h. The dried zeolites (around 1.6 kg) were packed in the column.

2.3. Experimental set-up

Fig. 1 showed the schematic of the zeolite pre-treatment unit. The feed solution in the feeding tank was pumped continuously into the zeolite column reactor, which had a height of 0.55 m, an internal diameter of 0.06 m in the reaction zone and an effective volume of 1.5 L. The purified recycled water can then be sent to a washing machine for laundry water supplies (Fig. 2). The system could be operated with by-pass controllers under three scenarios.
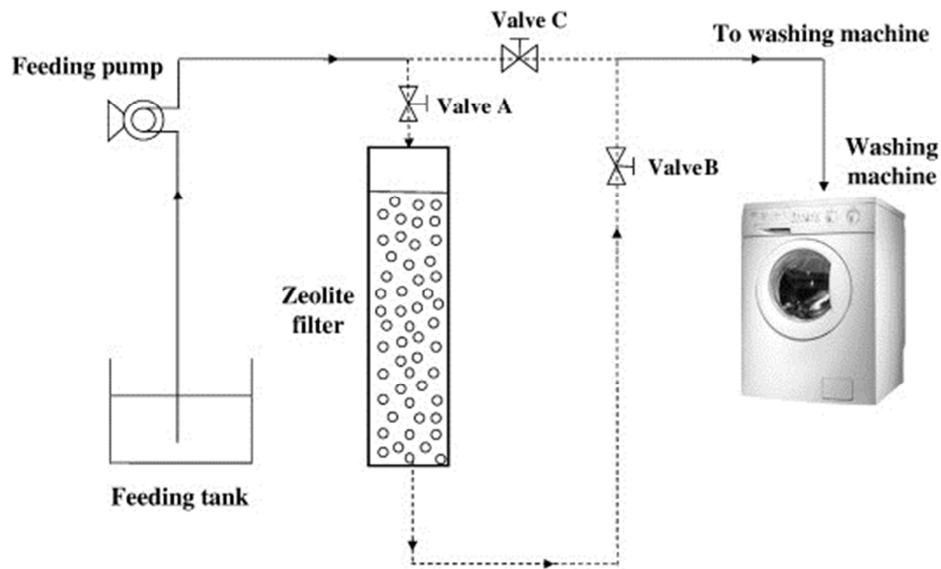

Fig. 1. Schematic diagram of the pre-treatment unit.

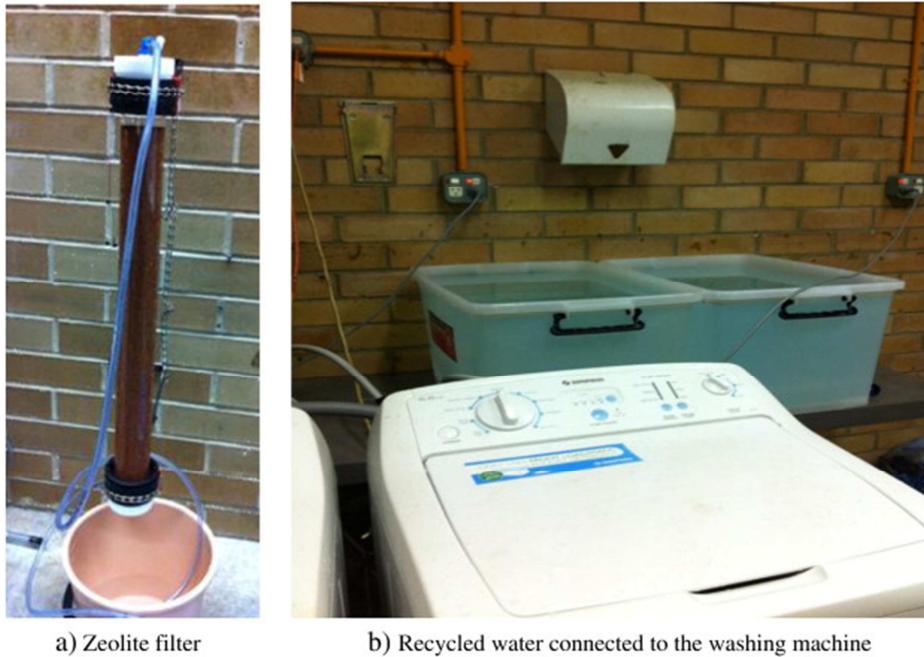a) Zeolite filter   b) Recycled water connected to the washing machine

Fig. 2. Zeolite column experiment in the laboratory.

For scenario 1, the recycled water was delivered directly to the washing machine without any further treatment (valves A and B closed, valve C open). Under scenario 2, the recycled water fully passed through the zeolite filter column prior to entering the washing machine (valves A and B open, valve C closed). With regard to scenario 3, the recycled water partially went through the zeolite filter column based on a bypass percentage before entering the washing machine (valves A, B and C open partially). To ease the observation of the filtration effectiveness, the experiment was operated under scenario 2 with a continuous influent pumping rate at room temperature (25 °C).

2.4. Zeolite regeneration with sodium chloride solution

The whole experiment also included two zeolite regeneration phases. High solubility, low cost and safety of sodium chloride make it suitable as an effective regenerant for removal of hardness ions from the saturated ion exchange resin. Under the regeneration phases, 10–15% of sodium chloride is generally deemed to be a good concentration of salt in the feed solution. At this concentration, good capacity of the regenerated ion exchange reactor can be achieved, without excessive consumption of salt (Wist et al., 2009). Consequently, sodium chloride solution (100 g/L) was adopted as the feed solution and the zeolite column reactor was operated in fluidized condition at the up flow mode. The regeneration pump worked

continuously at 0.3 L/h for 24 h. The regeneration proceeds according to Eq. (2) (GE, General Electric, 2012).

$$\text{Zeolite} \cdot \begin{bmatrix} Ca \\ Mg \end{bmatrix} + 2NaCl \rightarrow Na_2 \cdot \text{Zeolite} + \begin{bmatrix} Ca \\ Mg \end{bmatrix} \cdot Cl_2 \qquad (2)$$

After regeneration, the zeolite column was washed thoroughly with deionised water until the washings showed no more excessive sodium chloride; and this made the column now ready for the next cycle of water softening. Noticeably, small residual amounts of hardness might remain in the zeolite column.

2.5. Analytical techniques

The pH was measured with a portable pH meter (HANNA Instruments HI 9125, Australia). Alkalinity was determined by titrator (HANNA Instruments HI 84431, Australia), where titrations were conducted using the low range reagent HI 84431-50 (10 to 500 mg/L as $CaCO_3$). Both nitrogen and phosphorus were analysed by a photometric method, the Spectroquant® Cell Test (NOVA 60 Merck, Germany). Total nitrogen (TN) was derived by measuring the ammonium nitrogen (NH_4–N), nitrite (NO_2–N) and nitrate (NO_3–N) individually and adding the components together. Turbidity was measured by a portable turbidimeter (HACH 2100Q, USA).

The surface morphology of the zeolites was observed by Scanning Electron Microscope (SEM, Zeiss EVO® LS 15, Germany). The elemental compositions of zeolite specimens were determined by Energy Dispersive X-ray Spectroscopy (EDS, Bruker XFlash® Detector 5030, Germany). The images and chemical characterizations of the natural zeolites under raw material, pre-conditioning and adsorption completion conditions were compared to see the changes. Total hardness was measured by hardness meter (HANNA Instruments HI 93735 Hardness Ion Specific Meter, Australia). The required reagents for measurement include: hardness indicator reagent LR (HI 93735A-0), hardness buffer reagent (HI 93735B-0) and fixing reagent (HI 93735C-0). All experiments followed the measurement procedures described in the analyser user manuals.

3. Results and discussion

3.1. Recycled water quality

As can be seen from Table 2, according to the Western Treatment Plant recycled water quality monthly reports, all heavy metal concentrations in CWW recycled water are lower than guideline values that are set for Australian drinking water (ADWG (Australian Drinking Water Guidelines), 2011 and SRW (Southern Rural Water), 2013). As these chemical parameters are at acceptable levels both from health and aesthetic perspectives, heavy metal removal is not the main target of the pre-treatment unit.

Table 2. Performance measure for chemical characteristics.

Chemical characteristics	CWW recycled water (mg/L)	ADWG guideline values (mg/L)	
		Health	Aesthetic
Aluminium	0.015	0.1	0.2
Antimony	0.001	0.003	–
Arsenic	0.0015	0.01	–
Barium	0.005	2	–
Beryllium	< 0.001	0.06	–
Boron	0.17	4	–
Cadmium	< 0.0002	0.002	–
Chromium	< 0.001	0.05	–
Copper	0.006	2	–
Iron	0.045	–	0.3
Lead	< 0.001	0.01	
Lithium	< 0.02	–	–
Manganese	0.024	0.5	0.1
Mercury	< 0.0001	0.001	–
Molybdenum	0.0025	0.05	–
Nickel	0.0075	0.02	–
Selenium	< 0.001	0.01	–
Silver	< 0.001	0.1	–
Zinc	0.025	–	3

Abbreviation: ADWG = Australian Drinking Water Guideline.

Besides, according to Table 3, the concentrations of physical, microbial, nutrient and aesthetic indicators in CWW recycled water samples all satisfy the corresponding guideline values (ANZECC-ARMCANZ (Australian and New Zealand Environment and Conservation Council and Agriculture and Resource Management Council of Australia and New Zealand), 2000, EPA Victoria, 2003 and ADWG (Australian Drinking Water Guidelines), 2011). Thus, treatment measures for the further improvement of the physical and microbial performances of recycled water will not be discussed in detail in this paper. As the hardness level in CWW recycled water approaches the guideline level, the viability and effectiveness of employing a zeolite column for recycled water purification prior to use in the washing machine have been investigated in detail in the following sections. After reaching the adsorption equilibrium in the reaction phase, the zeolite column has been regenerated twice to restore the zeolite ion exchange capacity.

Table 3. Performance measure for water quality indicators.

Indicators	CWW recycled water	EPA Victoria guideline for recycled water	ANZECC-ARMCANZ STV limit[a]	ADWG guideline for drinking water
pH	7–7.5	6–9	–	–
Alkalinity (mg/L as CaCO$_3$)	115–125	–	–	–
BOD/SS (mg/L)	< 2/2[b]	< 10/5	–	–
Chlorine residual (mg/L)	≥ 1 after 30 min[b]	≥ 1 after 30 min	–	≥ 0.2 throughout the distribution system
E. coli (per 100 mL)	0[b]	< 10	–	–
Total nitrogen (mg/L)	13–25	–	25–125	–
Total phosphorous (mg/L)	8.5–10	–	0.8–12	–
Turbidity (NTU)	< 2	< 2	–	–
Colour (PCU)	8–12[b]	–	–	15
Hardness (mg/L as CaCO$_3$)	175–200	–	–	< 200

[a]   STV is the short-term trigger value of agricultural irrigation water that has minimized risk to the environment up to 20 years.

[b]   Note: Adapted from SRW (Southern Rural Water) (2013).

3.2. Characterization of zeolite samples

The SEM images demonstrated the changes in surface morphology of the natural zeolites after pre-conditioning and ion exchange reaction. As illustrated in Fig. 3, with a pre-conditioning stage, the surface of the modified zeolite (Fig. 3b) became rougher, more irregular and highly porous compared with the surface of the original zeolite (Fig. 3a). After the ion exchange reaction, as calcium and magnesium ions were preferentially adsorbed, displacing the existing sodium ions, the surface structure of zeolite in the saturated column had further changed and appeared to include larger crystals (Fig. 4) than the fresh zeolites.
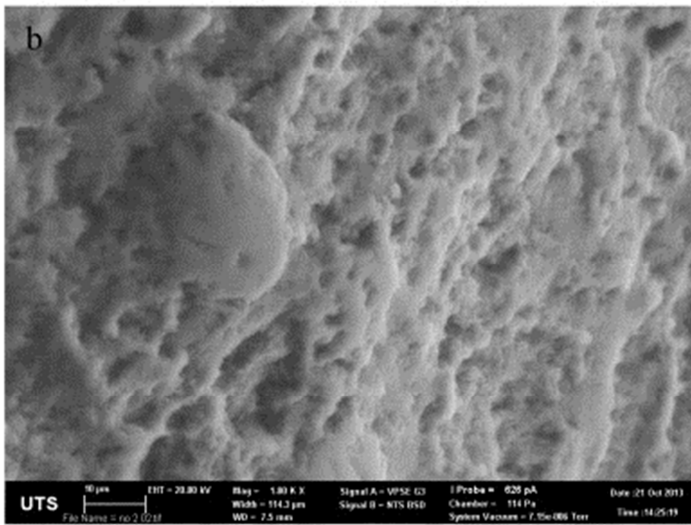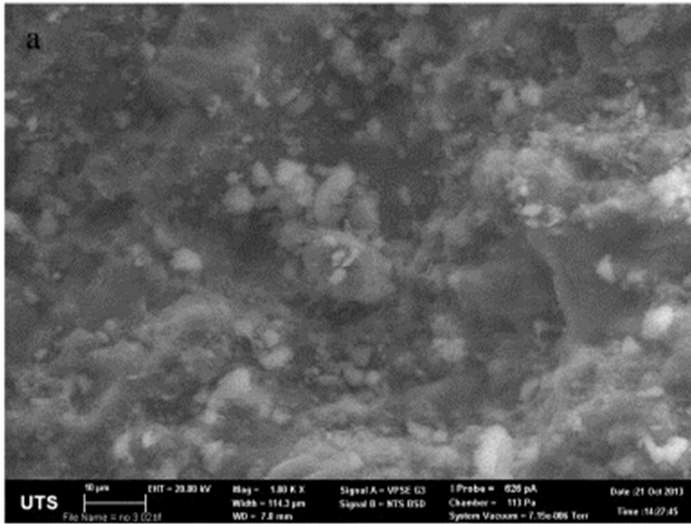
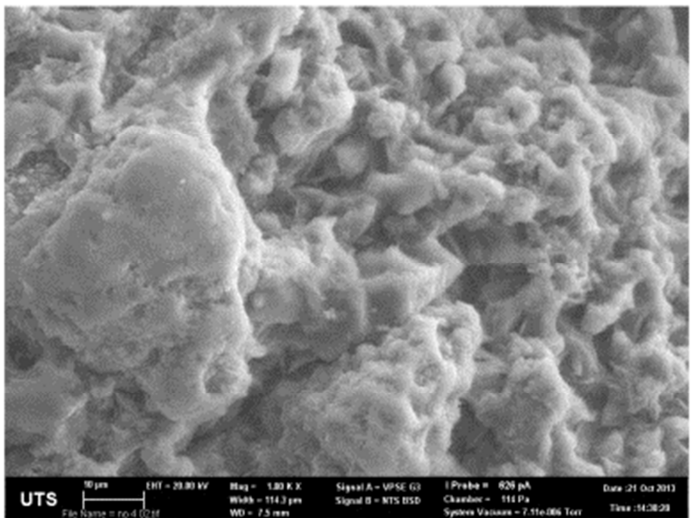Fig. 3. SEM images of the raw natural zeolite (a) and after pre-conditioning (b).

Fig. 4. SEM image of the zeolite after the column reached saturation.

The EDS analyses further verified the ion exchange mechanism of hardness ion adsorption by comparing the chemical composition changes of samples in different processes (Table 4). After pre-conditioning, sodium content on the zeolite surface increased by 243% whereas calcium and magnesium contents decreased by 78% and 65% respectively. These results indicate that the pre-conditioning using sodium chloride is an effective approach to attain a higher sodium form as well as increase the specific surface and porosity of zeolites, which is beneficial for the subsequent ion exchange reaction (Lin et al., 2013).

Table 4. Chemical element compositions of the natural zeolites under raw material, pre-conditioning and adsorption completion conditions by EDS.

Chemical elements (weight %)	Natural zeolite	Zeolite after pre-conditioning	Zeolite after adsorption
Oxygen (O)	47.64	47.93	51.09
Silicon (Si)	31.20	33.42	36.99
Aluminium (Al)	8.82	8.84	5.63
Sodium (Na)	1.06	3.64	1.05
Magnesium (Mg)	0.60	0.21	0.45
Calcium (Ca)	1.57	0.34	2.26
Potassium (K)	0.36	0.28	0.31
Carbon (C)	6.85	3.29	2.09
Iron (Fe)	1.77	1.49	–
Others	0.13	0.56	0.13

Note: To minimize the accidental error, each group of zeolite samples from three different conditions were analysed at least three times by EDS.

Furthermore, when the column reaction reached the adsorption equilibrium, sodium content on the surface of saturated zeolites was detected to be low, while calcium and magnesium contents increased by 565% and 114% respectively compared with that of the pre-conditioned zeolites. With the depletion of exchangeable sodium ions, hardness ions would be unlikely to be attached to the insoluble solids and regeneration of the zeolite resin is required.

3.3. Optimal contact time and maximum operation capacity

3.3.1. Optimal contact time

The operation under the optimum contact time (or service flow rate) will minimize the impact of the film mass transfer resistance and consequently shorten the length of the mass transfer zone (Crittenden et al., 2005). To determine the optimal condition, three breakthrough curves, which represent the evolution of the hardness ion concentrations in the function of adsorption contact time, have been obtained by passing the process stream through a full fresh zeolite column. In these curves, the loading behaviours of total hardness to be adsorbed from solution in the column were expressed in terms of normalized concentrations which are defined as the ratio of effluent ion concentration to its inlet concentration (C/C_0) as a function of time for a given bed height (Sivasankar and Ramachandramoorthy, 2011). During each run, samples of the effluent are collected and analysed until the effluent total hardness concentration reaches 200 mg/L as $CaCO_3$, which is equal to the influent concentration. At this point, no more sodium-form zeolite existed to take up hardness ions so that calcium and magnesium ions made breakthrough into the effluent.

For operational simplicity and ease of observation, the experiments were conducted under scenario 2. The contact time of less than 3 min was not evaluated as the high service rate might reduce the mobility of zeolite material inside the column, generating operational problems. As can be seen from Fig. 5, service time of the zeolite column for a given removal increased as contact time was increased. Breakthrough times ($C/C_0 = 0.1$) were found to be 15, 30 and 390 min for the contact time of 3, 4 and 5 min with the flow rate of 31.2, 23.5 and 18.6 L/h, respectively.
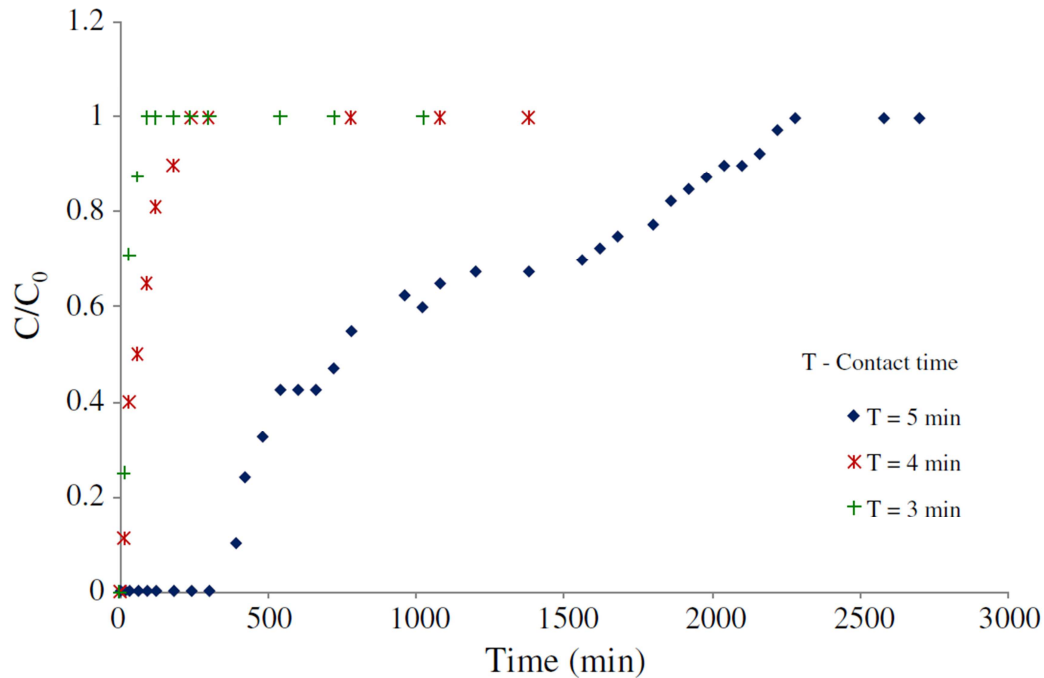
Fig. 5. Breakthrough curves for recycled water softening process with different contact times.

At the contact time of 3 and 4 min, the breakthrough was premature and almost immediate so that the column exhibited lower exchange capacity, whereas under a contact time of 5 min, the column reached the saturation after 38 h of service time. This is due to the fact that at a low flow rate of influent, the hardness ions had more time to be in contact with the adsorbent, which resulted in a greater removal of total hardness in the column. Comparatively, at higher flow rates, the adsorption capacity was low as the solute left the column before equilibrium occurred because of the insufficient residence and diffusion time of the solute in the pores of zeolites (Han et al., 2009 and Nidheesh et al., 2012).

These results are consistent with another research study conducted by Cinar and Beler-Baykal (2005) which showed that contact times over 5 min in the zeolite column could achieve considerable amounts of calcium ion removal. Despite that better performances may be expected for higher contact times and low flow rates in the range of 5–10 bed volumes per hour (BV/h), it would be very unlikely for household members to afford a long period of time for each laundry activity (Inglezakis, 2005). Considering the time efficiency and practical issues, a contact time of 5 min has been regarded as the optimal contact time. Under this contact time, the influent pump was operated at a continuous pumping rate of 18.6 L/h. Hence, the calculated service flow rate was 12.4 BV/h.

3.3.2. Maximum operation capacity (MOC)

The MOC of the zeolite column (mg/g), which is the weight of hardness ions adsorbed per gramme of zeolite, can be calculated from Eq. (3).

$$MOC = \frac{(V_{eff,T} - \int_{V_{eff,O}}^{V_{eff,T}} X(V_{eff})dV_{eff})C_0}{\rho_z V_c}$$

(3)

where, $V_{eff,O}$ is the effluent volume until the first appearance of the solute in the exit stream, $V_{eff,T}$ is the effluent volume until the exit solute concentration is equal to the inlet feed concentration, $X(V_{eff})$ is the function of the changing effluent volume versus time, C_0 is the influent concentration, ρ_z is the bulk density of zeolites, and V_c is the effective volume of the zeolite column (Inglezakis, 2005). At a contact time of 5 min, the solute first appeared at the reaction time of 370 min and reached the equilibrium at the time of 2280 min. Based on other known information, the MOC of the zeolite column under study is calculated to be 35 mg/g (or 1.87 meq/g).

As shown in Table 5, the practical MOC of zeolites from this experimental study is lower than the theoretical exchange capacities of the natural zeolites. This is due to the fact that the achieved capacity was influenced by the real operational conditions including the contact time, flow rate and quality, and temperature. Some of the zeolite cations cannot be removed from the zeolite structure in specific experimental states because of low mobility and strong bonding forces within the crystal structure of the material (Inglezakis, 2005).

Table 5. Ideal exchange capacity of some natural zeolites.

Zeolite type	Cation exchange capacity (meq/g[a])
Chabazite	3.84
Clinoptilolite[b]	2.16
Erionite	3.12
Ferrierite	2.33
Heulandite	2.91
Laumontite	4.25
Mordenite	2.29
Phillipsite	3.31
Faujasite	3.39

This study	1.87

Note: Adapted from Inglezakis (2005).

[a]   meq/g is the milliequivalents of negative charges available per gramme of zeolite.

[b]   Ideal exchange capacity was estimated from the chemical formula of pure species.

Noticeably, the intermittent operation mode of the column, under which the system was implemented continuously for 2 h followed by a few hours of non-production time, was found to increase the MOC. This is because high speed flows in continuous running mode may suffer from non-ideal states such as channelling, axial dispersion, bed compaction, density currents, leakage, and/or insufficient wetting of the zeolite material (Clifford, 1999). When being operated intermittently, zeolite particles gained opportunities to partially eliminate packing and channelling during the non-production time, thereby facilitating the uniform distribution of the feed solution over the zeolite resin surface for the next running cycle. Nevertheless, since the main compositions of the studied zeolites are clinoptilolite-rich minerals, this practical MOC value was demonstrated to be close to the ideal cation exchange capacity of natural clinoptilolite zeolite.

3.4. Cost-effectiveness and operational feasibility of zeolite column in a household laundry

3.4.1. Laundry use frequency and water consumption in a typical household

In the Werribee area of Melbourne, a recent social survey indicated that about 34.8% of local households employed front loading washing machines, compared with 65.2% of top loading machines (Chen et al., 2013). These two types of washing machines have a number of different characteristics including loading type and capacity, water and energy consumption per wash, brand and model name (ABS, Australian Bureau of Statistics, 2011). Front loaders are considered to use less water and energy and require only half the detergent that top-loading machines (1–3 star rating) consume (Gato-Trinidad et al., 2011 and Chen et al., 2012). However, water consumption varies significantly due to large differences of family makeup patterns and wash settings (e.g., size of the load, the number of cycles and clothing texture) in different households. On average, over 37% of households conducted 1–2 loads or less of washing per week, compared with 29% of households with 3–4 loads of washing per

week. A small proportion of people washed 5 or more loads a week (Chen et al., 2013). However, the frequency of use would also change depending on the weather, water restrictions and household income conditions.

In this research, for calculation simplicity, the average volume of water used per wash for a typical washing machine is assumed to be 80 litres (L) and the washing machine use frequency is considered to be 1 time per week. Remarkably, the zeolite ion exchange column can usually produce a hardness-free effluent at the initial treatment stage (e.g., first 360 min of reaction time under a contact time of 5 min in Fig. 5) that is much more pure than that required by the guidelines, namely 80–100 mg/L as $CaCO_3$ as the acceptable level. Therefore, to minimize treatment costs, bypass blending can be implemented, which is a common procedure in water treatment applications.

3.4.2. Mass balance of the pre-treatment system

As shown in Fig. 6, to produce a final effluent with total hardness level approaching the guideline value for satisfactory water quality (i.e., 100 mg/L as $CaCO_3$), part of the feed water can be bypassed around the process (through valve C) and blended with the treatment effluent under scenario 3.
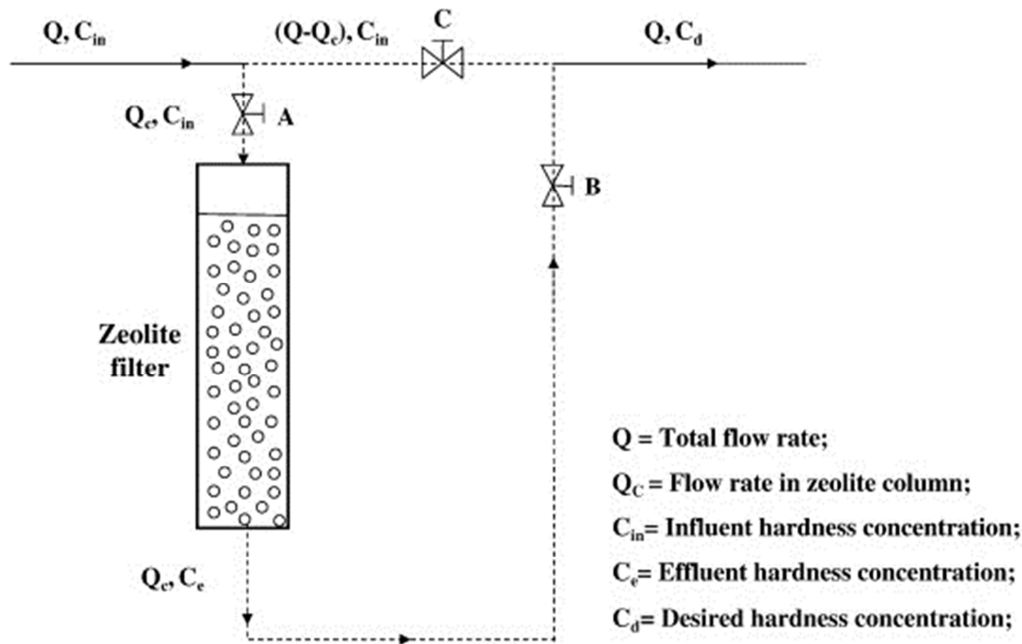

Fig. 6. Schematic diagram of water flows in the zeolite pre-treatment system.

To calculate the percentage of bypass volume, the mass balance equation (Eq. (4)) can be employed (Clifford, 1999).

$$Q_c \cdot C_e + (Q - Q_c) \cdot C_{in} = Q \cdot C_d \tag{4}$$

where some assumptions were made; there is no water accumulation and no reactions at the pipe joint, the influent hardness concentration (C_{in}) is 200 mg/L as $CaCO_3$, and the desired hardness concentration in blended product water (C_d) is 100 mg/L as $CaCO_3$. During the first 360 min of the reaction time, the effluent hardness concentration from column (C_e) was zero. The bypass fraction can be easily obtained from Eq. (5).

$$f_B = \frac{Q - Q_c}{Q} = \frac{C_d}{C_{in}} \tag{5}$$

The fraction that must be treated by the zeolite column is:

$$f_F = 1 - f_B = 0.5 \tag{6}$$

In this situation, the designed volume of recycled water per load of washing that should be passed through zeolite column is calculated to be 40 L. To attain an overall hardness level of less than 100 mg/L as $CaCO_3$ prior to use in the washing machine, it would take approximately 2 h in households to purify the recycled water in the zeolite column. The column can maintain a high service capacity up to 3 loads of washing for a typical washing machine.

3.4.3. Calculation of zeolite column service life

However, after the breakthrough point which is defined as the critical time when the exit hardness concentration equals approximately 10% of the inlet concentration (i.e., the reaction time of 390 min), the effluent concentration increased very rapidly with the increment of time (Inglezakis, 2005). This indicated that to maintain the same quality of blended product water, the bypass fraction should be reduced and an additional amount of feed water was required to be delivered through the zeolite column. When C_e reached 90 mg/L as $CaCO_3$, around 90% of raw recycled water (72 L) should be treated through the column for one laundry activity. As depicted in Fig. 5, by the reaction time of 660 min, the blended product water can still meet the desired hardness level. Nevertheless, for the 4th load of washing, due to a surge in water purification demand, the laundry activity can last for 4 h. Although the column could

continue to absorb the hardness ions in the feed water, the treated effluent could then no longer satisfy the guideline value. Consequently, given that the overall use frequency of the washing machine is once a week, the zeolite column service life without regeneration was shown to be one month.

3.4.4. Breakthrough capacity (BC)

The BC of the zeolite column (mg/g), which is the loading of the zeolite column when the hardness concentration in the effluent reaches the breakthrough point, can be evaluated using Eq. (7).

$$BC = \frac{(V_{eff,B} - \int_{V_{eff,O}}^{V_{eff,B}} X(V_{eff})dV_{eff})C_0}{\rho_z V_c} \tag{7}$$

where, $V_{eff,O}$ is the effluent volume until the first appearance of the solute in the exit stream, and $V_{eff,B}$ is the effluent volume until the breakthrough point (Inglezakis, 2005). Accordingly, the BC is estimated as 14 mg/g. Compared with MOC, the BC only considers the reaction time from the beginning of the experiment to the breakthrough point. This might be of greater importance for the design of column operations and determination of selectivity series, as after the breakthrough point, the treatment unit often becomes far less effective and time-consuming and therefore makes insignificant contributions in practice.

3.5. Zeolite column regeneration

The regeneration process can restore the capacity of the zeolite column and can make it ready for reuse in the next running period. The driving force for this reaction is the large excess of sodium ions in the regenerant solution so as to flush the retained calcium and magnesium ions to the waste stream. Thus, the waste brine after exiting contained a mixture of calcium chloride, magnesium chloride along with excess sodium chloride. When regeneration proceeded toward completion, the calcium and magnesium ion concentrations became lower (Wist et al., 2009). Fig. 7 gives three breakthrough curves corresponding to the column performances after zero, first and second regeneration cycles. As can be seen, after each run, the breakthrough curve possessed similar shape and features as previous ones and no large difference was observed. Only a slight deterioration of hardness removal was noted during

the second regeneration cycle. This may be because some ionic sites associated with slow diffusion within the zeolite structure were saturated with hardness ions in previous service cycles. The hardness ions might have difficult access to exchange with sodium ions, especially when regeneration occurred over a short time frame (Sivasankar and Ramachandramoorthy, 2011). Notwithstanding, the zeolite material can be reused several times before it must be replaced due to irreversible fouling.

Although the regeneration process fully demonstrated the cost effectiveness and durability of the zeolite material, there are also some challenges regarding the storage and treatment of spent regenerant. While reuse of spent regenerant is a good means of reducing costs and minimizing waste disposal, the concentration of trace contaminants is likely to be built up as the number of regenerant reuse cycles increases, triggering difficulties in environmental remediation (Wist et al., 2009).
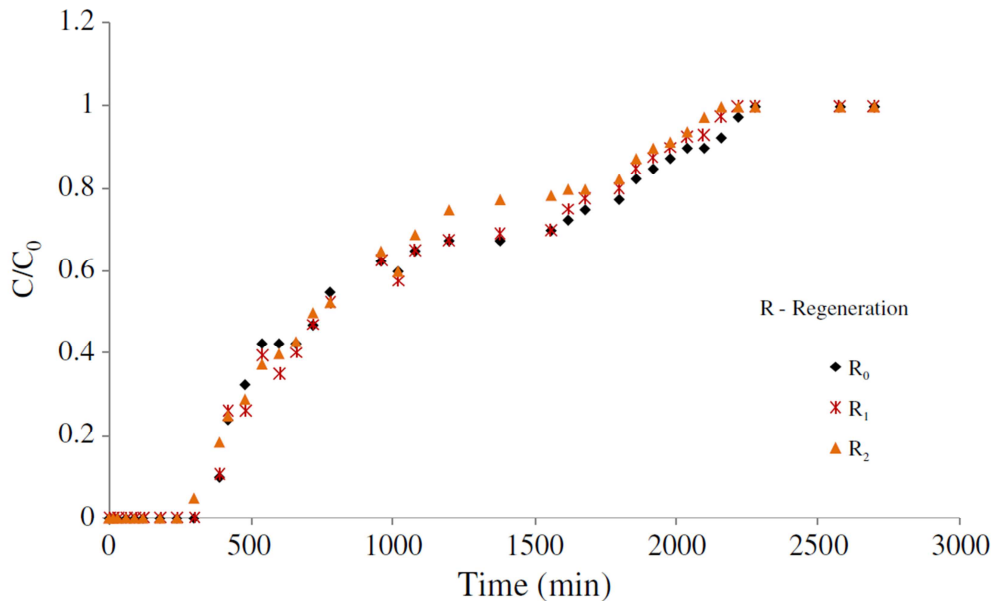

Fig. 7. Breakthrough curves for recycled water softening process under the contact time of 5 min with successive regenerations.

3.6. Pilot-scale column design and considerations

The experimental data derived from this small column study form the basis for the field trial operations and onsite scale-up pilot studies. To extend the current service life of 1 month to a longer period, the column height and/or diameter can be scaled up directly. Based on the existing column breakthrough data, when the pilot study is conducted under the same operating flow rate (i.e., 18.6 L/h), the increase of column volume would not change the

shape of the breakthrough curve nor enhance the breakthrough capacity (Crittenden et al., 2005). Alternatively, the adsorption columns can be connected in series to improve the service life and regenerant usage. It is worth noting that the MOC and BC obtained in pilot studies might be slightly higher than the values from experimental analyses owing to the intermittent operation mode coupled with prolonged non-production time in real-life situations of clothes washing. Overall, the optimal design option and specific parameters as well as the potential practical problems encountered in the pilot-scale studies could lead to precautionary procedures in the further development of full-scale designs and following application, maintenance and replacement in local households. The zeolite column is believed to contribute to the improved recycled water quality, enhanced public acceptability and increased use of recycled water in household laundries significantly.

4. Conclusions

This paper demonstrates the feasibility, operability and cost-effectiveness of applying the natural zeolite material as an effective ion-exchange resin for recycled water softening prior to use in washing machines. The column experiment results revealed that the pre-conditioning of natural zeolites contributed to improved surface morphology and increased sodium contents on particles, resulting in higher ion exchange capacity. Under the contact time of 5 min, the process was shown to be a promising water purification pre-treatment unit with a considerable hardness ion removal. Moreover, both maximum operational capacity and breakthrough capacity data were generated to present a quantitative assessment of the proposal, which were found to be 35 and 14 mg hardness ions/g of zeolites respectively. The zeolite column service life for a typical washing machine was shown to be one month without material regeneration. The regeneration process further guaranteed the simplicity of maintenance and durability of operation for actual application at household levels. After accomplishing a series of scale-up pilot studies, the pre-treatment unit can be put into practice, which is likely to play a significant and positive role in changing the public perception on the safe use of recycled water.

Conflict of interest

On behalf of all the co-authors, I declare that: (1) we have no financial and personal relationships with other people or organizations that can inappropriately influence our work;

and (2) there is no professional or other personal interest of any nature or kind in any product, service and/or company that could be construed as influencing the position presented in the manuscript entitled "A new optional recycled water pre-treatment system prior to use in the household laundry".

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