INVESTIGATION ON WATER SOFTENING USING SURFACTANT MODIFIED BENTONITE ADSORBENT COATING

by

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LIST OF SYMBOLS

b_T	Temkin isotherm constant
C_o	The initial concentration (mg/L)
C_e	The final concentration (mg/L)
G	Gram
k_L	Langmuir constant relate to energy of adsorption
K_f	Freundlich constant
k_T	Temkin isotherm equilibrium binding constant
k_1	Pseudo first order rate constant
k_2	Pseudo second order rate constant
ml	Milliliter
mV	Millivolts
n	Degree of non-linearity between solution concentration and adsorption
rpm	Rotational per minute
R^2	Correlation coefficient
SMB	Surfactant modified bentonite
q_e	The adsorption capacity at equilibrium
q_m	The maximum adsorption capacity
q_t	The adsorption capacity at any contact time
V	The volume of the solution
W	The mass of the adsorbent
ΔG^0	Gibbs free energy change
ΔH^0	Enthalpy change
ΔS^0	Entropy Change

%	Percentage
^{o}C	Temperature

LIST OF ABBREVIATIONS

AHT	Adsorptive heat transformer
AB	N-Decyl-N-benzyl-N-methylglycine
Al_2O_3	Aluminium dioxide
CD	N-Dodecyl-N-benzyl-N-methylglycine
CTAB	Cetyl trimethylammonium bromide
CPB	Cetyl pyridinium bromide
CPC	Cetylpyridinium chloride
CS	Chitosan
DBT	Dibenzothiophene
DBS	Dodecylbenzene sulfonate
DS	Dodecylsulphate
Fe_2O_3	Iron (III) oxide
HDTMA	Hexadecyltrimethyl ammonium bromide
H_2SO_4	Sulphuric acid
KCl	Potassium chloride
KOH	Potassium Hydroxide
MDC	Microbial desalination cells
MFC	Microbial fuel cell
MO	*Moringa oleifera*
MgO	Magnesium oxide
NF	Nanofiltration
NaCl	Sodium chloride
NaOH	Sodium hydroxide

OS	1-octanesulfonates
PEI	Polyethyleneimine
PES	Polyethersulfone
PVAc	Polyvinyl acetate
PVAl	Polyvinyl alcohol
SiO_2	Silicon dioxide
SDBS	Sodium dodecylbenzene sulfonate
SPAN	Suruhanjaya Perkhidmatan Air Negara
TiO_2	Titanium dioxide
TECI	The Essential Chemical Industry
TTAB	Tetradecyltrimethyammonium bromide
WHO	World Health Organiaztion

PENYIASATAN KE ATAS PELEMBUTAN AIR KERAS DENGAN MENGGUNAKAN LAPISAN PENJERAP SURFAKTAN DIUBAHSUAI DENGAN BENTONIT

ABSTRAK

Lapisan penjerap bentonit (SMB) yang telah diubahsuai dengan meggunakan surfaktan sodium dodecylbenzene sulfonate (SDBS) telah dihasilkan bagi penyingkiran ion Ca^{2+} dan Mg^{2+} daripada air keras. Penjerap telah dianalisis dengan menggunakan SEM, EDX, Zeta-meter dan FTIR analisis. Lapisan penjerap mempunyai potensi untuk menggantikan teknik rawatan pelembutkan konvensional yang mahal serta dapat mengurangkan penggunaan bahan kimia yang berlebihan (pemendakan kimia) dengan mengaplikasikannya ke kawasan rawatan. Rumusan bagi lapisan penjerap SMB telah dijalankan dengan merangkumi kesan penilaian nisbah surfaktan, kesan pengikat yang berlainan jenis, dan kesan nisbah penjerap ke atas pengikat, dan formulasi terbaik telah diperolehi dengan menggunakan pengikat polyvinyl acetate (PVAc) dengan nisbah penjerap kepada pengikat 0.75:1.0 (w/w). Keadaan optimum pelembutkan air keras telah diperolehi dengan penyingkiran tertinggi iaitu 66.6% (29.27mg/g) dengan menggunakan 120 mg/L air keras, kelajuan 300 rpm, pH 6.8, dan pada suhu 30°C. Lapisan penjerap SMB boleh digunakan semula untuk dua kali sahaja. Kajian berasingan bagi kalsium dan magnesium telah dijalankan dan magnesium lebih mudah disingkirkan daripada kalsium kerana adanya tapak aktif antara magnesium dan kumpulan berfungsi anionik pada permukaan SMB. Kajian menunjukkan penjerapan telah mengikut model isoterma Langmuir dan mengikut pseudo-tertib kedua. Parameter

termodinamik ($\Delta H°$,$\Delta S°$, dan $\Delta G°$) yang dinalalisis telah menyifatkan keadaan penjerapan adalah eksotermik dan tindak balas adalah spontan. Dalam kajian penyahjerapan, 0.1M H_2SO_4 menunjukkan penyahjerapan tertinggi dan kitaran penyahjerapan dicapai sehingga kitaran ketiga. Berdasarkan kapasiti penyingkiran yang baik terhadap ion Ca^{2+} dan Mg^{2+}, lapisan penjerap SMB boleh digunakan dengan berkesan untuk melembutkan air keras.

INVESTIGATION ON WATER SOFTENING USING SURFACTANT MODIFIED BENTONITE ADSORBENT COATING

ABSTRACT

Adsorbent coating of bentonite modified (SMB) sodium dodecylbenzene sulfonate surfactant (SDBS) has been developed for the removal of Ca^{2+} and Mg^{2+} ions from hard water. The adsorbent was characterized using SEM, EDX, Zeta-meter and FTIR analyses. It has potential to replace the expensive conventional softening treatment techniques as well as reduce the usage of excess chemicals (chemical precipitation) by applying onto treatment area. Formulation of SMB was carried out including evaluation effect of surfactant ratio, effect of different type of binder and effect of adsorbent to binder ratio with best formulation by using PVAc binder, with adsorbent to binder ratio 0.75:1.0 ratio (w/w). The optimum condition of softening hard water was obtained with highest removal efficiency 66.6% (29.27mg/g) using 120 mg/L hard water, 300 rpm mixing speed, pH 6.8, and 30°C. SMB adsorbent coating can be reused for two times only. The separate calcium and magnesium solution were conducted and magnesium is preferable than calcium due to the availability active sites between magnesium and anionic functional group of SMB surface. The adsorption in this study was fitted with Langmuir isotherm and pseudo-second order model. Thermodynamic parameters ($\Delta H°$, $\Delta S°$, and $\Delta G°$) revealed exothermic nature and reaction is spontaneous. In desorption study, 0.1M H_2SO_4 provide the highest desorption and adsorption/desorption cycle achieved up to third cycle. On the basis of good removal capacity towards Ca^{2+} and Mg^{2+} ions, SMB adsorbent coating can be effectively used for softening of hard water.

CHAPTER ONE

INTRODUCTION

1.1 Clean and Hard Water

Water is one of the important sources which contributes improvements in social well-being and growth of billions livelihoods. Clean and safe water is needed in daily life especially for drinking, cooking, bathing and cleaning task including laundering, dishwashing and some for watering plant. Clean water source are from ground water, under river flow, desalination of sea water and also surface water such as lake, river and wetland. Water will be treated by removing particulates, bacteria and various other pollutants before distributed to the residents. Natural fresh water contains small amount of dissolves solid such as calcium, magnesium, sodium, potassium, bicarbonates, sulfate, and chloride. It is safe to use directly. Piping system is generally needed to deliver water to the residential areas. However along this process, it is possible for water contamination to occur. Water with high number of undesirable contaminants such as metal salts, fluoride, chlorine, and also hardness will make it unsafe to be used.

Todays, the demand of clean water all over the world keeps increasing from time to time. This is due to the population increment and also contamination of supply. The population in Malaysia increased from 29,683,685 million (2014) of people compared in year 2013 which is 29,243,656 million (Countrymeters, 2016). Meanwhile, the total water consumption for year 2014 is about 211 litre per capita per day compared to 2013 (210 litre per capita per day) and expected to increase by year (SPAN, 2014). On the other hand, other countries such as North Africa and

Middle East have limited water resources due to the increasing population and water pollution problem (Emi *et al*. 2016.,; Heinrich Boll Foundation, 2012). This is the reason why the demand of fresh water is kept increasing. Thus, clean water is required all over the world for their daily consumption.

Water problem not only being created by industries, but also naturally such as hard water problem. The existence of hard water cations especially Ca^{2+} and Mg^{2+} in water supply have created problems. Hard water issue in countries such as Malaysia (Issa *et al*., 1998; Fahmi *et al*., 2011), United Stated (SALT Institute, 2013), England (Bristan, 2016), Ireland (Aquasafe, 2008), Netherland (Target Map, 2011) and many more create major problem to the residents as well as the relevant responsible bodies. This problem cause residents failed to obtain clean water for their daily used.

Water hardness is the measurement of the water capacity to react or bind with soap to form foam (WHO, 2011). The hardness of water is caused by variety of dissolves substances such as calcium, magnesium, aluminium, barium, iron, manganese, strontium and also zinc ions. Although other ions also contributes to the formation of hard water, but the dominant contributor are calcium and magnesium ion. Water that considered ‘hard’ refers to the high content of mineralized ion which is calcium and magnesium. These ions together with carbonate ion present in many sedimentary rocks especially limestone and chalk. When water passes through these areas, ions will be dissolves and form hard water. The degrees of hard water depend on the amount of dissolved calcium and magnesium ions. High concentrations of these ions increase the degree of water hardness.

1.2 Hard Water in Community

Hard water problem has become one of the main water issue in overseas countries such as United States, England, Canada, Ireland and Netherland. Some of the area in Malaysia especially Perlis also facing hard water problem. The allowable hard water for tap water supposed to have below 30mg/L. Table 1.1 shows the ranges of hard water concentration in few oversea countries and Malaysia.

Table 1.1: Hard water range in Malaysia and in oversea countries.

Country	City	Hard Water Concentration	Reference
United States	Most of the cities	>121 mg/L	(SALT Institute, 2013.; USGS Water-Quality Information, 2016)
England	Bristol, Lincoln, London, Brighton	>121 mg/L	(Bristan, 2016)
Ireland	Most of the cities except Donegai, Belfast, and Killarney.	>122 mg/L	(Aquasafe, 2008)
Netherland	Most of the Cities	>121 mg/L	(Target Map, 2011)
Malaysia	Titi Tinggi (Perlis)	530mg/L	(Issa *et al*., 1998)
Malaysia	Timah Tasoh Dam (Perlis)	314-362mg/L	(Fahmi *et al*., 2011)

United States have the most critical hard water problem. As shown in Figure 1.1, most of the cities in U.S have hard water more than 121 mg/L. Cities with red coloured on the map have very hard water which is more than 181 mg/L and cities with white coloured have 121 mg/L until 180mg/L hard water. The cities that have the hardest water are Indianapolis, Las Vegas, Minneapolis-St. Paul, Phoenix, San Antonio and Tampa (Homewater101, 2016).

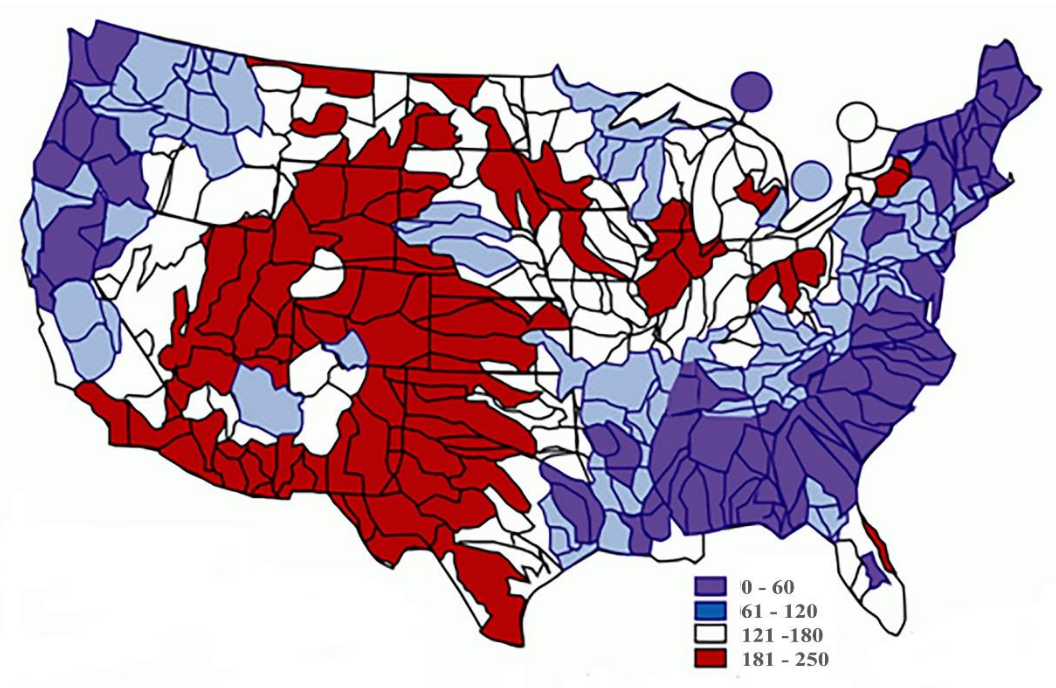

Figure 1.1: Hard water area in United States

Not only United States, England and Wales also faced the same water issue. Figure 1.2 shows the hard water in England and Wales. There are few cities that have more than 200 mg/L hard water such as in London, Southampton, Lincoln, Brighton and Bristol. Manchester, Birmingham and New Castle have moderately hard water which between 100 mg/L until 200 mg/L. Meanwhile water in Leeds considered soft.