

New Approach of Heavy Metal (Chromium, Iron, Copper and Nickel) Removal Using Surfactant Modified Zeolite for Tin Mining Wastewater

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Abstract: The adsorption capacities of cationic and oxyanionic metal ions, such as chromium, nickel, copper and iron of mining wastewater collected from Pengkalan Hulu, Perak, using surfactant modified zeolite (SMZ) prepared using the amphoteric surfactant of Miranol C2MSF and cationic surfactant of Uniquat QAC-50, were investigated. The adsorption capacities of chromium, copper, nickel and iron by SMZs, as a function of the zeolite concentration, were determined at room temperature by varying the SMZ concentration from 10 mg/L to 120 mg/L for each wastewater sample, of each set of experiments. During the process, all the other parameters were kept constant with respect to the initial concentration of heavy metals in the wastewater sample, pH of the wastewater sample and contact time. In the experiment performed, the results revealed that all heavy metal elements, through the adsorption process, whether with amphoteric or cationic SMZ, can be removed from the initial concentration by up to 85% or more. Both SMZs have the ability to remove at that range, although cationic SMZ has a higher removal capacity for heavy metals at a lower optimum adsorbent dose compared to amphoteric SMZ.

Key words: Amphoteric SMZ • Cationic SMZ • Zeolite • Adsorption • Heavy metal

INTRODUCTION

Rapid industrialization has led to an increase in the dispersal of heavy metals into the environment. Due to their toxicity, persistency and bioaccumulation tendency in nature, water contamination caused by the dumping of metals is a serious environmental problem [1]. According to Amuda *et al.* [2] at least 20 metals are classified as toxic and half of these are discharged in quantities that place human health at risk. Heavy metals are elements that exhibit metallic properties and these include transition metals, some metalloids, lanthanides and actinides.

Wastewater from mining operations, electroplating plants, power-generating plants, electronic appliance factories and tanneries, contain several toxic heavy metals [3]. Certain heavy metals are known to be very toxic and prolonged exposure to these metals can be hazardous for human beings and other biological systems, as it can be absorbed by marine animals and enter directly into food chains [4]. The constant discharging of wastewater by

industrial sectors has led to the presence of increasing amounts of toxic metals in the environment. The release of contaminated water is a major contributing factor to the high levels of cadmium, chromium, copper, lead and mercury [5] in the environment.

In Malaysia, as well as in most Asian countries, mining has been a major contributor to the economy and tin mining has been singled out as the most environmentally unfriendly process as it discharges wastewater with a high content of heavy metals.

Typically, non-ferrous metal mining activities include removal, transportation and selective smelting, with each process producing castoff in the form of solid, liquid and gas. In the initial stage of the mining process, when ore is crushed, some heavy metals are discharged onto the ground and heavy metals carried by the wind eventually settle on the soil and water through air diffusion. Some heavy metals contaminate ground and surface water by sap drainage, while dust released during transportation on and under the ground, settle on soil and water.

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The mining sites usually contain deleterious heavy metals such as copper, zinc, mercury, manganese, lead and cadmium, which can cause complex pollution problems. Recent research has identified five main contributors to heavy metal pollution from mining activities, which are river accepted mine drainage, well settling dust in winds, tailings, transportation of ore by rail and transportation of minerals by vehicles.

The usual methods used for removing heavy metals from wastewater include chemical precipitation, flotation, adsorption, ion exchange and electrochemical deposition [6]. Lately, adsorption has become a popular alternative treatment technique for wastewater loaded with heavy metals. Basically, adsorption is a mass transfer process, by which a substance is transferred from the liquid phase to the surface of a solid and becomes bound by physical or chemical interactions, or both [7].

Activated carbon, for example, has undoubtedly been the most popular and widely used adsorbent in wastewater treatment applications throughout the world. However, activated carbon remains an expensive material, with a low level of selectivity and requires complexing agents to improve its removal performance for inorganic matters. Thus, due to the above reasons, the use of activated carbon as an adsorbent is no longer appealing to small scale industries [8]. Among the various treatment processes available, ion exchange is considered to be cost-effective if low-cost ion exchangers such as zeolites are used [9]. The ion exchange capacity is a key factor in identifying adsorptive behaviours [10].

Zeolites are naturally occurring hydrated aluminosilicate minerals characterized by cage-like structures [11]. Natural zeolites also gained significant interest among scientists, mainly because of valuable properties such as ion exchange ability and high surface areas [12]. It has been studied as a means of removing metal ions and its adsorption capacity for zinc and copper were ranged as 0.04-5.5 mg/g and 0.37-5.1 mg/g, respectively [13]. During the last decade, various novel modifications have been exploited to attribute zeolites with new properties that extend their spectrum of application [14]. Recently, interest in the adsorption of anions and neutral molecules by surface-modified zeolites increased. However, zeolites possess a net negative structural charge resulting from isomorphous substitution of cations in the crystal lattice. This negative charge sometimes results in zeolites having little or no affinity for anions [15]. Zeolites in their original form can adsorb only cations, but some heavy metals such as chromium and arsenic are present in cations, anions and non-ionized

species [16]. Therefore, the external surface charge of natural zeolites can be altered with a surfactant to make it suitable for adsorbing oxyanions of arsenic, chromium and selenium [17].

Most of the previous studies focused on using cationic surfactants to sorb organic matter or metallic anions; e.g. the sorption of phenol and alkylphenols on HDTMAB (hexadecyltrimethylammonium bromide)-modified montmorillonite and anion-cation organobentonite [18]. Moreover, SMZs can be used to target four major categories of contaminants, namely, anions, cations, organics and pathogens [19]. However, two types of SMZs used in this study, namely amphoteric and cationic, were modified from natural zeolite to perform experiments on heavy metals such as chromium, nickel, copper and iron, for their removal efficiency pertaining to mining wastewater.

The aim of this study is to measure the effectiveness and ability of amphoteric SMZ and cationic SMZ in the removal of heavy metal concentrations of chromium, copper, iron and nickel from mining wastewater. The experiments involved the determination of the optimum dosage of amphoteric SMZ and cationic SMZ required for the removal of chromium, copper, iron and nickel from wastewater, while keeping all the other parameters constant.

MATERIAL AND METHODS

The mining wastewater for this study was collected from a pond of the Rahman Hydraulic Tin Mining site located in Pengkalan Hulu, Perak. Forty litres of wastewater samples were collected from the wastewater pond and subsequently preserved in the Environmental Laboratory cold room at a temperature of 4°C to minimize microbiological decomposition of solids. The container of wastewater was thoroughly shaken before samples were taken for experiments.

Surfactant Modified Zeolite (SMZ): The natural zeolite used in this study was obtained from Indonesia and the characteristics of this zeolite are shown in Table 1.

To change the surface properties of natural zeolite in order to increase electrostatic attraction and to improve adsorption capability, the surface of the natural zeolite was modified by covering it with Miranol C2MSF amphoteric surfactant and Uniquat QAC-50 cationic surfactant. The surfactant solutions can be prepared by dissolution of both surfactant liquids in distilled water at the rate of 78 mg/L for Miranol C2MSF and 5.6 mg/L for Uniquat QAC-50 [20].

Table 1: The characteristics of the natural zeolite

Components	Percentage Chemical Composition (%)
SiO ₂	62.75
Al ₂ O ₃	13.63
Fe ₂ O ₃	2.12
CaO	3.42
MgO	0.87
Na ₂ O	1.32
K ₂ O	1.39
MnO	0.05
TiO ₂	0.35
P ₂ O ₅	0.04
H ₂ O	0.38

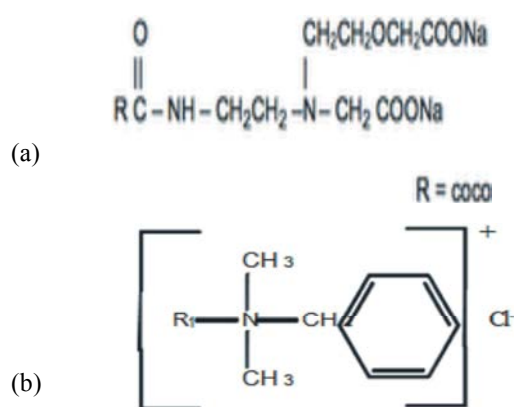


Fig. 1: The chemical structure of (a) Miranol C2MSF amphoteric surfactant and (b) Uniquat QAC-50 cationic surfactant

Prior to use, natural zeolite was grounded and sieved to pass through sieve size 2.00 mm and retained at 1.18 mm. To remove the impurities in natural zeolite, it was dissolved in 0.5N hydrochloric acid solution for 30 minutes and then washed with distilled water. The same process is repeated with the 1N NaOH solution. The zeolite was then placed in an oven for drying at a temperature of 105°C for 15 hours.

After the drying process, 100gms of natural zeolite was added to the Miranol C2MSF solution. The mixture was then stirred at room temperature for 4 hours at 300 rpm [21] before the zeolite was separated from the mixture by filtration and washing with distilled water. The drying process was carried out in an oven at a temperature of 105°C for 15 hours. The same process is repeated for the Uniquat QAC-50 solution. The modified zeolites are designated as Miranol C2MSF – zeolite and Uniquat QAC-50 – zeolite and stored for further use in experiments. The chemical structure of Miranol C2MSF (Cocoamphodiacetate) amphoteric surfactant and Uniquat QAC-50 cationic surfactant are as shown in Fig. 1 (a) and (b).

Laboratory Test: After the modification of natural zeolite to Miranol C2MSF zeolite and Uniquat QAC-50 zeolite, it is ready to be used in laboratory experiments. The initial concentration value of each heavy metal component such as chromium, copper, nickel and iron in the mining wastewater collected earlier, was determined in order to ascertain removal efficiency after the addition of the adsorbent. All the initial concentrations were determined using Hanna Instrument COD and multiparameter bench photometer, model HI 83099 [22]. The precision of the heavy metals was determined by analysing (in duplicate) the metal concentration for all the samples. All methods were adapted from the Standard Methods for the Examination of Water and Wastewater [23].

Batch Experiments: Batch experiments are experiments conducted at ambient temperature using the optimum conditions of all factors that influence adsorption such as adsorbent dose, pH, initial ion concentration, particle size and agitation time [2]. The adsorption of chromium, copper, nickel and iron by SMZs as a function of the zeolite concentrate, was done in room temperature by varying the SMZ concentrate from 10 mg/L to 120 mg/L for each wastewater sample of each set of SMZs, keeping all other parameters constant with respect to initial concentration of heavy metals in wastewater sample, pH of sample and contact time.

The mining wastewater sample was filtered with filter papers before being used in experiments, in order to remove any impurities which could compromise the efficiency of data measuring instruments. A conventional jar test apparatus was used to perform these batch experiments. Each set of batch testing involves a series of six beakers together with six-spindle steel paddles. Mining wastewater was measured to 500 ml and placed in each jar. The pH of the wastewater is adjusted to 7 with H₂SO₄ or NaOH. Then, the required dosage of adsorbent Miranol C2MSF zeolite and Uniquat QAC-50 zeolite were added separately into each jar.

The mixture was mechanically agitated at 80 rpm (rapid mixing) for 1 minute and 30 rpm (slow mixing) for 15 minutes using the jar test apparatus. After agitation, the suspensions were allowed to settle for 24 hours before the sample was analysed for heavy metal concentration after adsorption. The heavy metal concentrations of chromium, nickel, copper and iron after adsorption were analysed using Hanna Instrument COD and multiparameter bench photometer, model HI 83099.

RESULTS AND DISCUSSION

The removal efficiency of each heavy metal element was calculated by the following equation:

$$\text{Percentage of heavy metal removal} = \frac{C_i - C_f}{C_i} \times 100\%$$

where,

C_i = Initial heavy metal concentration in the mining wastewater

C_f = Final chromium concentration after adsorption process

The initial concentration of chromium, copper, nickel and iron in the raw mining wastewater collected from Rahman Hydraulic Tin, Pengkalan Hulu, Perak, are shown in Table 2.

Fig. 2 (a) to (d) show the effect of amphoteric SMZ on chromium, nickel, iron and copper respectively, while Fig. 3 (a) to (d) show the effect of cationic SMZ on chromium, nickel, iron and copper respectively. Graphs generated from the experiments show that both amphoteric SMZ and cationic SMZ can completely remove chromium from wastewater. The optimum dosage needed for complete removal of chromium elements in mining wastewater using amphoteric SMZ is slightly less than that for cationic SMZ as shown on Fig. 2 (a) and Fig. 3 (a). These may be attributed to the fact that both zeolites can act as an ion exchange. The operating adsorbent capacity depends upon parameters such as concentration of adsorbent, contact time, particle size and pH. According to Fig. 2 (b) and Fig. 3 (b), the nickel optimum removal rate for both SMZs is 85%, but cationic SMZ can achieve this at 20 mg/L which is much less than the optimum dose for amphoteric SMZ which is 50 mg/L. The positively charged cationic SMZ will allow the molecules to bind with the negatively charged surface via ionic or hydrogen bonding. This process will further reduce, or neutralize the particles surface charge. The destabilization of particles by the modified cationic surfactant zeolite occurs through the charge neutralization mechanism, which makes the modified zeolite surface more hydrophobic and this neutralizes the negative charges.

96% of copper can be removed from mining wastewater with the optimum dose of cationic SMZ at 50 mg/L, as shown in Fig. 2 (d). This removal rate is significantly higher than the optimum dose of 40 mg/L for amphoteric SMZ which can only remove 91% of copper from mining wastewater. It is apparent that the equilibrium concentration in the solution phase decreases with an

Table 2: Initial heavy metal concentration in raw wastewater sample

	Heavy Metal Component	Initial Concentration ($\mu\text{g/L}$)
1	Chromium 6^+ (Cr^{6+})	110
2	Copper (Cu^{2+})	19.7
3	Nickel(Ni)	3.35
4	Iron (Fe)	9.1

increase in the amount of zeolite for a given initial metals concentration, as the percentage of metal removed from the aqueous phase increases as the amount of sorbent is increased in the batch vessel with a fixed initial solute concentration [24]. This result was anticipated because for a fixed initial solute concentration, an increasing amount of adsorbent provides for a greater surface area (or adsorption sites). Based on Fig. 2 (c) and 3 (c), the highest level of removal for iron is 91% by using the cationic SMZ at an optimum dose of 10 mg/L compared to 90 mg/L for amphoteric SMZ, which could only achieve 88% removal. All the results from optimum dose of SMZ and reduction percentage of metals did not vary too much, except in the case of iron.

The initial concentration of the selected heavy metal elements for experiments was lower than the permissible discharge standard, resulting in very high removal rates with the utilization of both the amphoteric and cationic SMZ. The results obtained show that the zeolite exchanger binds more of a particular metallic ion even if the ion is mixed with another metallic ion [12]. Furthermore, zeolites do not equally prefer all ions. This variability in preference can be expressed semi-quantitatively as a position in the selectivity sequence. Several authors have mentioned that zeolites are well known materials for the removal of heavy metals such as cadmium, lead and nickel. The summary of reduction percentage for amphoteric SMZ and cationic SMZ is shown in Table 3.

Adsorption is a mass transfer process by which a substance is transferred from the liquid phase to the surface of a solid and becomes bound by physical and/or chemical interactions [25]. Recently, adsorption has become one of the alternative treatment techniques for wastewater laden with heavy metals. Zeolites can transfer a heavy metal contamination problem of many thousands of litres, to a few kilos of easily handled solid which can be effective exchanger regeneration, or can be cement stabilized or vitrified [12]. Modifying the surface of zeolites can increase its capacity for adsorption. Surfactant modification allows the zeolites to sorb non-polar organic solutes and anions for which untreated zeolites have little affinity [12].

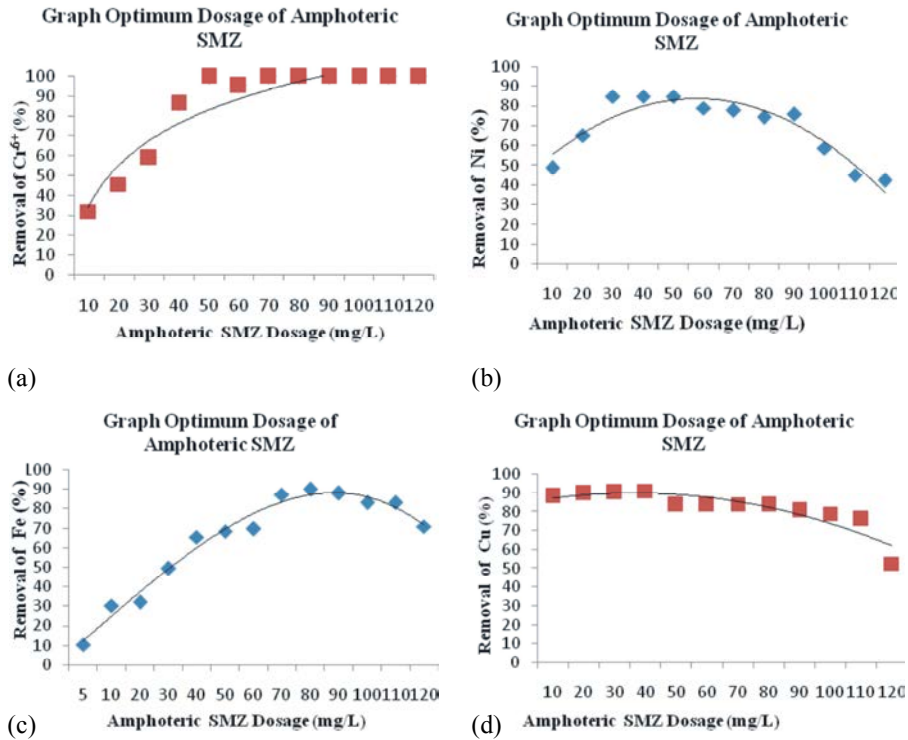


Fig. 2: Effect of amphoteric SMZ on (a) chromium, (b) nickel, (c) iron and (d) copper

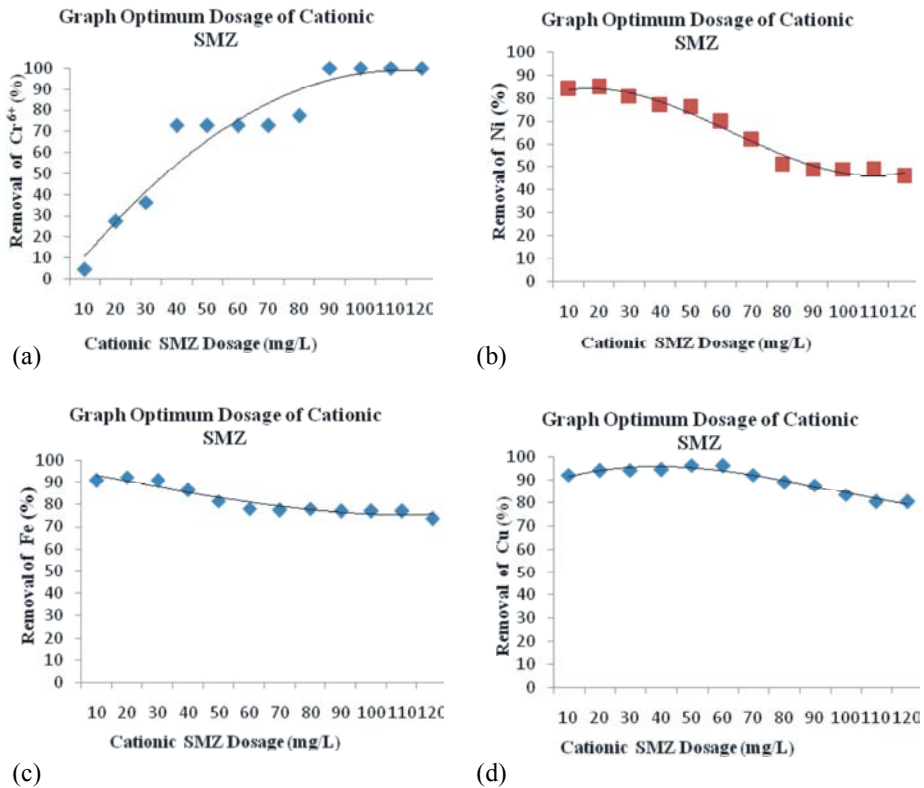


Fig. 3: Effect of cationic SMZ on (a) chromium, (b) nickel, (c) iron and (d) copper

Table 3: Summary of percentage reduction for amphoteric SMZ and cationic SMZ

Heavy Metal	Amphoteric SMZ		Cationic SMZ	
	Optimum Dose (mg/L)	% Reduction	Optimum Dose (mg/L)	% Reduction
Chromium 6+	90	100	110	100
Nickel	50	85	20	85
Copper	40	91	50	96
Iron	90	88	10	91

CONCLUSIONS

In the laboratory studies conducted, the removal of heavy metals such as chromium, nickel, copper and iron from mining wastewater collected from Pengkalan Hulu, Perak, using amphoteric and cationic SMZ was accomplished. The SMZ is a surface active agent which, when dissolved in water, takes on the ability to remove dirt from surfaces such as human skin, textiles and other solids. Every surfactant molecule has a hydrophilic (water loving) head which is attracted to water molecules and a hydrophobic (water hating) tail that resists water and instantly attaches itself to oil and grease in dirt.

The results obtained indicate that a small quantity of SMZ is favourable in the removable of heavy metals from mining wastewater. From the experiments performed, it was found that all the elements, through the adsorption process with either amphoteric SMZ or cationic SMZ, can be removed by up to 85% or more from the initial concentration. Both SMZs have the ability to remove heavy metals in that range. However, cationic SMZ appears to have a higher ability to remove heavy metals using a lower optimum dose compared to amphoteric SMZ. The cationic surfactant SMZ seems to have better removal of Ni, Cu and Fe compared to amphoteric SMZ which is better in removing Cr⁶⁺ in mining wastewater. Nevertheless, all the results on the optimum dose of SMZ and the reduction percentage are almost the same for both amphoteric and cationic SMZs, except in the case of iron. The highest removal of iron was achieved at an optimum dose of 10 mg/L with the percentage reduction of 91% by using cationic SMZ while 88% of iron was removed by amphoteric SMZ at an optimum dose of 90 mg/L. Treatment of natural zeolites with large cationic surfactants dramatically alter their surface chemistries. These large organic cations exchange selectively with native inorganic cations to form a stable, organic rich coating on the external surface of the zeolite.

Ion exchange by zeolites is considered to be one of the main processes for the removal of toxic metals from solutions. The data reported after the experiments

suggest that cationic SMZ can be considered a potential sorbent for the removal of heavy metals from mining wastewater.

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