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Low-Cost Adsorbent in Treatment of Acid Mine Drainage in Cambodia: Chong Phlah, Mondulkiri

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Abstract: *Acid mine drainage (AMD) is a major environmental distributed pollutant due to the exposure of air and water from tailing and overburden produced from metals mining activity. AMD might degrade water to strong acidity, sulfide, iron (Fe), and other heavy metals contents due to the chemical consumption during the mineral extraction process. Thus, this study aimed to investigate the effectiveness of neutralization acid mine drainage caused by artisanal and small-scale mining at Chong Phlah, Mondulkiri, Cambodia. In this study, eggshell, limestone, and Calcium Carbonate (CaCO₃) were applied as the adsorbent. The adsorbent was grounded to the size of less than 75µm, however, the eggshell was calcined at 900 ºC for 2 hours before grinding. Limestone source was obtained from Battambong province, Cambodia. The experiment was conducted to study the influence of adsorbent dosage, varied time, adsorption kinetic, removal behavior, and stability of sample after treatment. Batch adsorption results showed that the maximum removal of As, Fe, and Mn was greater than 98%, 95%, and 83%, with eggshell, limestone, and CaCO₃, respectively. The optimum contact time of As, Fe, and Mn removal was 480, 180, and 5 min, respectively. The pH between 5.8 and 6.6 was obtained after the adsorption process. In addition, As, Fe, and Mn following the pseudo-second-order kinetic model. The stability of arsenic and iron was arsenate and hematite, respectively. This demonstrated that the neutralization of acid mine drainage by the eggshell, limestone, and CaCO3 could be obtained. The application of this neutralization method using eggshell and limestone was considered cost-effective, readily available, and environmentally friendly to remove the heavy metals from acid mine drainage caused by tailing waste from artisanal and small-scale mining. The commercial CaCO3 in neutralization showed great effectiveness over eggshell and limestone, however, it is an expensive material..*

Keywords: Acid Mine Drainage; Adsorbent; Calcination; Neutralization; Eggshell; Limestone; Calcium carbonate; Cambodia

1. INTRODUCTION

Regionally, Cambodia occupies the south-central region of the Indochina peninsula, mainland of Southeast Asia. The Indochina Terrane was made up of several tectonic units hosted by mineralization belts such as Truong Son Fold Belt (TSFB), Loei Fold Belt (LFB), Dalat-Kratie Belt (DKB). The Dalat–Kratie and Southeast China magmatic belts may have been closely associated during the Jurassic-Cretaceous and were later separated by Cenozoic SE Asia extrusion as the result of the Himalaya-India collision. Ore deposits in the DKB are mostly intrusion-related Au systems (Okvau, Mondulkiri in Cambodia), porphyry Cu-Au, skarn Pb-Zn, sediment-hosted Au deposits (North Kratie in Cambodia), and

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porphyry Cu-Mo, porphyry Cu-Mo-Au porphyry (Halo prospect, Canada Wall and Okalla East, Ratanakiri, Cambodia) (Fig. 1).

The waste soils from mineral processing to extract a specific metal from ore and unmanaged acidic related waste rock can cause environmental problems if no right wastemanagement. The main source of acid mine drainage formation was the oxidation of sulfides (iron pyrite). The acid mine drainage becomes the potential cause of water pollution in which sulphuric acid has dissolved and releases metals in wastes. In most cases, it tends to produce acidic leachates (low pH) and contains high concentrates of metals and sulfate from the tailing waste dump. Without certain management of artisanal tailing and waste rock, the surrounding ground and surface waters will contaminate the leachate [1].

Currently, there are many small-scale and artisanal mining activities in Cambodia (Fig. 2). Most of those are doing precious metal mining like gold in most provinces such as Ratanakiri, Mondulkiri, Kratie, Kampong Cham, Preah Vihear, etc [2]. These mining activities are often practiced by some locals and small private companies. Specifically, artisanal mining is most likely following the traditional way of ore extraction technique using family tools and a labor force of not more than seven people. Small- scale mining usually upgrades its extraction tools with more labor forces. Yet, these mining businesses are not following the regulation of the country and do not consider the environmental problem caused of the mining activities.

According to Radio Free Asia (RFA) reports, small-scale mining had continuously released toxic wastes into the rivers, which could affect the public health and living conditions of the local villagers Chemical toxic waste was released into the nearby river, affecting the whole stream. Recently, AMD treatment systems had been developed based on chemical, physical, and biological alone or in combination process of those two or all together. Generally, the development of the system was categorized depending on either passive or active processes [3]. For as long as twenty years, the modern and rural byproducts have been effectively used as adsorbents for treating industrial effluents [4]. Thus, the research aims to study the treatment of acid mine drainage in the application of low-cost adsorbents. The study area was the active and abandoned artisanal and small-scale mine sites in Chong Phlah, Mondulkiri. The most commonly used adsorbent is activated carbons. Their high surface area, pore volume, and pore size distribution are the key adsorption efficiency in most of organic pollutants. Effectiveness of adsorption depends on their pore texture and surface area, the physicochemical properties of the adsorbate, ionic strength, temperature, and pH [5]. Thus, the best surface is of adsorbent which has an influence on reactions on surface would depend on its nature structure, greater area, and more pore. In the current study, eggshell, limestone, and $CaCO_3$ had been used to neutralize the acid mine drainage produced by tailings and its

effectiveness in As, Mn, and Fe removal at different adsorbent doses and contact times.

2. METHODOLOGY

2.1. Site description and sampling

The study area consists of the tailings impoundment contained in a narrow and tension-gash valley. The physical properties of Acid Mine Drainage (AMD) were collected seasonally in both dry and rainy seasons. The sampling sites in this study were in Chong Phlah, Mondulkiri province, Cambodia (Fig. 2). The weather in Chong Phlah was around 28 to 35°C with an average of 31.5°. The precipitation is approximately 20%, humidity is 64%, and wind speed is 8 km/h [6].

2.2. Sample preparation

Tailings were collected from both active and abandoned mine sites and stored in the refrigerator at a temperature of 4 ºC before the adsorption experiment. Tailing then was dried at room temperature for evaporating water content for 10 days until crispy or dried [7].

Chicken eggshell (ES) was collected from household waste located in Phnom Penh city. Eggshell was rinsed several times with tap water to remove dirt and dust. Then, the eggshell was sun-dried under the temperature of around 40 °C for 2 days [8]. Eggshell was grounded using mortar and later pulverizing and sieving to obtain the fine powder of less than 75 µm. The eggshell was then calcinated at 900 °C for 2 h [9]. After the calcination process, calcined eggshell powder (CES) was stored at room temperature in a ziplocked container.

Limestone was obtained from Battombang province, Northweatern Cambodia. Fresh limestone was crushed before grinded with pulverizer to obtained the size of less than 75 µm.

2.3. Batch adsorption experiment

2.3.1. Adsorption ratio

The effect of varied dosages (0.2, 0.4, 0.6, 0.8, 1, 1.2 and 1.5 g) was investigated to optimize the removal of heavy metals. Batch adsorption experiments were conducted to determine the effect of varied ratio of eggshell, limestone, and $CaCO_3$ with the tailing sample. In this experiment, various ratio was put into a conical centrifuge tube and shaken using an orbital shaker (shaking speed = 200 rpm, contact time = 360 min). After shutting down of the machine for 30 min, 10 ml of samples were drawn from supernatant for heavy metal analysis using AAS.

2.3.2. Study on contact time

The effect of various contact times (5, 10, 15, 30, 60, 180, 300, 480, and 1440 min) was studied. A series of batch adsorption experiment was conducted by shaking optimum adsorbents (eggshell, limestone, and CaCO$_3$) in the tailing sample (optimum ratio) in conical centrifuge tube. The flasks were agitated at 200 rpm for certain contact time mention above. After shaking process, the samples were allowed to settle for a few minutes and then were analyzed using AAS. The percentage removal, R (%) and adsorption capacity, q_e (mg/g) of heavy metals can be expressed in the following equation.

$$R (\%) = \frac{C_o - C_e}{C_o} \times 100 \qquad \text{(Eq. 1)}$$

$$q_e = \frac{C_o - C_e}{m} \times V \qquad \text{(Eq. 2)}$$

where, C_o and C_e (mg/L) represent heavy metals concentration at initial and equilibrium, m is the mass of eggshell, limestone and CaCO$_3$ adsorbents (g) and V is the volume of the distilled water (L). The first and second order equation were applied to investigate the reaction mechanism and potential rate of the adsorption of heavy metals onto adsorbents powder.

3. RESULTS AND DISCUSSION

3.1. Characteristic of adsorbents

Calcite was presented in all diffraction of XRD patterns [10]. X-ray diffraction pattern of the eggshell calcination at 900°C for 2 h was presented in Fig. 3. The Fig. 3 recorded the diffraction patterns in 20-65 degrees (2θ) range using Cu Kα (alpha) radiation with the wavelength of 1.54056 Å. Eggshell demonstrated a major peak at 2theta = 29.5 which indicates that calcite is a major constituent of the eggshell. In the calcined eggshell at 900 °C, regular peaks were obtained at 2theta = 23.5, 26.5, 39.5, 47 and 48, showing the conversion of CaCO$_3$ to CaO [11].
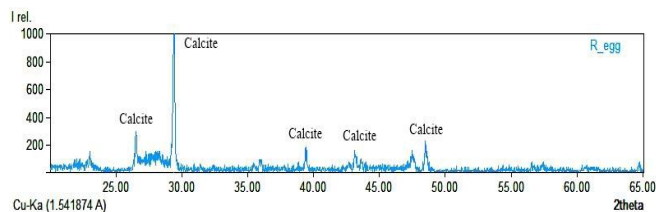

Fig. 3. XRD pattern of CES powder

Fig. 4 represents the XRD patterns of limestone from Battambong province, Cambodia. There are several components such as coleimanite, kyanite, calcite, kaolinite, and corundum. The major component is calcite.

Fig. 5 represents the XRD patterns of the tailing sample. The peak value of tailing was categorized by quartz (SiO$_2$) as

the main mineral occurance, and other associate related iron mineral such as lumanite, clinozoisite, serpentinite, and chlorite.
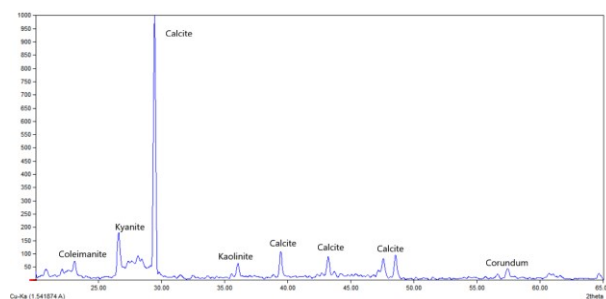

Fig. 4. XRD composition of limestone

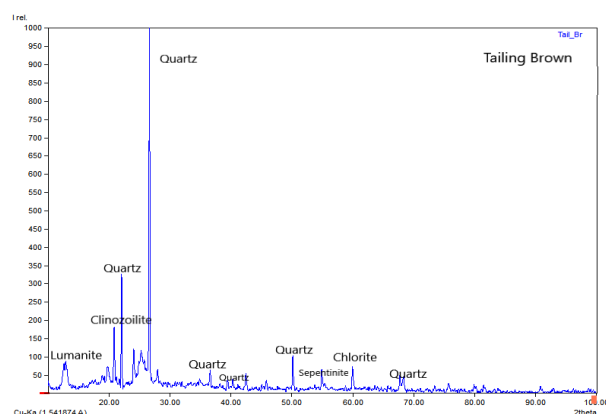**Fig. 5.** XRD composition of tailings

The chemical composition of eggshell, limestone, and tailing is shown in Table 1. Calcium carbonate (CaCO$_3$) was the main component of eggshell and limestone. On the other hand, tailing consisted mainly of silicon dioxide (SiO$_2$), aluminium oxide (Al$_2$O$_3$), arsenic trioxide (As$_2$O$_3$) and iron (III) oxide (Fe$_2$O$_3$).

3.2. Influence of ratio

The effect of adsorbent dose on adsorption of heavy metals onto eggshell, limestone, and calcium carbonate was determined by keeping size, initial concentration, contact time, and shaking speed to be constant. The adsorption of arsenic, iron, and manganese was determined by varying adsorbents dosage from 0.2 to 1.5 g. Fig. 6 demonstrated the influence of the adsorbents ratio on removal efficiency of heavy metals. According to Fig. 6, removal efficiency of arsenic keep increasing over adsorbents dose added in. The removal efficiency of As was 99.375, 98.541, and 99.958 percent at 0.2g of eggshell, limestone, and CaCO$_3$, respectively. The significant removal of eggshell was at 0.6g, which is shown 99.98 percent removal. At adsorbents dose of 0.2g, CaCO$_3$ adsorbents was indicated the highest removal. And at 0.4g dose, equilibrium

point of limestone removal was achieved.

Table 1 XRF composition of adsorbents

| Composition	Eggshell (%)	Limestonese (%)	Tailing (%)
$CaCO_3$	98.6748	97.5546	0.50
Fe_2O_3	0.0077	0.2257	16.13
SiO_2	0.0223	1.1821	8.61
Al_2O_3	0.0036	0.6196	1.33
As_2O_3	-	-	11.64
SO_3	0.4297	0.0346	15.51
K_2O	0.045	0.0327	0.30
Na_2O	0.118	0.0349	0.04
SrO	0.0256	0.0176	-
P_2O_5	0.3641	-	0.02
LOI	46.0231	38.4456	45.82

Note: (-) not detected
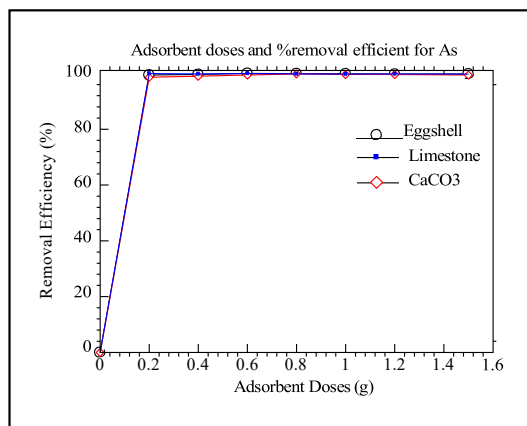
Fig. 6. Influence of adsorbents doses on As removal efficiency

Fig. 7 illustrated the removal efficiency of iron with eggshell, limestone, and $CaCO_3$. At first dose of 0.2g of eggshell, limestone, and $CaCO_3$, iron removal was at 99.179, 97.238, and 83.358 %, respectively. All adsorbents at 0.6g showed the highest removal then it remain slightly decreasing after that points. All adsorbents, a rapid increment of heavy metals removal at the first dose occurred due to the increase of driving force in groundwater solution that might increase the number of available active sites on the surface of adsorbent media.

Fig. 8 indicated the influence of adsorbents dose on the removal efficiency of manganese. The removal efficiency of manganese rapidly at the first dose to 97.82, 98.36, and 96.73% of eggshell, limestone, and $CaCO_3$, respectively. At 99.5%, eggshell removal efficiency reached the highest removal at 1g. On the other hand, a small amount of limestone and $CaCO_3$ was used to remove manganese effectively. It reached an equilibrium point at 0.2g for limestone and 0.4g for $CaCO_3$ and the removal efficiency was 98.36% and 97.28%, respectively.
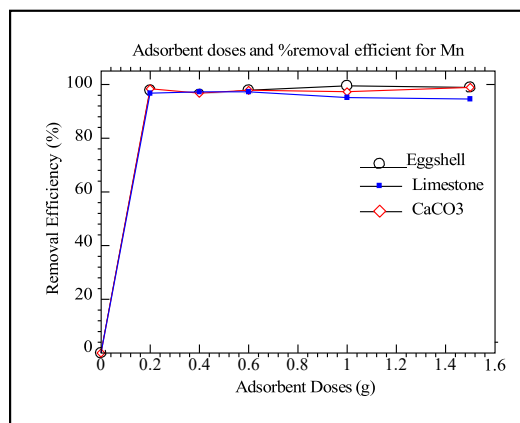
Fig.7. Influence of adsorbents doses on Fe removal efficiency
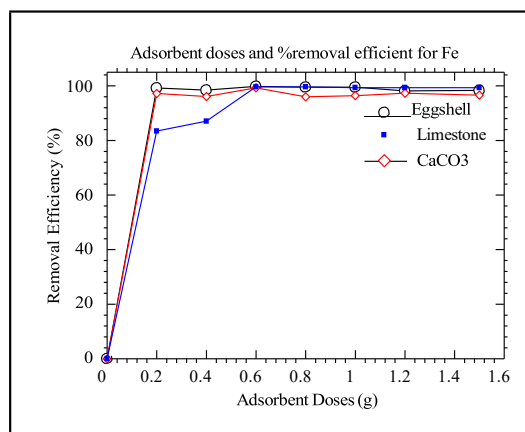
Fig. 8. Influence of adsorbent doses on percentage removal of manganes

Initially, the adsorbents showed dramatically increase until reaching the maximum removal and then decreasing. As shown in Fig. 8, the percentage removal was increased due to the increase of adsorbents. The high active sites of adsorbents will stop the removal activities meaning the equilibrium state was achieved [12]. According to the research data of Gupta et al. [13], increasing adsorbent ratio generally resulted in the increase in the removal efficiency of metals due to high adsorbent-to- sample surface area and large free site attraction between CES and metals. The increasing the surface area of adsorbent was another mechanism. Meanwhile, the research of Subbareddy et al. [14] found that adsorption increases rapidly in the beginning and decreases slowly later. It is assumed that the adsorption decreases with an increase in concentration of adsorbents.

3.3. Influence of contact time

The effect of the contact time on adsorption of heavy

metals onto CES, limestone and $CaCO_3$ was determined by keeping the size, adsorbent dose, initial concentration, and shaking speed to be constant. In the study, the adsorption of arsenic, iron and managenese was determined by varying contact time from 5 min to 24 h.

Fig. 9 illustrated the influence of contact time on arsenic removal efficiency. The arsenic removal was reached the maximum at 480 min, 99.979, 99.958, and 99.985% of eggshell, limestone, $CaCO_3$, respectively.
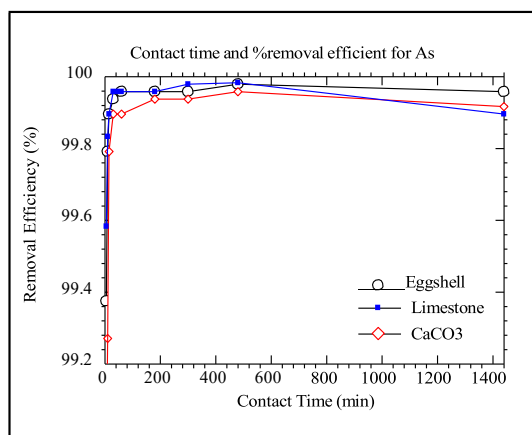

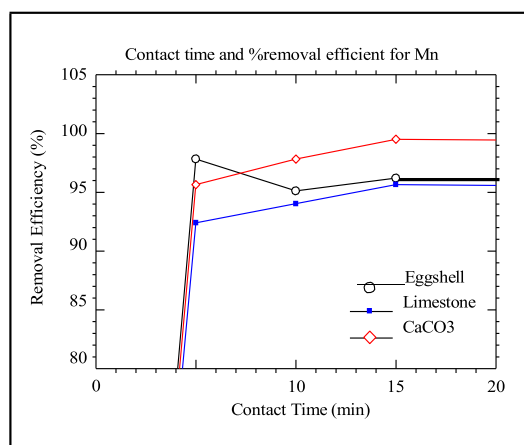**Fig. 9.** Effect of contact time on percentage removal of As

Fig.10. Effect of contact time on percentage removal of iron

Fig. 10 demonstrated the percentage removal of iron with different contact times. For eggshell adsorbents, the highest removal was at 180 min, 99.253 %. Nevertheless, limestone was observed to be at equilibrium at 1440 min. For chemical $CaCO_3$ was 99.70% at 300 min and remain stable.

Fig. 11 indicated the effect *p*f contact time on the removal efficiency of manganese. In the first 5 min, eggshell adsorbent reached 97.82 % where it remains to decrease after all. On the other hand, limestone and $CaCO_3$ reached the maximum at 15 min at 99.51 and 95.65 %, respectively.
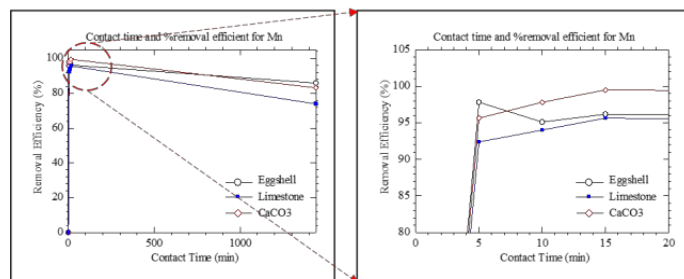

Fig.11. Effect of contact time on percentage removal of manganese

Determination of the optimum contact time is intended to determine the duration of metals to adsorbent by the eggshell, limestone, and $CaCO_3$. The longer of the contact time, the better of adsorption power [15], yet the longer contact time could result in decreased adsorption. This was due to the active site of eggshell, limestone, and $CaCO_3$ which had been saturated so that it could not bind any further [16]. As illustrated in Figs. 9, 10, and 11, the longer the contact time, the better adsorption, yet, it might reach the point where it will not bind anymore.

3.4. Adsorption kinetics

The two kinetic models, pseudo-first order and pseudo second-order models were applied to investigate the reaction pathways and potential rate-limiting steps of the adsorption of heavy metals onto eggshell, limestone, and $CaCO_3$. Adsorption kinetic was done by maxing adsorbents with the tailing sample at room temperature (303K) under the shaking of 200 rpm.

Adsorption rate and mechanism could be determined by defininf adsorption rate through kinetic study. The pseudo-first order and pseudo-second order models can be expressed by:

$$\log(qe - qt) = \log(qe) - \frac{tk_1}{2\,303}$$
$$\frac{t}{q_t} = \frac{1}{k_2 q_e^t} + \frac{t}{q_e}$$

Therefore, As, Fe, and Mn removal efficiency seemed to correspond to the second-order kinetic. This showed that the adsorption process involved with chemisorption, which indicates the nature of the ion exchange process [17].

Fig. 12 (a) and (b) indicated the kinetic model of arsenic onto eggshell, limestone and CaCO3. It shew the linear plot of ln(qe-qt) versus contact time (*t*) for the first order model and *t*/*q*t versus contact time (*t*) for the second-order model. The Kinetic study had achieved following the pseudo- second-order model rather than the pseudo-first order model arsenic.

Fig. 13 (a) and (b) indicated the kinetic model of iron onto eggshell, limestone and CaCO3. The Kinetic study had

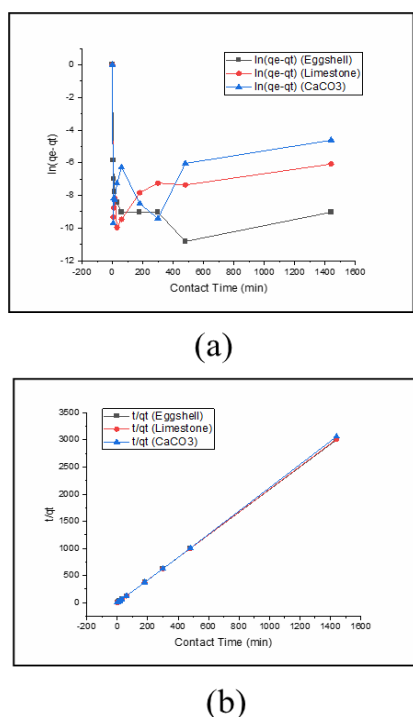achieved following the pseudo-second-order model rather than the pseudo-first-order model for iron.

(a)

(b)

Fig.12. Pseudo first order (a) and Pseudo second-order (b) model of arsenic

Table 2 demonstrated the overall result of kinetic parameter calculated by applying pseudo first and second order for the adsorption of heavy metal onto eggshell, limestone and CaCO3. Correlation coefficient (R^2) in pseudo-second order was greater than pseudo-first order in all heavy metals. This shows that the adsorption process involved with chemisorption, which contributed to the Fe removal in the groundwater sample [17].

Kinetic study had achieved following the pseudo-second order model rather than pseudo-first order model for both metals. According to Lui, the pseudo-second order equation for adsorption is much similar to the universal rate law for a chemical reaction [18].

3.5. Removal behavior

The behavior of As, Fe and Mn removal in the study was shown the effect of contact time over pH and equilibrium concentration of metals. Fig. 15 indicated the behavior between pH, equilibrium concentration and contact time of aresenic, iron, and manganese. When pH was increased, the concentration of heavy meatals was declined to prolong the time. In addition, the increase in concentration would result in a decrease in pH.
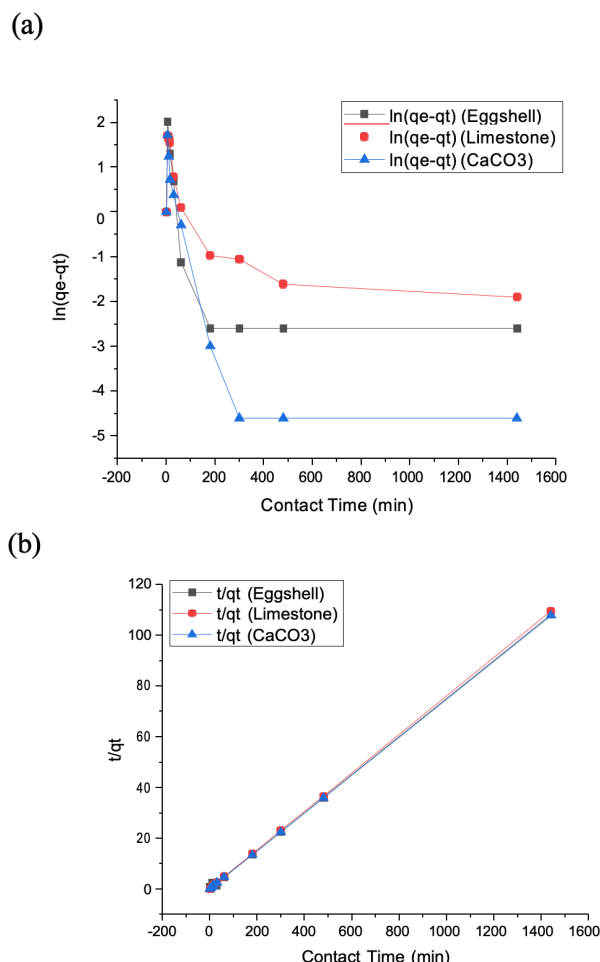
(a)

(b)

Fig.13. Pseudo first order (a) and Pseudo second-order (b) model of iron

The result shown the decrease of removal concentration of arsenic, iron and manganese with the increase of pH over the certain contact time. The result of removal behavior was expressed the lower concentration of treated sample, the better removal efficiency of heavy metals.

3.6. Stability of As and Fe in treated samples

Redox potential and pH are particularly demonstrated metals speciation and oxidation states which are shown in the Eh-pH diagram. Fig. 16 illustrated the redox potential. Eh–pH diagram for As and Fe species at 30°C and 1.013 bar total pressure. All contact time in experiment showed oxidation state of arsenic at As (V) in the form of $HAsO^{2-}$ hydrogen arsenate. Hematite was found in the diagram of speciation of iron in all contact time (from 5 to 1440 minutes). In most research, Fe (II) found mostly dissolved under acidic conditions pH < 2, and Ferrous iron Fe (III) is obtained at pH > 2 [19]. Fe_2O_3 and is widely found in rocks and soils.
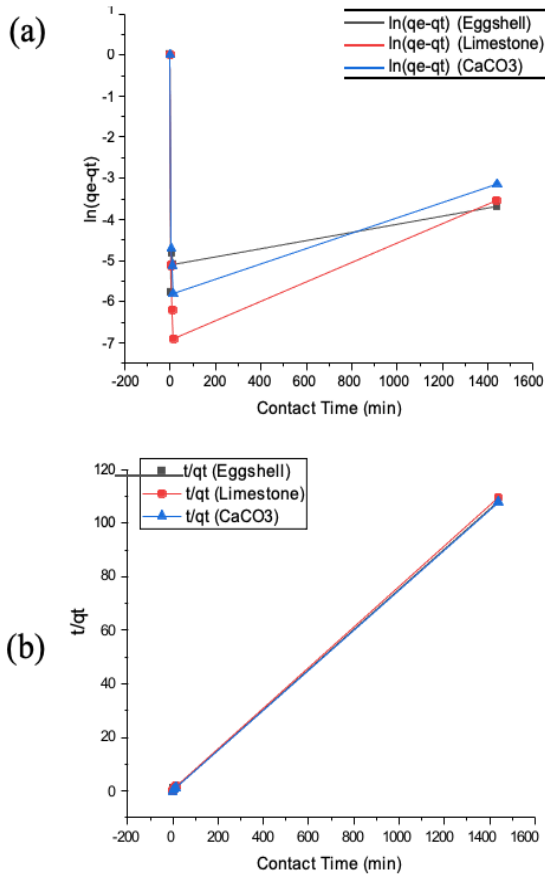
Fig.14. Pseudo first order (a) and Pseudo second order (b) model of managanese

Table 2 Kinetic model of eggshell, limestone and CaCO$_3$ on adsorption

	Order of Reaction		As	Fe	Mn
CES	Pseudo 1st order	$q_{e\ exp}$	0.4799	13.3746	0.1831
		$q_{e\ cal}$	0.000931	1.09168	0.01988
		k^1	-1.70×10^{-6}	-1.84×10^{-6}	1.00×10^{-7}
		R^2	0.0254	0.29417	-0.3312
	Pseudo 2nd order	$q_{e\ cal}$	0.4798	13.3440	13.3422
		k^2	75.7293	715.5705	505.768
		R^2	1	0.99996	0.99998
Limestone	Pseudo 1st order	$q_{e\ exp}$	0.4799	13.3	0.182
		$q_{e\ cal}$	0.000473	1.78976	0.01051
		k^1	6.59×10^{-7}	-1.53×10^{-6}	-3.16×10^{-3}
		R^2	0.02195	0.46434	-0.29998
	Pseudo 2nd order	$q_{e\ cal}$	0.4777	13.19261	13.1891
		k^2	-0.30695	502.2219	524.4768
		R^2	1	0.99997	0.99997
CaCO3	Pseudo 1st order	$q_{e\ exp}$	0.47998	13.35	0.179
		$q_{e\ cal}$	0.000771	0.77197	0.02014
		k^1	9.44×10^{-7}	-2.88×10^{-6}	3.51×10^{-7}
		R^2	0.04486	0.44666	-0.30731
	Pseudo 2nd order	$q_{e\ cal}$	0.47044	13.38867	13.3833
		k^2	-0.05889	1018.272	970.5899
		R^2	0.99996	0.99999	0.99999

* $q_{e\ exp}$ (mg/g); $q_{e\ cal}$ (mg/g); k1 (min-1); k^2 (g.mg-1.min-1)

Eh-pH is an important factor to know the redox stability of As (III) and As (V). Oxidation and iron are important controls on arsenic speciation in water. Arsenate was seen to be more attracted to the surfaces of hematite or with electrostatically than other surfaces. Moreover, arsenate is less mobile than As (III) in the environment [20].
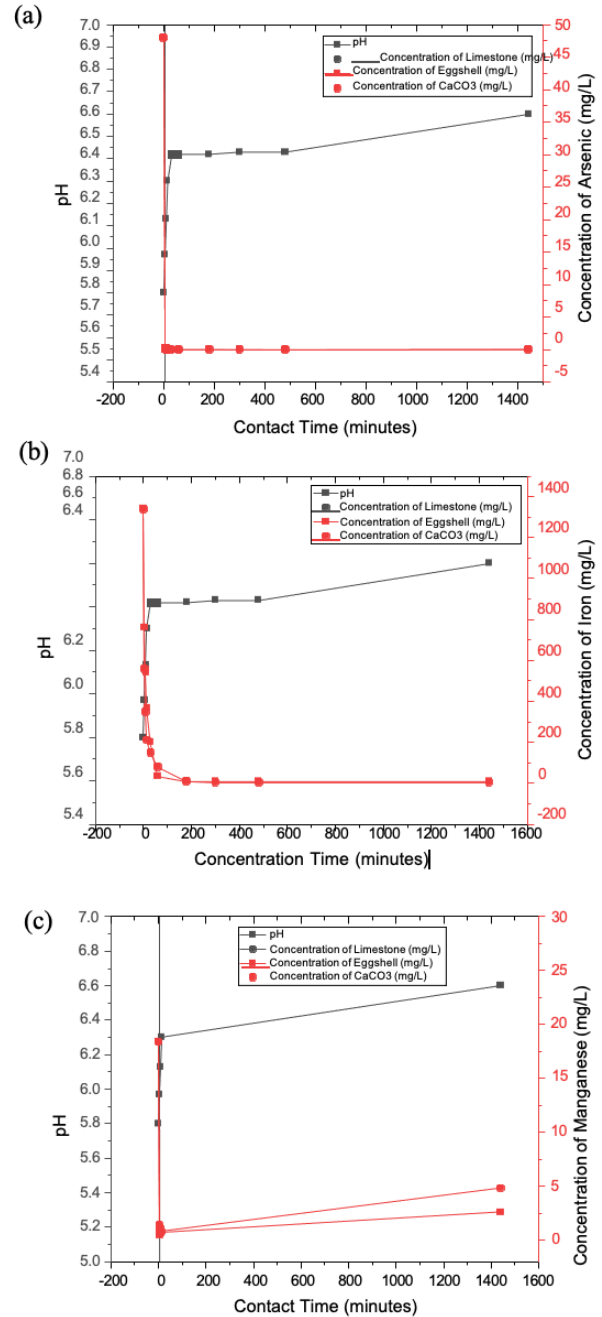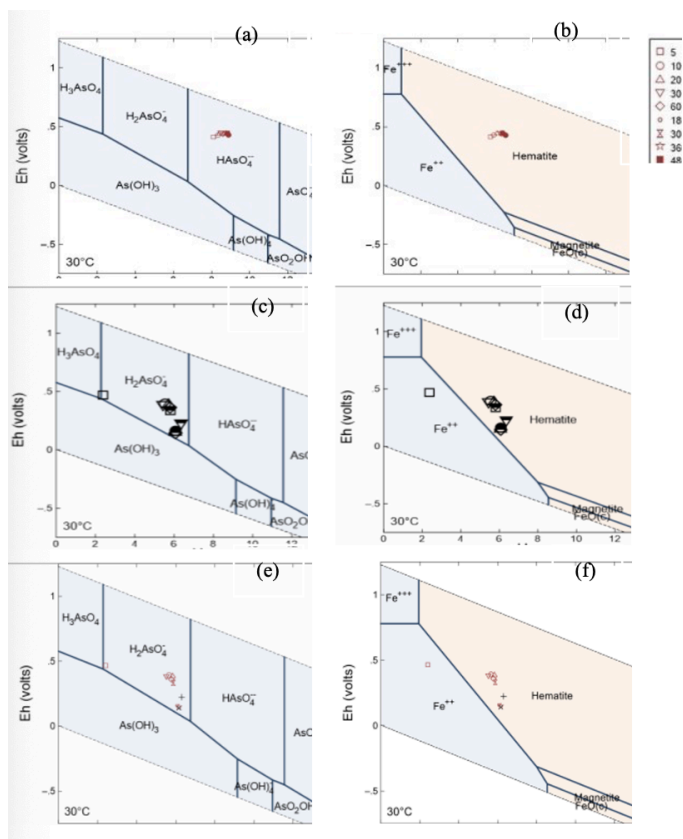

Fig. 15. Removal behavior of arsenic (a), iron (b), manganese (c) concentration, pH and contact time

Fig.16. Speciation diagram of As in eggshell (a), Fe in eggshell (b), As in limestone (c), Fe in limestone (d), As in $CaCO_3$ (e), Fe in $CaCO_3$ (f), in T = 30 °C and P = 1.013 bars, a [main] = 10^{-6}, a [H_2O] = 1

4. CONCLUSIONS

This study showed the great potential of eggshell, limestone, $CaCO_3$ in neutralization acid mine drainage produced by tailing waste. The result indicated 99.983, 98.958, and 99.958% removal of As with eggshell, limestone, and $CaCO_3$.

The removal of iron was achieved at 99.81, 99.25, and 99.62% with eggshell, limestone, and CaCO3, respectively. As well as Mn removal, 99.51%, 98.36% and 97.28%. The optimum contact time of As, Fe, and Mn removal was at 480, 180, and 5 min, respectively. Moreover, the adsorption kinetic study showed the adsorption of heavy metals followed the second order model. The eggshell, limestone, $CaCO_3$ was found to be an efficient adsorbent which can be used as alternative adsorbents for removing heavy metals from tailing. In addition to high efficiency, the eggshell and limestone were considered as a cheap and environmental-friendly adsorbent. $CaCO_3$ showed a great result than eggshell and limestone, however, it is a chemical and expensive material to used. Therefore, utilization of eggshell and limestone adsorbents should be considered as heavy metal removal application.

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