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Kinetics of Batch Adsorption of Fe^{2+} Ions from Textile Industry Wastewater onto Calcium Carbide Residue

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Abstract

This research was conducted to study the efficiency of calcium carbide residue as an adsorbent for the removal of iron (II) from textile industry wastewater in a batch adsorption process. In this study, the iron (II) content in textile industry wastewater was synthetically prepared using $Fe_4.7H_2O$*. The iron (II) content in the effluent was characterized using atomic absorption spectrometry (AAS), while the functional groups responsible for the adsorption of iron on the surface of the calcium carbide residue surface were observed using SEM and Fourier Transform Infra-red (FTIR) spectrophotometry. The SEM images of the calcium carbide residue revealed a highly porous particle morphology. Meanwhile, the FTIR revealed the presence of various functional groups (OH, CH, C=C, and C-C). Factors affecting adsorption, e.g., contact time, adsorbent dose, pH, and iron concentration, were also studied. The maximum iron (II) ion adsorption was observed to occur at pH 6. The data obtained from the adsorption process most closely matched the Langmuir isotherm model with a correlation value of* $R^2 = 0.9959$ *and* $q_e=1.697$ *mg/g with the pseudo-second-order kinetic model was found to be the most suitable adsorption kinetic model with a correlation coefficient value* (R^2)*, which is 0.9962 for an adsorbent mass of 7.5 g. The adsorption of iron ions from textile wastewater onto calcium carbide residue particles exhibits a physisorption mechanism.*

Keywords: adsorption, calcium carbide, solid waste, textile waste

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INTRODUCTION

Textiles are widely used in various fields, such as clothing, basketry, container making, fabrics, etc. Textile industry is one of the major industries that employ most workforce in the developing countries. Hence, it gives an important contribution to the world economy. However, textile industry is also the major contributor to environmental pollution in the world. Surveys in various parts of the world show that 20 to 30% of fresh water have been polluted by the textile industry wastewater. Textile industry uses millions gallon of water daily. Water laden with many chemicals, either in the form of heavy metals, organic toxicants, and infectious agents that are discharged without appropriate treatment has become the serious threat to the environment. Therefore, the reduction of these pollutants in textile wastewater is one of the requirements regulated by the Environmental Act

(ACT1974) before final disposal into the environment can be made. Iron (II) ion is one of the toxic compounds contained in textile wastewater. Even though it has low toxicity, if its content in the water system around the residential area has exceeded the safe threshold it will be very dangerous. Heavy metal poisoning can be experienced by humans through contamination of drinking water and air resulted from transportation, industrial, households and agricultural activities.

The wastewater generated during textile processing contains large amounts of dyes and chemicals containing metals, such as iron, copper, selenium, zinc, which cannot be degraded naturally. As a result, they can potentially damage the environment and become harmful to human health. In addition to their effects on the biota of the rivers, lakes and other water systems in their paths (Johnson and Hallberg, 2005), they can also be accumulated in the living organisms and trigger the development of various diseases (Akcil and Koldas, 2006; Damian et al., 2013).

Several technologies have been applied to reduce the iron content in groundwater, including adsorption and electrochemical technology (Luptakova et al., 2012), electrodialysis (Buzzi et al., 2013), as well as ultra-filtration technology, electrolysis, reverse osmosis, extraction (Motsi et al., 2011). However, the choice largely depends upon the type and concentration of the absorbent that is also associated to the cost. Among those methods, the adsorption method is the most commonly used for its excellent metal ion removal efficiency. In this process also can be an alternative to conventional methods, such as precipitation or coagulation due to a faster adsorbate separation from the wastewater to the achievement of the desired water quality, simple design, inexpensive, effective and efficient, environmentally friendly, and economical (Fu and Wang, 2011; Guptaand Ali, 2013; Yavuz et al., 2003).

Several inexpensive adsorbents for removing heavy metal ions from aqueous solutions have been discovered. Recent efforts have been made to use cheap and usable agricultural wastes, such as egg shells, banana peels, rice husks, pellets, etc. as adsorbents to remove heavy metals from wastewater due to the presence of various functional groups such as hydroxyl, amino, carboxyl, and ether, which serve as active sites (Yu. B et al., 2001). The potential material to be developed as an adsorbent material for metal ions is the solid waste from the welding industry, namely calcium carbide. The carbide waste has an alkaline pH ranging from 12 - 13, with a $Ca(OH)_2$ content of 97%, a large surface area, fine grain, insoluble, easy to obtain, and relatively inexpensive. Based on these characteristics, the solid calcium carbide residue can be used as an adsorbent in the removal of metal ions in acidic water. The use of calcium carbide waste as an adsorbent is expected to neutralize pH and reduce heavy metal levels so that the quality of acidic water can be improved and can be safely discharged into water bodies. Calcium carbide residue was used as an adsorbent in this study to remove iron (II) present in an aqueous solution. This process involves the transfer of heavy metals (iron) from groundwater to the surface of a porous solid material (calcium carbide residue).

The purpose of this study was to examine the ability of calcium carbide residue to remove ferrous (II) metal ions from textile wastewater. The physicochemical characteristics of calcium carbide residue were determined using SEM-EDX and FTIR, while the adsorption process was evaluated using two equilibrium models, namely the Langmuir and the Freundlich adsorption isotherm models. For the adsorption kinetics, the pseudo first order and second order kinetic models were employed. The results of this study are expected to obtain a model of adsorption isotherm equilibrium and adsorption kinetics equations as well as the characteristics of solid waste calcium carbide as a good and cheap adsorbent.

MATERIALS AND METHODS

Adsorbent preparation

In this study, calcium carbide residue was used as the adsorbent. The waste from the calcium carbide welding process is in the form of wet lumps was sun dried, and sieved using an 80-mesh sieve. The waste carbide powder was then soaked in demineralized water for 24 hours, drained, and printed in the form of tablets with a thickness of 2 mm and a diameter of 3 mm. Before being used as an adsorbent, the calcium carbide tablets were heated using an oven at a temperature of 150ºC for 120 minutes. The resulted adsorbent is well depicted in Figure 1.

Chemicals and Equipment

The chemicals used in this study included synthetic acid wastewater made from pro-analytical grade $FeSO_4.7H_2O$ compounds, 0.1 M HCl and 0.1 M NaOH solutions, and filter papers. The chemical formula used in this study was of standard analytical grade and manufactured by MERCK.

Preparation of iron (II) synthetic waste solution

In this experiment, the synthetic wastewater used was made using $FeSO_4$. $7H_2O$. with a concentration of 1000 mg/L with necessary dilution.

Batch adsorption method.

In batch adsorption systems, several models describing the diffusion of solutes on the surface and in the pores of the adsorbent have been developed (film diffusion model, intra-specialized diffusion model, extra-specialized diffusion model, pore diffusion model, etc.) to explain the adsorption kinetics. However, pseudo-first-order and pseudo-second-order it has been widely used to describe the rate of Adsorption in liquid-on interactions.


(a)

(b)

(c)

Figure 1. Manufacturing process (a) calcium carbide chunks residue from welding (b) 80 mesh calcium carbide powder (c) calcium carbide tablets made into tablets with a thickness of 2 mm and a diameter of 3 mm. The average weight of the adsorbent is 0.5 g

Adsorption of Fe(II) using calcium carbide

In this research, textile wastewater used is synthetic liquid waste made from $FeSO_4.7H_2O$ compound with the following stages. The adsorption process was carried out in batches using a beaker containing 100 mL of synthetic iron (II) ion solution and 5 g calcium carbide particles at ambient temperature. The effect of pH on adsorption was evaluated by varying the pH from 2 to 10 using 0.1M HCl and 0.1M NaOH for pH adjustment and measured using a pH meter (pH-2601). Initial concentrations were set at 20, 40, 60, 80, 100 mg/L. Stirring was done using a shaker at a speed of 200 rpm for 1 hour. Samples were withdrawn at 10, 20, 30, 40, 50, and 60 minutes. After adsorption, the adsorbent was separated from the liquid using filter paper. The concentration of iron (II) ions in solution was analyzed at a wavelength of 324.7 nm with an atomic absorption spectrometer (MODEL: AA-700, Shimadzu, Japan).

Analysis of heavy metals (Fe II) adsorption

The amount of adsorbed iron (II) metal ions per mass of calcium carbide residue at a specific time (q_t) is calculated based on the formula in equation 1 (Vijayaraghavan et al., 2004):

$$q_t = \frac{(C_0 - C_t) * V}{m} \tag{1}$$

At equilibrium, q_t= q_e and C = C_t; therefore, the amount of adsorbed iron (II) ions, q_e, is calculated from:

$$q_e = \frac{(C_o - C_t)V}{W} \tag{2}$$

Calculation of the percentage removal of iron (II) ions from aqueous solution was estimated using:

$$\% R = \frac{(C_o - C_t)100}{C_o} \tag{3}$$

Where C_o, C_t, and C_e are the initial concentrations, the concentration at any time and the equilibrium concentration of the iron (II) metal ion solution (mg/L), V is the volume of the solution (L), and W is the mass of activated carbon (g).

Adsorbent Characterization

Scanning electron microscope (SEM) analysis

Scanning Electron Microscope (SEM) analysis of the sample was carried out to determine the morphological structure of the calcium carbide particles before and after Adsorption (HITACHI S-5500, Japan).

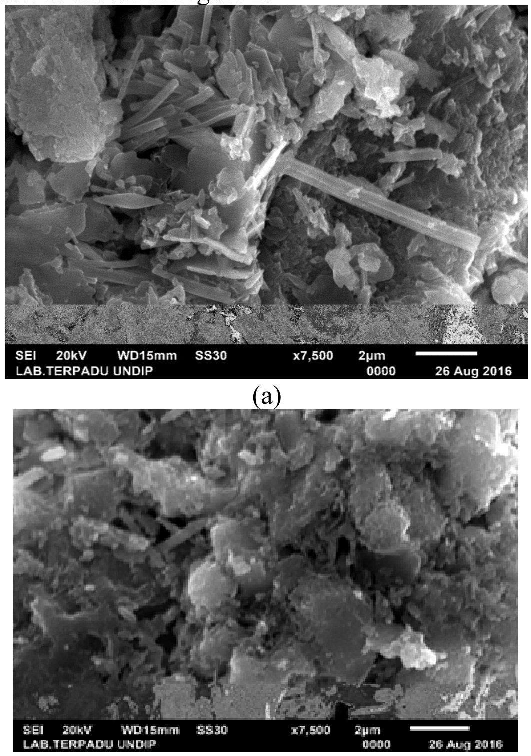
FTIR analysis.

Fourier transform infrared (FTIR) analysis of the sample was carried out to find the functional groups present on the absorbent surface using an FTIR spectroscope (Perkin Elmer Spectrum one v3.02 FT-IR Spectrometer, India).

RESULTS AND DISCUSSION

Characterization of calcium carbide as adsorbent

The morphology of the calcium carbide solid waste is shown in Figure 2.



(a)

(b)

Figure 2. Surface morphology of adsorbent particles (a) before and (b) after use

Figure 2.a shows SEM micrographs of solid waste calcium carbide before being used for the adsorption process. From the SEM micrograph, it is clear that the adsorbent surface of the calcium carbide particles is rough, uneven with several small visible pores, and the surface is clean with a number of macro pores. Hence, it is confirmed that the calcium carbide residue has many pores and cavities, so it has a high ability to absorb metal ions and is very suitable as an adsorbent.

Figure 2.b shows the results of the SEM micrograph of the surface of the calcium carbide particles adsorbent upon the adsorption of Fe (II) ions. From the SEM micrograph it can be revealed that there are pores with a rough surface with a narrow thickness between the fibers which is an important factor to facilitate the mass transfer rate of Fe (II) metal ions to the adsorbent surface so as to increase the adsorption capacity (Yilmaz et al, 2014). This observation shows that the calcium carbide particles partially lose their porosity so that their surfaces look smoother that resemble crystal-like solid, due to $Fe^{2+} = O$ bonding on the surface. As a result, the the surface of the adsorbent is enlarged and solid, the particles are densely arranged forming a nearly spherical shape. This condition indicates that the surface of the adsorbent after adsorption has a pore density, the surface structure of the adsorbent is larger and more irregular. The polarity of the residual calcium carbide adsorbent is higher, so it is better able to absorb Fe (II) ions which are also polar

Quantitative and qualitative analysis of the chemical composition of the adsorbent surface was carried out using EDX in the SEM tool. The mass percentage results obtained from the study of the chemical composition contained in the calcium carbide residue before and after being used as an adsorbent to reduce the metal ion content of Fe (II) in a batch process shown the Table 1 and Table 2.

Table (2) shows that 20.66% Fe (II) oxide (FeO) was formed after the adsorption process. This shows that the ability of solid waste calcium carbide to bind Fe (II) ions is quite good. The formation of iron oxide is influenced by several factors, including pH and the concentration of ferrous metal ions in solution. Iron oxide is formed from a solution of Fe (II) ions through the reaction of the formation of $Fe(OH)_2$ that occurs in an alkaline environment. A blackish green $Fe(OH)_2$ precipitate will appear in an alkaline environment.

Under alkaline conditions, a blackish green $Fe(OH)_2$ precipitate will occur. Precipitated Fe (II) hydroxide is formed in an alkaline environment by reaction (Vogel, 2000):

$$Fe^{2+} + 2OH \rightarrow Fe(OH)_{2\downarrow}$$

The precipitate $Fe(OH)_{2\downarrow}$ can form iron (II) oxide, FeO through the reaction:

$$Fe(OH)_{2\downarrow} \rightarrow FeO + H_2O$$

The concentration of ferrous metal ions in solution, either as Fe^{2+} or Fe^{3+} ions, can form iron oxides, depending on the ability of ferrous metal ions to react with OH^- ions in solution. The more concentrated the concentration of Fe metal ions and the more alkaline in the solution, the greater the ability to react to produce iron oxide.

Another thing that happens is the sharp removal of calcium oxide (CaO). The removal of calcium oxide (CaO) occurs because the CaO compound reacts with water to form calcium hydroxide. Calcium hydroxide which has a fairly high pH can increase the pH of the Fe ion solution, with the equation 4.5:

$$CaO(s) + H_2O\ (l) \rightarrow Ca(OH)_{2\downarrow}\ (aq)$$

Table 1. Composition of calcium carbide before the Fe (II) ion adsorption

Element	(keV)	Mass %	Sigma	Mol %	Compound	Mass %	Cation	K
C	0.277	13.84	0.20	43.35	C	13.84	0.00	8.3901
O		26.19						
Al	1.486	1.26	0.10	0.88	Al_2O_3	2.38	0.68	1.2212
Si	1.739	1.22	0.11	1.64	SiO_2	2.61	0.64	1.4394
S	2.307	0.66	0.08	0.77	SO_3	1.65	0.30	0.9410
Ca	3.690	56.84	0.43	53.36	CaO	79.53	20.79	88.008
Total		100.00		100.00		100.00	22.42	

Table 2. Composition of calcium carbide after the Fe (II) ion adsorption

Element	(keV)	Mass%	Sigma	Mol%	Compound	Mass%	Cation	K
C	0.277	27.53	0.33	66.73	C	27.53	0.00	8.3901
O		23.20						
Al	1.486	0.94	0.09	0.51	Al_2O_3	1.78	0.58	1.2212
Si	1.739	0.75	0.09	0.78	SiO_2	1.61	0.44	1.4394
S	2.307	3.94	0.18	3.57	SO_3	9.83	2.03	0.9410
Ca	3.690	27.58	0.29	20.03	CaO	38.59	11.39	88.008
Fe	6.398	16.06	0.33	8.37	FeO	20.66	4.76	
Total		100		100		100	19.20	

This causes the CaO component which is the main component in the calcium carbide residue to decrease gradually from 79.53% to 38.58%, while carbon (C) increases from 13.84% to 27.53%. For neutralization there is a reaction between sulfuric acid H_2SO_4 and calcium hydroxide $Ca(0H)_2$, as shown in reactions

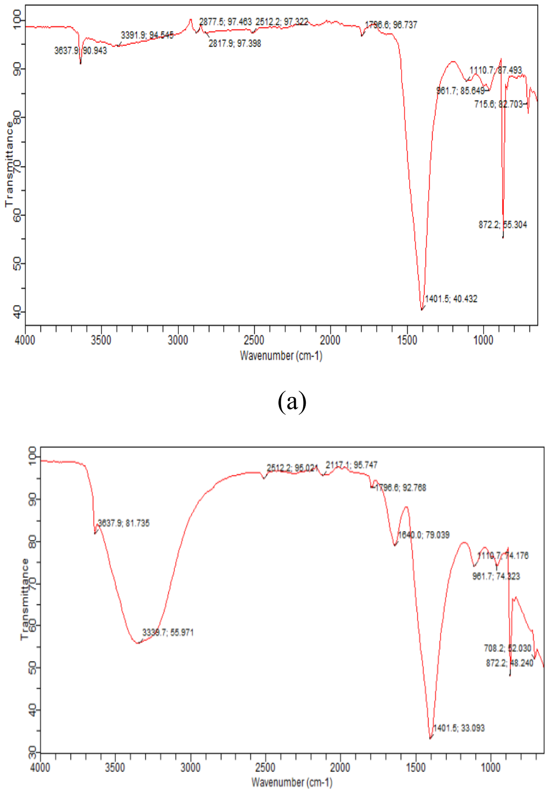
$$H_2SO_4 + Ca(0H)_2 \rightarrow CaSO_4 + 2\,H_20$$

$$CaSO_4 + 2\,H_20 \rightarrow SO_3 + Ca(0H)_2$$

From this reaction, it can be seen that there is also sulfite (SO_3) formation on the surface of the calcium carbide residue adsorbent, resulting in an increase in sulfite from 1.65% to 9.83%.

FTIR Analysis

The FTIR spectra of calcium carbide residues before and after adsorption are depicted in Figures 3. a and 3.b. Figures 3 show that all FTIR spectra contain several significant peaks that are almost similar; each type of functional group has a very close wave number range. Significant heights ranged from 2800-2900 cm^{-1}, 1500-1650 cm^{-1}, and 1000-1200cm^{-1} associated with C–H stretching of alkanes, C=C aromatic stretching, C–O–C stretching of ester vibrations, ether and phenol groups. Stretch vibrations at a bandwidth between 3400-3800cm^{-1} indicate the presence of O–H vibrations from alcohols, phenols, and carboxylic acids (Liang et al., 2010). However, the peak shifts to a lower or higher frequency level than that observed in the FTIR spectrum of the calcium carbide residue that has not been used as an adsorbent to adsorb Fe (II) ions, which can bind cations. Absorption at a wavelength of 3637.9 cm^{-1} indicates the presence of CaO (Namduri and Nasrazani, 2008). The bandwidth at the wavelength of 3391.9 cm^{-1} corresponds to the hydroxyl stretch and serves for the O–H bond.



(a)

(b)

Figure 3: FTIR spectrum of solid waste calcium carbide (a) before Adsorption & (b) after Adsorption

On the inside of the vibration, the absorption wavelength of 2877.5–2817.9 cm^{-1} is a vigorous intensity indicating the presence of C–H alkane groups. Meanwhile, at a peak bandwidth of 2512.2 cm^{-1}, it represents OH vibrations and can also be a symmetrical COO^ stretching vibration indicating the presence of a hydroxyl group (Huang and Zhu, 2013; Li et al., 2014). At the peak of the functional groups with absorption wavelengths of 1796,6 $cm^{-1}$and 1640.0 cm^{-1}, the mountains of symmetrical aromatic C=C bonds constantly change. It implies the presence of an alkene element. In Figure 4.16. and 4.17, there is a band peak as high as 633.63 cm^{-1}, indicating the presence of Fe-O groups (Rachel et al., 2015). Then the sharp peaks at 1401.5 cm^{-1} and 1110.7 cm^{-1} were caused by the Si-O strain vibration, for the height of the absorption band 961.7 cm^{-1} and 872.2 cm^{-1} associated with bending vibrations indicating the presence of Al-O groups (Vempati et al., 1996).

Contact time effect

Contact time is an essential parameter because this factor determines the adsorption kinetics of the adsorbate at a given initial concentration. Equations 1, 2, and 3 can calculate the amount of adsorbed Fe (II) metal ions per mass of solid calcium carbide residue at equilibrium (q_e). Calculations were carried out at different initial concentrations of Fe (II) ions, i.e. 20 to 100 mg/L during the adsorption process as shown in Figure 4.

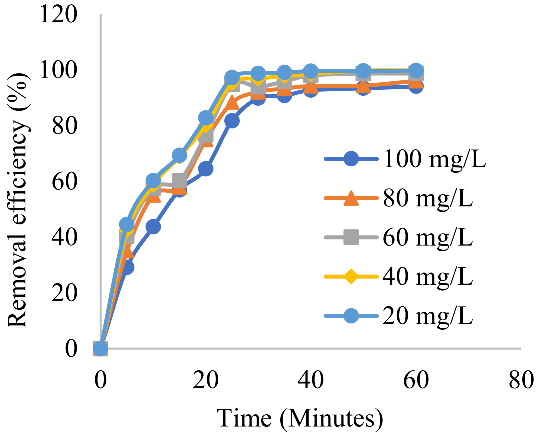


Figure 4. Percentage (%) removal of Fe (II) ions.

By using equation 3, the percentage rate of adsorption can be determined. It can be seen that in Figure 4, it shows that the percentage of Fe (II) ion adsorption quickly reaches equilibrium at a contact time of 30 minutes for a concentration of 20 mg/L. Under these conditions, the percentage of Fe (II) ion adsorption was close to 100%, indicating that Fe (II) ions were completely removed from the solution.

Experiments conducted showed that, for C_o = 100 mg/L Fe (II) ion removal increased from 29.1% to 81.7%, for C_o = 80 mg/L Fe (II) ion removal increased from 35.03%. to 88.0%, C_o = 60 mg/L the Fe (II) increased from 20.22 to 90.66%. Meanwhile, when C_o = 40 mg/L Fe (II) increased from 42.38% to 95.25% and for C_o = 20 mg/L the removal of Fe (II) ions increased from Fe (II) ions increased from 44.53% to 97.14% with variations in contact time from 5 to 25 minutes. However, at contact times from 25 to 60 min, the percentage of Fe (II) ion removal remained constant (98%), indicating that equilibrium was reached at a contact time of 25 min. Thus, these results illustrate that the optimal contact time for the maximum removal of Fe (II) ions (98%) is 30 minutes. This result is important because the equilibrium time is one of the determining parameters of an economical wastewater treatment system. The process shows that the release of Fe (II) metal ions increases with increasing contact time before equilibrium is reached. All parameters, such as adsorbent dose and solution pH were kept constant. The amount of adsorbate adsorbed per solid mass of calcium carbide residue at equilibrium (q_e) tends to increase with increasing contact time and increasing initial concentration of Fe (II) ion solution. This indicates that the ability of calcium carbide particles to adsorb metal ions Fe (II) can still be utilized up to a concentration greater than that used in this study. The adsorption capacity of calcium carbide particles to adsorb Fe (II) ions increased with increasing time the equilibrium was reached for each concentration. At low Fe (II) metal ions concentration range, the adsorption percent is high due to the availability of more reactive sites. However, at a higher concentration of Fe (II) metal ions, more surface sites have been covered, resulting in an adsorbent capacity decrease due to the less availability of active surface sites.

Effect of Initial pH on Adsorption of Iron (II) Ions.

The initial solution acidity or pH value is an essential parameter for the absorption of metal ions because it affects both the chemical properties of the adsorbent surface and the chemical properties of the dissolved metal ion solution. Usually, the acidity of the solution affects both the dissociation of the calcium carbide surface site and the condition of the chemical solution of heavy metal ions, including hydrolysis, complexation by organic or inorganic ligands, redox reactions, precipitation, speciation, and availability of heavy metal ion adsorption. Esposito et al., 2002; Wang, 2010). At a low acidity, heavy metal ions generally tend to bind to the adsorbent rather than precipitate in the form of hydroxide (Schneider et al., 2001).

The effect of the initial pH of the ferrous (II) metal ion solution on the rate of iron (II) ion adsorption at pH values of 2.5; 4.0, and 6.0 with initial concentrations (20 to 100mg/L), an adsorbent mass of 5 g and contact time of 60 minutes and temperature of 30°C are presented in Figure 5.

In Figure 5. it can be seen that the effect of increasing the initial concentration of Fe (II) ions on the percentage of removal of iron (II) ions resulted in a significant increase in the rate of removal (q_e) of iron (II) ions in synthetic acid solution by calcium carbide residues.

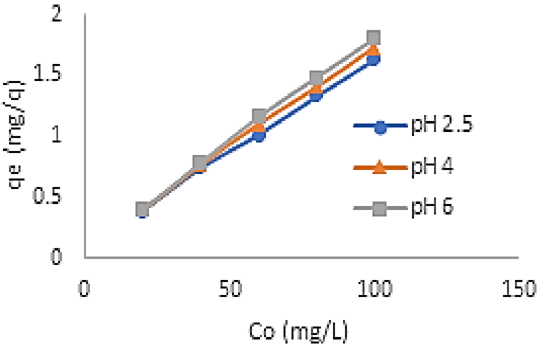


Figure 5. Effect of initial concentration of iron (II) ions at different pH on the rate of removal of iron (II) ions

The increase in the percentage of Fe (II) metal ion removal was from 0.3989 mg/g Fe (II) ion at an initial concentration of 20 mg/L to 1.8809 mg/g Fe (II) ion at a concentration of 100 mg/L. The higher the iron (II) ion solution concentration, the more iron (II) ions are absorbed. Meanwhile, the adsorption rate decreased from 99.735% to 94.048% when the concentration of iron (II) ion increased from 20 mg/L to 100 mg/L at a contact time of 60 minutes. This shows that increasing the initial concentration of iron (II) metal ions will increase the driving force and is supported by the presence of more reactive sites in the pores of the adsorbent calcium carbide residue so that Fe (II) ions will move from the outer surface to the pores of the calcium carbide residue. Micro size. Iron (II) ions can exchange cations not only on the outer surface of the adsorbent but also on the interior of the calcium carbide residue adsorbent. Equilibrium is reached when all Fe (II) metal ion exchange and cations on the outer and inner surfaces of the calcium carbide residues have been reached.

According to Wang (2008), at a high pH of the solution, the presence of H^+ ions as a competitor to metal ions will decrease because the metal ion solution is alkaline. It was further explained that the concentration of H^+ ions could accelerate the maximum metal ion adsorption. At the initial concentration of 40 mg/l, at a contact time of 5 minutes, the pH increased from 4.3 to 10.2 at a contact time of 60 minutes, and the value of q_e also increased from 0.179 mg/g to 0.798 mg/g. This means that the increase in pH and the initial concentration of iron (II) ions increased the adsorption capacity (q_e) of the calcium carbide residue adsorbent.

Effect of Residual Mass of Calcium Carbide on the Adsorption Rate of Fe (II) ions

The concentration of Fe (II) ions in acid solution with an initial concentration of 100 mg/L were adsorbed using different residual doses of calcium carbide, starting from 2.5 grams, 5.0 grams, and 7.5 g in 100 mL of iron ion (II) solution with a period of 5 to 60 minutes. The effect of the residual dose of calcium carbide on the Adsorption of iron (II) ions is presented in Figure 4.

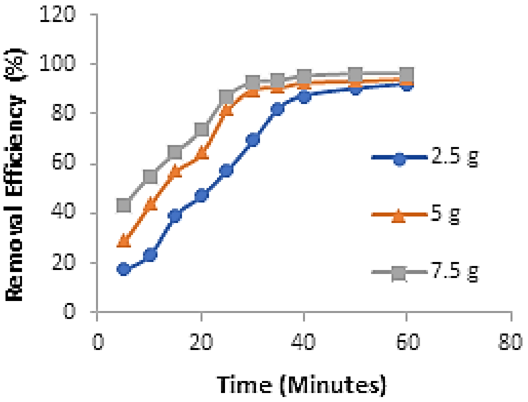


Figure 4. Effect of calcium carbide residue adsorbent mass on percent removal of Fe (II) metal ions

From Figure 4 it can be seen that there is a significant increase in the percentage of Fe (II) ion removal in the solution with an increase in the residual dose of calcium carbide at the initial concentration of Fe 100 mg/L in the adsorption contact time of 60 minutes. This is due to the increased availability of active adsorption sites arising from an increase in the effective surface area due to an increase in adsorbent dose or adsorbent conglomeration. Furthermore, it is known that increasing the amount of residual calcium carbide adsorbent can significantly increase the removal efficiency of the Fe (II)) ion concentration because it can remove more than 98% of the Fe (II) ion content in the solution. However, at a contact time of 30 minutes to 60 minutes, it was seen that the percentage of Fe (II) ion removal using calcium carbide residue adsorbent was relatively constant. This could be attributed to the fact that increasing the adsorbent dose increased the removal of Fe (II) adsorption. There are more sites for Adsorption, which leads to unsaturated adsorption sites.

ADSORPTION ISOTHERM

The mode of interaction between adsorbent molecules and metal ions and the accumulation rate were studied using an isothermal model. Equilibrium data, often called adsorption isotherms, form the basis for the design of adsorption systems, this study modeled equilibrium data using the Langmuir and Freundlich model. The Langmuir model assumes that single-layer Adsorption occurs at a finite number of uniform sites on the adsorbent (5). The linear form of the Langmuir equation, when plotted, gives a good picture of the interaction between adsorbate and adsorbent can be expressed as:

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \qquad (4)$$

where q_m is the maximum number of metal ions per unit mass, K_L is Langmuir's constant, C_e is the equilibrium concentration at time t ($C_e = C_t$), and qe is the equilibrium adsorption capacity.

The values of K_L and q_m are obtained from the plot of 1/q_e against $1/C_t$. The linear form of the Freundlich isotherm adsorption method is expressed by the Freundlich isotherm correlation describing Adsorption in a non-uniform (multilayer) system and is represented linearly as:

$$\ln q_e = \ln K_f + \frac{1}{n}(\ln C_e) \qquad (5)$$

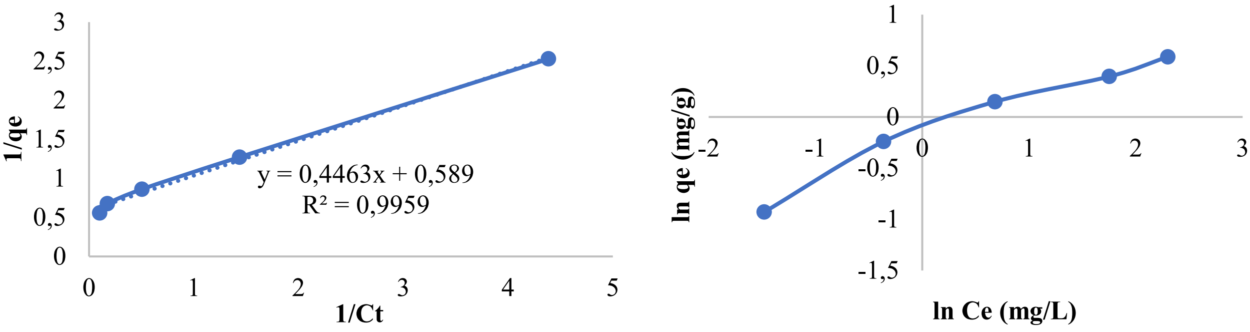
where *K, F*, and *b*, respectively, show the adsorption capacity and intensity (Freundlich's constant).

The plot of ln q_e versus ln $C_e$gives a linear graph with a slope of 1/n and an intercept K_f. The isothermic adsorption model, which shows a linear relationship between the amount of substance adsorbed per gram of adsorbent calculated using the Langmuir equation and the Freundlich equation, can give the result that both can be applied to the Fe (II) ion adsorption process using calcium carbide residue as shown in Figure (6).

Figure 6 A. shows that the plot of $1/q_e$ against $1/C_e$ from experimental data at a contact time of 25 minutes, Langmuir isothermic adsorption to adsorb Fe (II) ions with a residual mass of calcium carbide 5 g, shows a straight line so that the constant can be calculated. Langmuir model (Table 3).

In Table 3. The Langmuir isothermic adsorption equilibrium for the adsorption of Fe (II) ions gives a straight line. This means that the obtained linearization matches the experimental results as expressed by the value of the correlation coefficient, R^2, which ranges from 0.95 to 0.99. The adsorption capacity generally increases as the pH of the initial solution increases. The maximum adsorption capacity of iron (II) ions, q_{max}, which represents the mono-layer coverage of the adsorbent with adsorbate according to the Langmuir model, occurred at pH 6 of 1.697mg/g.

Meanwhile, the maximum adsorption capacity, q_{max} of iron (II) at pH 4 was 1.341mg/g and the maximum adsorption capacity at pH 2.5, q_{max} of iron (II), was 1.317 mg/g. This means that the calculation of the adsorption capacity of ferrous metal ions (II) is suitable using the Langmuir Model, which effectively and significantly provides a correlation coefficient value (R^2) > 0.95.



(a) (b)

Figure 6. (a) Langmuir and (b) Freundlich adsorption isotherms for Fe (II) adsorption on calcium carbide residue.

Table 3 Langmuir and Freundlich isotherm constants for the adsorption of Fe (II) ions using calcium carbide residue adsorbent.

Metal	Initial pH	Langmuir Constants			Freundlich Constants		
		q_e (mg/g)	K_L (1/mg)	R^2	K_F (1/mg)	1/n	R^2
Ion Fe (II)	2.5	1.317	0.714	0.9541	0.182	0.394	0.983
	4.0	1.341	1.527	0.9514	0.590	0.363	0.997
	6.0	1.697	1.319	0.9959	0.350	0.383	0.963

The results of observations and calculations showed that when the initial pH of the solution was increased, the adsorption capacity of the calcium carbide residue also increased. The calculation results obtained show that the Langmuir model for isothermic Adsorption at pH = 6 is received by the equation $\boldsymbol{q_{e=}\frac{2.234C_e}{1.319C_e+1}}$. In contrast, the isothermic Adsorption of the Freundlich model occurs at pH 4 with the equation $\boldsymbol{q_e = 0.59C_e^{0.383}}$. This means that the isothermic adsorption pattern in the absorption of Fe (II) metal ions by the residual calcium carbide adsorbent follows the isothermic pattern of the Langmuir model and the isothermic design of the Freundlich model. This is because the active site on the surface of the calcium carbide residue adsorbent is heterogeneous, and the Adsorption occurs in a mono-layer surface layer.

Kinetic Model

In order to determine the mechanism of the Fe (II) ion removal process using calcium carbide solid waste adsorbent, various mechanisms controlling the adsorption process (chemical reactions, mass transfer, etc.), pseudo-first-order and pseudo-second-order Langergreen correlations were used to test the experimental data. The integral of Langergreen 's pseudo-first-order equation is given as:

$$\frac{dq_1}{dt} = k_1(q_e - q_t) \tag{6}$$

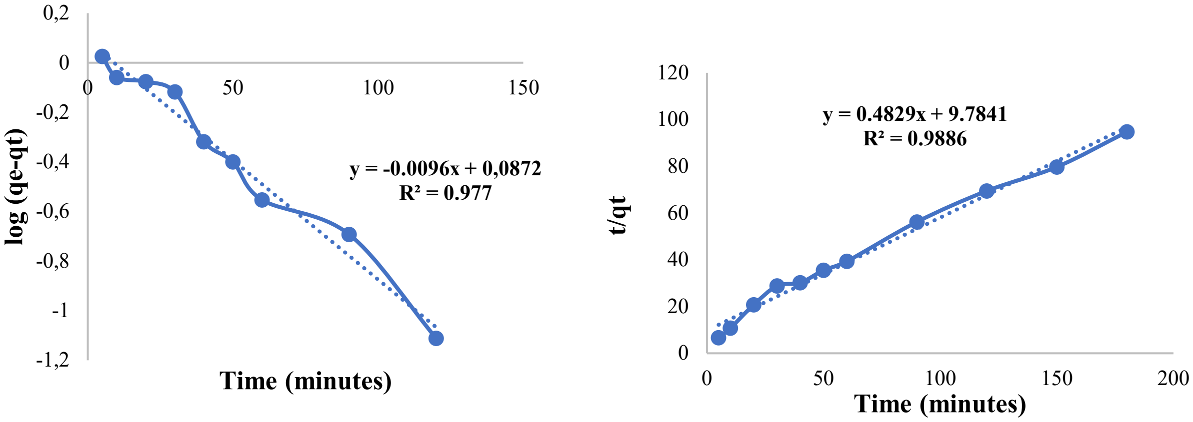
The q_e (mg/g) is the amount of Fe (II) ion adsorption per gram of adsorbent at equilibrium, q_t (mg/g) is adsorption capacity at time t (min) and k_1 (min-1) is the constant rate for kinetic model at the pseudo-first-order level. In linear form, the pseudo-first-order kinetic model can be expressed in equation 7.

$$\log(q_e - q_t) = \log q_e - \frac{K_1 t}{2.303} \tag{7}$$

where q_e is the amount of adsorbate adsorbed on the adsorbent at equilibrium, qt is the amount of adsorbate adsorbed on the adsorbent at that time, and k_1 is the pseudo-first-order Adsorption constant.

Figure (7) shows Langergreen's pseudo-first-order correlation plot for the adsorption of iron (II) from textile industrial waste at an initial concentration of 100 mg/L using calcium carbide residues with variations of 2.0 g, 5.0 g, 7.5 g. with a contact time of 5 to 180 minutes. The kinetic parameters for the adsorption process (pseudo first-order rate constant, k_1 can be obtained from the log plot of the gradient $(q_e - q_t)$ about t

Table 4 shows that the adsorption process for ferrous metal ions (II) takes place according to a pseudo-second-order kinetic model with a correlation coefficient (R^2) which is close to one, respectively, 0.9962 for an adsorbent mass of 7.5 grams; 0.9877 for an adsorbent mass of 5.0 g; and 0.9696 for an adsorbent mass of 2.0 g.



(a) (b)

Figure 7. (a) First-order pseudo adsorption kinetics and (b) second-order pseudo adsorptions

Table 4 Linear equation of Fe (II) ion adsorption kinetics model and correlation value (R^2)

Massa adsorbent (g)	First-order pseudo kinetic model				Pseudo-second order kinetic Model			
	Linear equation	q_e	R^2	k_1	Linear equation	q_e	R^2	k_2
2.0	y = -0.0095x + 0.5572	3.608	0.966	0.0218	y = 0.1867x + 6.9494	5.353	0.9696	0.0050
5.0	y = -0.0096x + 0.0872	1.222	0.977	0.0221	y = 0.4829x + 9.7841	2.071	0.9886	0.0243
7.5	y = -0.0120x – 0.0731	0.845	0.846	0.0276	y = 0.7436x + 7.2334	1.345	0.9962	0.0764

These conditions indicate that the more abundant the residual calcium carbide adsorbent will increase the value of the adsorption constant (k_2). However, there is an allowance for the value of q_e. Thus, the adsorption kinetics model that occurs in the Fe (II) metal ion adsorption process in a synthetic waste solution by the calcium carbide residue adsorbent is a pseudo-second-order kinetics model, which means that the mass of the adsorbent affects the reaction rate.

CONCLUSION

The results obtained in the process of removing Fe (II) ions using a solid waste calcium carbide adsorbent using a batch adsorption process are concluded as follows. Calcium carbide solid waste is suitable to be used as an adsorbent to reduce the concentration of Fe (II) ions, with an optimal time of 60 minutes, where there is a decrease of 99.728% for the initial concentration of 40 mg/L by 99.246% for the initial concentration of 60 mg/L, amounting to 98.766 % for the initial concentration of 80 mg/L, 98.836% for the initial concentration of 100 mg/L, and can increase the pH from pH 2.5 to 11.8.

The process of adsorption of Fe (II) ions by solid waste calcium carbide can follow the Langmuir isotherm adsorption model and Freundlich isotherm. The best adsorption process occurred at a contact time of 25 minutes, with the highest R^2 value of 0.9933 for the Langmuir isotherm equation and 0.9726 for the Freundlich isotherm equation. The results of calculations using the Langmuir isotherm adsorption model equation obtained: $\boldsymbol{q_{e=}\frac{1.1764C_e}{0.719C_e+1}}$. The results of calculations using the Freundlich isotherm adsorption model equation is obtained: $\boldsymbol{q_e}$ = 2,6705$\boldsymbol{C_e^{3.6296}}$.

The adsorption kinetics of Fe (II) ion in calcium carbide solid waste corresponds to pseudo-first order adsorption kinetics with adsorption rate constants k_1 = 0.0756 and R^2 = 0.9842 for an initial concentration of 100 mg/L, it is seen that the value of qe continues to increase. In line with the increase in the pH value from pH 2.5 to pH 12.8, the trend of an increase in the price of qe is still visible. The optimum interaction time occurred in the 25th minute which indicated the number of Fe (II) ions adsorbed per gram of calcium carbide solid waste with q_e values of 1.580 mg/L and 1.977 mg/L, respectively.

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