



**Study of Preparation and Properties of Gelatin/ Activated Carbon
Bead Form for Rhodamine B and Lead (II) Ions Adsorption**

Fareeda Hayeeye

**A Thesis Submitted in Fulfillment of the Requirements for the
Degree of Doctor of Philosophy in Chemistry
Prince of Songkla University
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Thesis Title Study of Preparation and Properties of Gelatin/ Activated
Carbon Bead Form for Rhodamine B and Lead (II) Ions
Adsorption

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I hereby certify that this work has not been accepted in substance for any degree, and is not being currently submitted in candidature for any degree.

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ชื่อวิทยานิพนธ์	ศึกษาการเตรียม และสมบัติของตัวดูดซับเชิงประกอบจาก เจลาติน/ ถ่านกัมมันต์ สำหรับการดูดซับสีย้อมโรดามีนบี และ ตะกั่ว
ผู้เขียน	นางสาวพาริดา หะยีเย๊ะ
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บทคัดย่อ

งานวิจัยนี้ได้ศึกษาการเตรียมตัวดูดซับเชิงประกอบจากเจลาติน (GE) และผงถ่านกัมมันต์ (AC) โดยขึ้นรูปในรูปแบบเม็ดเพื่อใช้ในการดูดซับสารพิษจากสารละลาย โดยเม็ด GE/AC ที่เตรียมได้ มีความสะดวกและง่ายต่อการใช้งานมากกว่า AC อีกทั้งยังมีประสิทธิภาพในการดูดซับสารละลายสีย้อมโรดามีนบี และ โลหะตะกั่วจากน้ำเสียสูงกว่าถ่านกัมมันต์แบบเม็ด (GAC) ทั่วๆไป

แผนงานวิจัยที่ 1 ได้ทำการเตรียมและศึกษาคุณสมบัติเฉพาะตัวของ GE/AC ซึ่งเป็น ตัวดูดซับแบบเม็ดที่มีประสิทธิภาพ สำหรับใช้ในการดูดซับที่ pH และ อุณหภูมิต่างๆกัน โดย อัตราส่วนมวลที่เหมาะสมในการขึ้นรูปแบบเม็ดของ AC : GE คือ 1 : 9 และจากภาพถ่ายอิเล็กตรอนแบบส่องกราด (SEM image) แสดงให้เห็นว่าเม็ด GE/AC ที่เตรียมได้เป็นทรงกลมขนาดใกล้เคียงกัน โดยมีเส้นผ่านศูนย์กลางประมาณ 4 มิลลิเมตร และจากผลการวิเคราะห์ค่าพื้นที่ผิวจำเพาะ (BET Surface area) พบว่าเม็ด GE/AC มีพื้นที่ผิว 34.75 ตารางเมตรต่อกรัม ซึ่งสูงกว่า GAC ทั่วๆไป นอกเหนือจากนี้จากผลการวิเคราะห์การหาค่า pH ที่ผิวเป็นศูนย์ (Point of zero charge, pH_{pzc}) โดยวิธี pH drift พบว่าค่า pH_{pzc} ของ GE/AC เท่ากับ 4.5

แผนงานวิจัยที่ 2 ได้ทำการศึกษาจลนศาสตร์ในการดูดซับของสารละลายสีย้อมโรดามีนบี และ โลหะตะกั่ว บนเม็ด GE/AC จากผลทางจลนศาสตร์พบว่าการดูดซับสารละลายสีย้อมโรดามีนบี และ โลหะตะกั่ว สอดคล้องกับการดูดซับแบบอันดับสองเทียม (pseudo-second-order) นอกจากนี้รูปแบบการดูดซับสารละลายสีย้อมโรดามีนบี และ โลหะตะกั่ว สอดคล้องกับแบบจำลองการดูดซับของแลงเมียร์ (Langmuir adsorption isotherm) และปริมาณการดูดซับสูงสุดของสารละลายสีย้อมโรดามีนบี และ โลหะตะกั่ว คือ 250.41 และ 370.37 มิลลิกรัมต่อกรัม ตามลำดับ จากผลการทดลองทั้งหมดแสดงให้เห็นว่า เม็ด GE/AC ที่เตรียมได้ สามารถใช้งานได้ง่ายกว่า AC และ ค่าปริมาณการดูดซับสารละลายสีย้อมโรดามีนบี และ โลหะตะกั่ว สูงสุด มีค่าสูงกว่า GAC ทั่วๆไป

Thesis Title	Study of Preparation and Properties of Gelatin/Activated Carbon Bead Form for Rhodamine B and Lead (II) ions Adsorption
Author	Miss Fareeda Hayeeye
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Abstract

The adsorbent from the gelatin (GE) and the powdered activated carbon (AC powder) in GE/AC bead form was prepared for the removal of pollutants from aqueous solution. The advantage of the GE/AC bead are easy handle than that one of AC powder and was higher adsorption capacity than that one of typical granular AC, in the removal of Rhodamine B and Pb^{2+} ions from waste water.

Strategy I: Preparation and characterization of GE/AC beads as an efficient granular adsorbent for adsorption at various pH and temperatures. The optimal weight ratio of AC and GE for the formation of GE/AC bead is 1: 9. By scanning electron microscopy (SEM), the result showed that the GE/AC bead is spherical with nearly equal size about 4 μ m. The BET surface area of GE/AC bead is $34.75 \text{ m}^2 \text{ g}^{-1}$ which is higher than some granular AC. Moreover, the result from the pH drift method presented that the point of zero charge (pH_{pzc}) of GE/AC beads is 4.5.

Strategy II: The kinetic studies of Rhodamine B and Pb^{2+} ions adsorption using GE/AC beads. The results from the kinetic of both adsorption data were best fitted with the pseudo-second-order model. Moreover, the adsorption isotherm of Rhodamine B and Pb^{2+} ions by GE/AC beads was the best fit by the Langmuir model, which predicted the maximum adsorption capacities are of 256.41 and 370.37 mg g^{-1} for Rhodamine B and Pb^{2+} ions, respectively. The experimental results showed that GE/AC beads are more convenient to use than AC powder and has higher adsorption capacity than typical granular AC, in the removal of Rhodamine B and Pb^{2+} ions from waste water.

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List of Abbreviations

AC	Activated carbon
GE	Gelatin
GE/AC bead	Gelatin/ Activated carbon composite bead form
GA	Glutaraldehyde
q_e	The amount of solute adsorbed per unit weight of adsorbent (mg g^{-1})
q_m	The amount of maximum adsorption capacity (mg g^{-1})
C_e	The equilibrium solute concentration conditions (mg L^{-1})
b	The Langmuir constant
K_F and n	The Freundlich constant
k_1	The rate constant of pseudo-first order model
k_2	The rate constant of pseudo-second order model
t	Time
ΔH°	Enthalpy
ΔS°	Entropy
ΔG°	Gibb's free energy
K_c	The ratio of C_A and C_e
R	The universal gas constant
T	The absolute temperature (K)

List of Publications

This thesis contains general summary (introduction, background information and conclusion) and the following papers which are referred indicated by their roman number.

Paper I **Hayeeye, F.,** Sattar, M., Chinpa, W. and Sirichote, O. (2017). Kinetics and thermodynamics of Rhodamine B adsorption by gelatin/activated carbon composite beads. *Colloids and Surfaces A: Physicochem. Eng. Aspects*, 513, 259–266.

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Paper II **Hayeeye, F.,** Yu, Q.J., Sattar, M., Chinpa, W. and Sirichote, O. (2017). Adsorption of Pb^{2+} ions from aqueous solutions by gelatin/ activated carbon composite bead form. *Adsorption Science & Technology*.

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Paper I

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1. Introduction

1.1 Background and rationale

Waste water streams from many activities in agriculture and industries such as chemical industry and mining metal processing contain dye, for example basic dye, anionic dye and reactive dye for heavy metals such as lead, copper and cadmium. They are generally toxic to environment and human health.

One of the most basic dye was used in factory is Rhodamine B. It is suspected to be carcinogenic and thus products containing it must contain a warning on its label (Ashly, et al., 2014). Moreover, the wastewater containing Rhodamine B was quite stable, which makes it difficult to biodegrade because of the complex aromatic structures of dyes. Thus, the extensive uses of dyes cause not only a severe public health concern but also many serious environmental problems (Shi, et al., 2014). Therefore, the removal Rhodamine B from waste water is very important because it takes effect to public health, aquatic life and ecosystem.

In parts of Pb^{2+} ions, pollution of the environment by Pb^{2+} ions is serious problem because of their toxic effects on human health and living organism. Pb^{2+} ions do not degrade into harmless end products and tend to accumulate in living organisms, causing various diseases and disorders. Lead and its compounds even at low concentration are poisonous to animals and humans. A lead concentration 0.006 mg L^{-1} in blood can damage the fatal brain, cause diseases of kidneys, circulatory system, and nervous system (Chuah, et al., 2005). Pb^{2+} ions contamination in water and wastewater is the result from many industries such as metal plating, mining, tanneries etc. (Zhang, et al., 2005 and Cay, et al., 2004). Therefore, it is also necessary to treat heavy metal-contain wastewater prior to its discharge to the environment.

Adsorption of dyes and heavy metal by activated carbon (AC) has been widely utilized as AC is one of the most effective adsorbent for heavy metal ions and organic substances. AC has very high surface area and porous structure, high capacity and high rate of adsorption (Sirichote, et al., 2008). There have been several reports that activated carbon can be used to adsorb Rhodamine B. These include activated

carbon prepared from the steel and fertilizer industries (Bhatnagar, et al., 2005) , pericarp of rubber fruit (Hayeeye, et al., 2014), thespusia populinia bark (Hema, et al., 2009), walnut shell (Sumanjit, et al., 2008), bagasse pith (Hamdi, et al. 2008), an indigenous waste (Arivoli, et al., 2008) and tamarind fruit shells (Edwin, et al., 2008). However, AC in fine powder form limits to its usage. Therefore, studies on the adsorption of Rhodamine B by granular AC have been also reported in the literature. Granular AC prepared from various materials such as cationic surfactant (hexadecyltrimethyl ammonium chloride) modified bentonite clay (Anirudhan, et al., 2015), oil palm empty fruit bunch AC (Manase, 2012) , black tea leaves pecan shell (Mohammad, et al., 2012), formaldehyde treated parthenium carbon (WC) and phosphoric acid treated parthenium carbon (PWC) (Hem, et al., 2009).

Moreover, there have been several reports that activated carbon can be used to adsorb heavy metal ions. These include activated carbon prepared from apricot stone (Kobyra, et al., 2005), date stones (Jamal, et al., 2013), coconut shell (Jyotsna, et al., 2004) and walnut wood (Ghaedi, et al., 2015). However, AC in fine powder form limits to its usage. Therefore, studies on the adsorption of Pb^{2+} by granular activated carbon have been also reported in the literature. Granular activated carbon prepared from various low-cost materials such as walnut shell (Kima, et al., 2001), pecan shell (Bansode, et al., 2003), peanut shells (Wilson, et al., 2006), coconut shell (Jyotsna, et al., 2005), red mud (Zue, et al., 2007) and cherry stones (Jaramillo, et al., 2009) have been studied, however, the maximum adsorption capacity of granular activated carbon is generally lower than that of powder activated carbon.

Therefore, in this study the combination of gelatin (GE) and AC powder in the formation of gelatin/activated carbon composite bead form (GE/AC bead) as an effective granular adsorbent for the adsorption of pollutants from aqueous solutions was interesting. Because it is a good material for making a bead form due to this biodegradable polymer was derived from collagen obtained from various animal by-products; in this work used the commercial GE which made from peptone primagen of animal tissue and was easy to make an adsorbent in bead form by basic method.

1.2 Objective of this research

The objective of this work is to develop the granular adsorbent performances for adsorption applications. The GE/AC beads were firstly prepared at different weight ratios of GE and AC and then were characterized to obtain the optimized ratio of the GE and the AC for adsorption study. These GE/AC beads were used to study adsorption of Rhodamine B dye and Pb^{2+} ions as follows.

1.2.1 The effects of GE/AC dose, contact time, and pH on the adsorption of Rhodamine B were studied to optimize the experimental controlling conditions. The kinetic models and adsorption isotherms of Rhodamine B were then investigated. Moreover, the study of thermodynamic parameters (enthalpy, entropy and Gibb's free energy) of Rhodamine B sorption on GE/AC beads was calculated at various temperatures (**Paper I**).

1.2.2 The adsorption of Pb^{2+} ions at various GE/AC dose, contact time, and pH was studied to optimize the experimental controlling conditions of Pb^{2+} ions. Also, the kinetic model and adsorption isotherm of Pb^{2+} ions have been studied (**Paper II**).

2. Preparation of GE/AC beads

2.1 Materials

2.1.1 Activated carbon (AC)

AC is used in a wide range of applications that include medicinal uses, gas storage, pollutant and odour removal, gas separations, catalysis, gas purification, metal extraction, water purification, chromatographic separation, chemical purification, trapping mercury, fuel cells and many other applications. Carbon adsorption has numerous applications in industrial processes such as spill clean-up, groundwater remediation, gold recovery, drinking water filtration, air purification, volatile organic compounds removal, gasoline dispensing operations, colour/odour correction in wines and fruit juices and additive in liquor ice and other processes (Kennedy, et al. 2011)

AC is classified in many ways, although a general classification can be made based on their size, preparation methods, and industrial applications which can be classified 5 categories: powdered, extruded, impregnated, polymers coated and granular AC. Granular AC are irregular shaped particles with sizes ranging from 0.2 to 5 mm which has a relatively larger particle size compared to powdered activated carbon and consequently, presents a smaller external surface. Granular AC which is an adsorbent derived from carbonaceous raw material, is used for water treatment, deodorization and separation of components of flow system. This type is used in both liquid and gas phase applications (TIGG Corporation, 2012). Many researches showed the maximum adsorption capacity of granular AC is lower than powder activated carbon. These have stimulated the developing the granular AC as an effective GE/AC adsorbent in bead form by using AC powder (Figure 1) compacted with GE for removal of Rhodamine B and Pb^{2+} ions in aqueous solutions. Evaluation and optimization of the experimental controlling conditions such as GE/AC dose, contact time and pH were carried out experimentally. The kinetic models and adsorption isotherms of Rhodamine B and Pb^{2+} ions on GE/AC composite bead form were also investigated.



Figure 1 The powder activated carbon

2.1.2 Gelatin (GE)

The light brown powder GE is a natural biodegradable as shown in Figure 2. The chemical structure of GE causes GE to dissolve in water as shown in Figure 3. The GE forms in a biodegradable film is flexible and transparent. GE structures have functional groups such as hydroxyl groups, amide groups and carbonyl groups (Ninan, et al., 2014). The functional properties of GE depend on their molecular weight distribution and the amino acid composition (See, et al., 2010).

GE is a protein derived by partial hydrolysis of animal collagen such as fish scales bone tissue and intestinal parts from cattle buffalo and pigs by heat or acids. During the thermal hydrolysis of collagen the cross-linkages between polypeptide chains bonds of the collagen along with some amount of polypeptide chain bonds are broken down (Yang, et al., 2008). The hydrolysis results in the reduction of protein fibrils into smaller peptides, which will have broad molecular weight ranges associated with physical and chemical methods of denaturation, based on the process of hydrolysis as shown in Figure 4.



Figure 2 GE powder

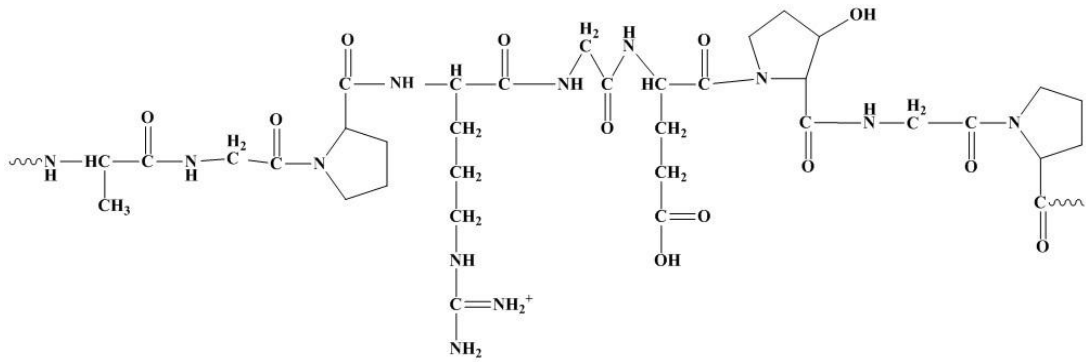


Figure 3 The chemical structure of GE

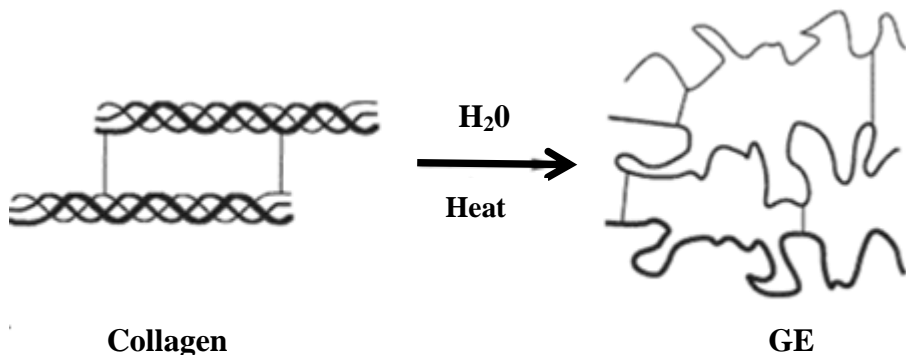


Figure 4 Preparation of GE (Kettle, 2016)

GE can be dissolved in hot water, and sets to a gel on cooling. When added directly to cold water, it does not dissolve well. However, it is also soluble in most polar solvents. GE swells in water and absorbs 5-10 times its weight of water to form a gel in aqueous solutions between 30-35°C (NOSB TAP Review, 2002). The melting point of the gel depends on GE grade and concentration but is typically less than 35 °C and the lower than freezing point, GE is become ice crystallizes.

To avoid the solubility of gelatin in the aqueous solution during adsorption study, the bead form of GE/AC were immersed in 1% v/v of glutaraldehyde (GA) aqueous solution for overnight to crosslink.

2.2 The ratio of GE solution and AC powder of GE/AC beads

The effect of GE and AC ratio and GA concentrations on the adsorption study was studied to optimize the ratio of GE and AC for preparation of bead form with high adsorption capacity. The composition of GE, AC and GA are listed in Table 1.

In this research, the optimal weight ratio of GE: AC is 9: 1 for forming GE/AC beads. After the formation of GE/AC beads, they were filtered and immersed in 1% v/v of GA aqueous solution for overnight to crosslink. Finally, the obtained GE/AC beads were dried at 60 °C for 6 h. Their characterizations were investigated by SEM, BET surface area and EDX: energy dispersive x-ray spectroscopy. Moreover, the kinetic models and adsorption isotherms for Rhodamine B and Pb²⁺ ions adsorbed by GE/AC beads were studied.

Table 1 The ratio of GE solution and AC Powder for preparation of GE/AC beads

GE Solution (% wt./wt.)	GE solution (g)	AC powder (g)	The GE/AC bead form	
			GA 0.5 % v/v	GA 1.0 % v/v
10	7	1	✗	✗
	8	1	✗	✗
	9	1	✗	✗
20	7	1	✗	✗
	8	1	✗	✗
	9	1	✗	✗
30	7	1	✗	✗
	8	1	✗	✗
	9	1	✗	✓

2.3 Characterization of GE/AC bead

Figure 5 shows the morphology of the GE/AC bead using SEM. The result in Figure 5(a) presented that the GE/AC beads are spherical with nearly equal size (diameter of 4 mm). It was also found that the adsorbent bead has a rough surface (Figure 5(b)). The higher magnification of GE/AC beads are shown in Figure 5(c) and 5(d), respectively, it can be seen clearly that there are many pores on the surface and internal cross-section of bead. This porous structure may affect the Rhodamine B sorption efficiency (**Paper I**).

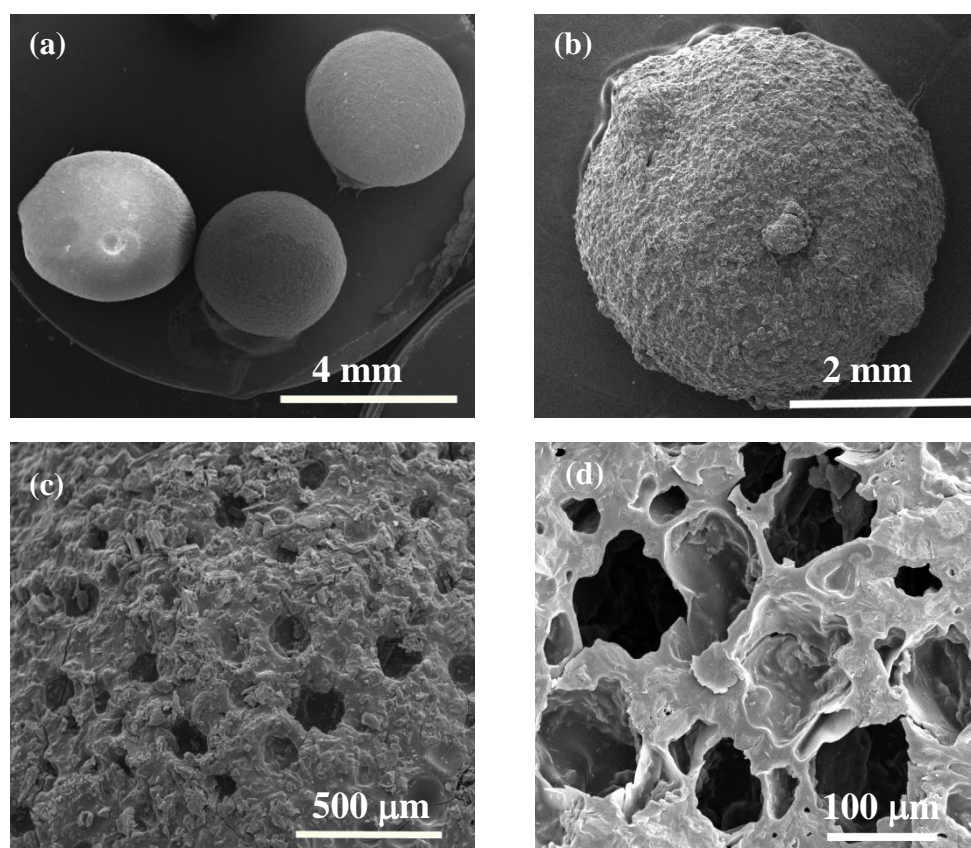


Figure 5 SEM images of GE/AC bead in magnitude (a) $\times 12$, (b) $\times 25$ and (c) surface and (d) a cross-section.

The elemental components for GE/AC bead were detected by SEM/EDX using a standard less qualitative EDX analytical technique. The peak heights in the EDX spectra are proportional to the elemental concentrations. The qualitative spectra for GE/AC bead are shown in Figure 6 indicated that C, N, and O are the main constituents (**Paper II**).

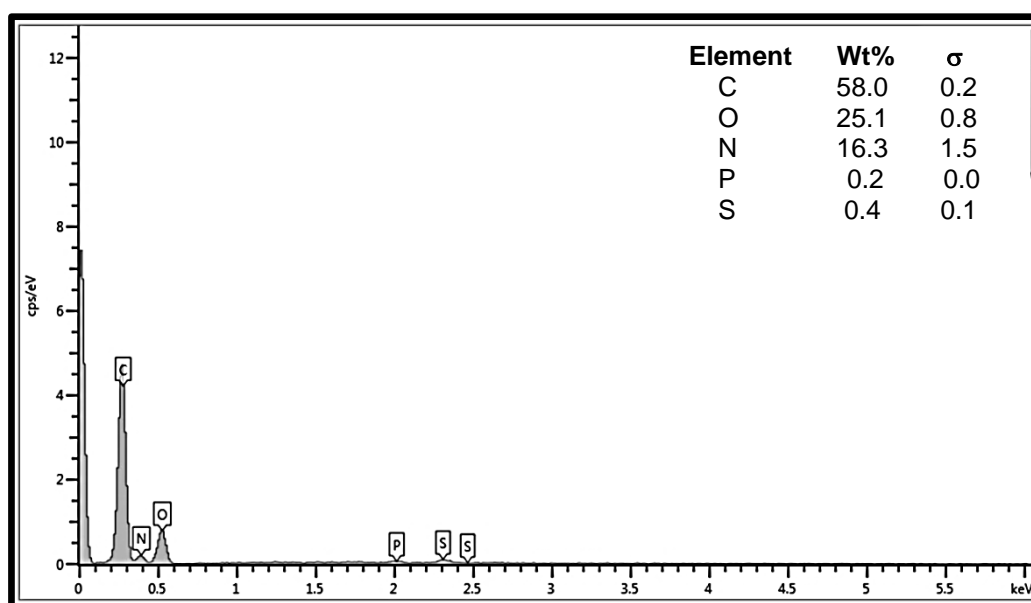


Figure 6 SEM/EDX spectra of GE/AC bead

By BET surface area measurement, the narrow pore size distribution and its average pore diameter of 3.25 nm were found for GE/AC bead. This result indicated that this bead adsorbed was in mesoporous scale (2 – 50 nm). The specific surface area for GE/AC bead is $34.75 \text{ m}^2 \text{ g}^{-1}$. The point of zero charge of GE/AC bead is 4.5 indicated that the surface nature of GE/AC is acidic as shown in Table 2 (**Paper I**).

Table 2 Characteristics of GE/AC bead and BET surface area of granular adsorbent from literature data.

Sample	BET surface area (m ² g ⁻¹)	Total pore volume (cm ³ g ⁻¹)	Average pore diameter (nm)	pH _{pzc}
GE/AC bead (This study)	34.75	0.028	3.25	4.5
AC from granular red mud (Zue, et al., 2007)	15.28	-	-	-
AC from calcined alunite (Özacar, et al., 2002)	26.40	-	-	-

3. Adsorbate for adsorption study on GE/AC beads

3.1 Rhodamine B

Rhodamine is a family of related chemical compounds, fluorone dyes. Examples are Rhodamine 6G and Rhodamine B. They are used as a dye and as a dye laser gain medium. It is often used as a tracer dye within water to determine the rate and direction of flow and transport. Rhodamine dyes fluoresce and can thus be detected easily and inexpensively with instruments called fluorometers. Rhodamine is used extensively in biotechnology applications such as fluorescence microscopy, flow cytometry; fluorescence correlation spectroscopy and Enzyme-linked immunosorbent assay (ELISA). Rhodamine is generally toxic, and is soluble in water, methanol and ethanol. The structure of Rhodamine is shown in Figure 7.

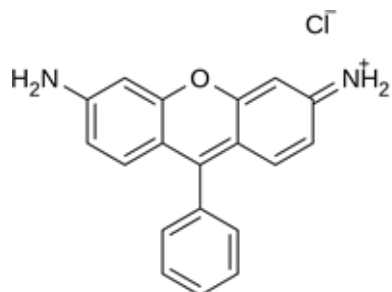


Figure 7 The structure of Rhodamine

The structures of Rhodamine 6G and Rhodamine B in aqueous solution are displayed below in Figure 8 (a) and (b), respectively.

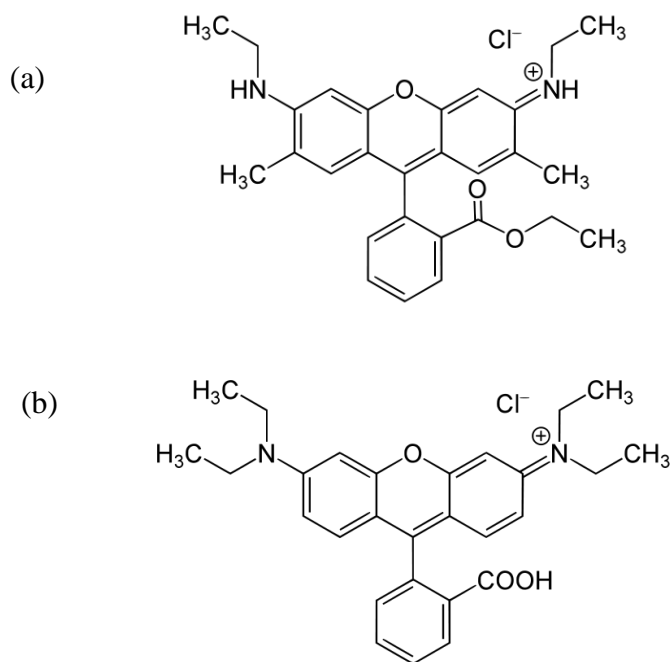


Figure 8 Structure of Rhodamine 6G (a) and Rhodamine B (b).

Properties of Rhodamine B

IUPAC name:	[9-(2-carboxyphenyl)-6-diethylamino-3-xanthenylidene]-diethylammonium chloride
Other names:	Rhodamine 610, C.I. Pigment Violet 1 or Basic Violet 10
Molecular formula:	$C_{28}H_{31}ClN_2O_3$
Molar mass:	479.02 g mol ⁻¹
Appearance:	Red to violet
Melting point:	210 - 211 °C (Decomposes)
Classification of dye:	Basic dye

Rhodamine B is cationic dye, water solubility in water is ~50 g L⁻¹. It mainly applied to acrylic fibers, but finds some use for wool and silk. Usually acetic acid is added to the dye bath to help the uptake of the dye onto the fiber. Basic dyes are also used in the coloration of paper. Discharges of Rhodamine B in natural waters can cause environmental degradation. In California, Rhodamine B is suspected to be carcinogenic, so products containing it must present a warning on the label (Ashly, et al., 2014). In this thesis, (**Paper I**) Rhodamine B, which was selected as a representative of the common cationic dyes in effluents from textile and food industries, from wastewater.

(a)



(b)



Figure 9 (a) Rhodamine B powder and (b) Rhodamine B solution

3.2 Lead (II) nitrate (Pb(NO₃)₂)

Lead (II) nitrate is an inorganic compound. It commonly occurs as a colorless crystal or white and unlike most other lead (II) salts, is soluble in water as shown in Figure 11. Lead (II) nitrate is the only common soluble lead compound. It readily dissolves in water to give a clear, colorless solution (Ferris, et al., 1959). As an ionic substance, the dissolution of lead (II) nitrate involves dissociation into its constituent ions. $\text{Pb}(\text{NO}_3)_2 (\text{s}) \rightarrow \text{Pb}^{2+} (\text{aq}) + 2 \text{NO}_3^- (\text{aq})$

Properties of Lead (II) nitrate

IUPAC name:	Lead (II) nitrate
Other names:	Lead nitrate, Lead dinitrate, Plumbous nitrate
Molecular formula:	Pb(NO ₃) ₂
Molar mass:	331.2 g mol ⁻¹
Appearance:	White colorless crystals
Melting point:	270 °C (Decomposes)

Lead (II) nitrate is toxic, an oxidizing agent, and is categorized as probably carcinogenic to humans. Consequently, it must be handled and stored with the appropriate safety precautions to prevent inhalation, ingestion and skin contact. Due to its hazardous nature, the limited applications of lead (II) nitrate are under constant scrutiny. They have been linked to renal cancer and glioma in experimental animals and to renal cancer, brain cancer and lung cancer in humans (World Health Organization, 2006) Hence, the removal of Pb²⁺ ions from aqueous solutions was applied in **Paper II**.

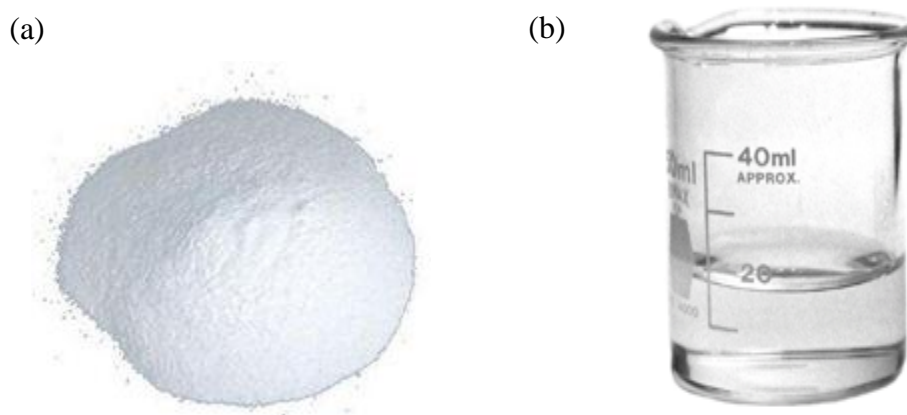


Figure 10 (a) $\text{Pb}(\text{NO}_3)_2$ powder and (b) $\text{Pb}(\text{NO}_3)_2$ solution

4. Adsorption study

Adsorption is present in many natural, physical, biological, and chemical systems, and is widely used in industrial applications such as activated charcoal, capturing and using waste heat to provide cold water for air conditioning and other process requirements (adsorption chillers), synthetic resins and increase storage capacity of carbide-derived carbons. Moreover, this process is commonly used to adsorb toxins in the environment in particular. The wastewater treatment plant of industries such as food, dyes, textiles, paper and plastic is use adsorption process which has a highly effective wastewater treatment. The adsorption is a process where molecules from the gas phase or from solution bind in a condensed layer on a solid or liquid surface. The molecules that bind to the surface are called the “adsorbate” while the substance that holds the adsorbate is called the “adsorbent”. The process when the molecules bind is called “adsorption”. There are two different types of adsorption:

1. Chemisorption is direct chemical bond between the adsorbate and the surface. This bond cannot be broken by only increased temperature. This behavior is usually irreversible process.

2. Physisorption is adsorption in the Vander Waals forces. These forces can be eliminated (removal of molecules from surface of adsorbent) when increasing temperature. Therefore, physisorption can be called reversible process.

Chemisorption and physisorption are usually distinguishable from each other without any great difficulty. Table 3 summarizes the main criteria.

Table 3 Criteria for distinguishing between Chemisorption and Physisorption.

(Bond, 1987)

Criteria	Chemisorption	Physisorption
Heat of adsorption (ΔH_{ads})	$> 40 \text{ kJ mol}^{-1}$ usually around $600-700 \text{ kJ mol}^{-1}$	$0 - 40 \text{ kJ mol}^{-1}$
Force of attraction	Chemical bond forces	Van der Waal's forces
Activation energy, E_a	Usually small	Zero
Increasing temperature	Irreversible	Reversible
Specific	It is highly specific	It is not very specific

4.1 Adsorption isotherm

The process of adsorption is usually studied through graphs which are known as adsorption isotherm, that is, the graph between the amount of adsorbate (q_e) on the adsorbent as a function of its pressure (if gas) or concentration (if liquid) at constant temperature.

Basic adsorption isotherm

In the process of adsorption, adsorbate gets adsorbed on adsorbent. According to Le Chatelier principle, the direction of equilibrium would shift in that direction where the stress can be relieved. In case of application of excess of pressure to the equilibrium system, the equilibrium will shift in the direction where the number of molecules decreases. Since number of molecules decreases in forward direction, with the increases in pressure, forward direction of equilibrium will be favored.

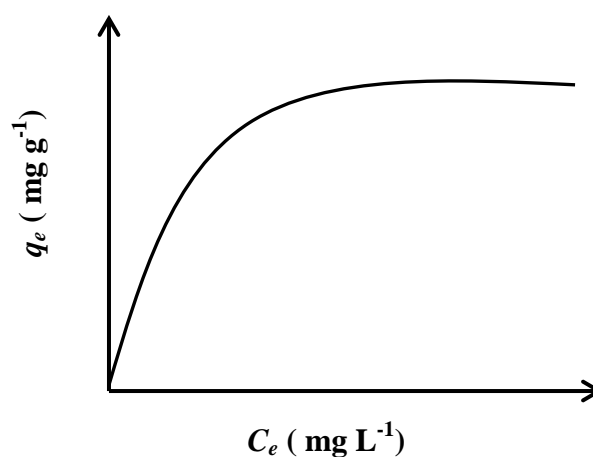


Figure 11 Adsorption isotherm graph

From the graph, we can predict that after saturation pressure q_e , adsorption does not occur anymore. This can be explained by the fact that there are limited numbers of vacancies on the surface of the adsorbent. At high concentration a stage is reached when all the sites are occupied and further increases in pressure does not cause any difference in adsorption process. At high concentration of solution, adsorption is independent of concentration. Adsorption isotherms of (a) Rhodamine B and (b) Pb^{2+} ions onto GE/AC beads were shown in Figure 12.

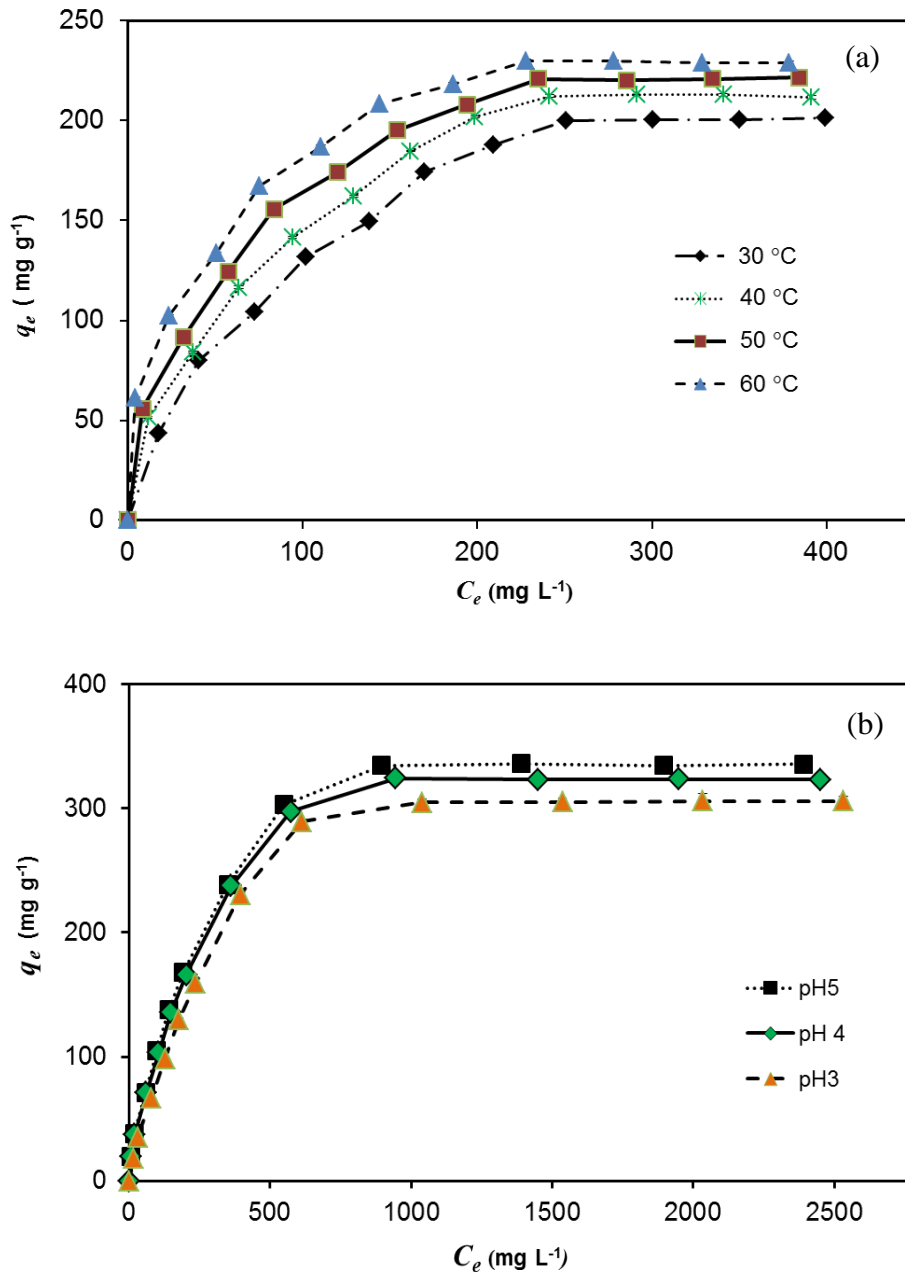


Figure 12 Adsorption isotherms of (a) Rhodamine B at 30, 40 50 and 60°C and (b) Pb²⁺ ions at pH 3, 4 and 6 onto GE/AC beads, GE/AC dose 0.15 g.

The adsorption characteristics in solution phase between the adsorbent and adsorbate were explained by the adsorption isotherm models in general. Several models can be used to describe adsorption data. The two most frequently used for dilute solutions are the Langmuir and Freundlich isotherms (Chuenchom, 2004)

Langmuir adsorption isotherm

In 1916 Langmuir proposed the adsorption isotherm known as Langmuir adsorption isotherm. This isotherm was based on a different assumption of which was that dynamic equilibrium existed between adsorbed gaseous molecules and the free gaseous molecules. Langmuir provided a means of determining surface area based on monolayer coverage of the solid surface by the adsorptive. Based on his theory, he derived Langmuir equation (Langmuir, 1916 and 1918) which depicted a relationship between the number of active sites of the surface undergoing adsorption and pressure.

$$q_e = \frac{q_m b C_e}{1 + b C_e} \quad (\text{Non-Linear form}) \quad (1)$$

Where q_e represents the amount of solute adsorbed per unit weight of adsorbent (mg g^{-1}); q_m is the amount of maximum sorption capacity corresponding to complete monolayer coverage of the surface, also called the monolayer capacity (mg g^{-1}); C_e is the equilibrium solute concentration conditions (mg L^{-1}); and b is an equilibrium constant related to the energy of sorption (Reddad, et al., 2002).

Equation (1) is usually linearized by inversion to obtain the following from:

$$\frac{C_e}{q_e} = \frac{1}{q_m b} + \frac{C_e}{q_m} \quad (\text{Linear form}) \quad (2)$$

Many researchers have usually used equation (2) to analyze batch equilibrium data by plotting C_e/q_e versus C_e , which yields a linear if data conform to the Langmuir isotherm (Zhengang et al, 2009).

(Paper I and II) Figure 13 shows the Langmuir adsorption isotherms of Rhodamine B (a) and Pb^{2+} ions (b) on GE/AC beads. The results indicate that the Rhodamine B and Pb^{2+} ions sorption on GE/AC beads were well fitted by the Langmuir model ($R^2 > 0.99$). The parameter values of Langmuir model of Rhodamine B and Pb^{2+} ions were shown in Table 4 and 5, respectively.

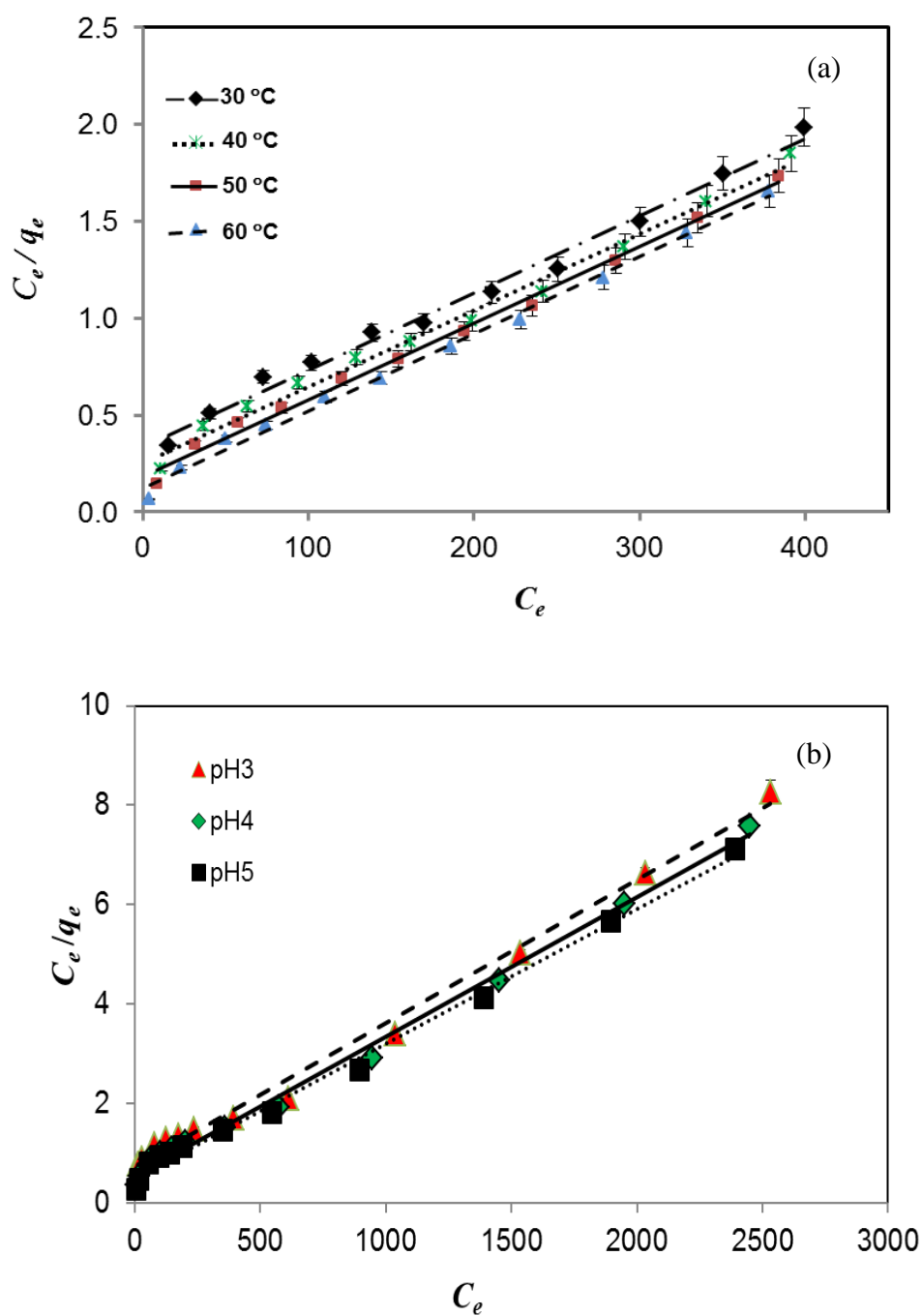


Figure 13 Langmuir adsorption isotherms for (a) Rhodamine B at 30, 40 ,50 and 60 °C and (b) Pb^{2+} ions at pH 3, 4 and 5 onto GE/AC beads, GE/AC dose 0.15 g.

Table 4 Fitted parameters in the Langmuir model for Rhodamine B adsorption by GE/AC beads at 30, 40, 50 and 60 °C, GE/AC dose 0.15 g.

Temp (°C)	Rhodamine B adsorption		
	q_m (mg g ⁻¹)	b (×10 ⁻³) (L mg ⁻¹)	R ²
30	243.90	0.13	0.990
40	250.00	0.16	0.991
50	256.41	0.19	0.994
60	256.41	0.32	0.995

Table 5 Fitted parameters in the Langmuir model for Pb²⁺ ions adsorption by GE/AC beads at pH 3, 4 and 5, GE/AC dose 0.15 g.

pH	Pb ²⁺ ions adsorption		
	q_m (mg g ⁻¹)	b (×10 ⁻³) (L mg ⁻¹)	R ²
3	345.00	3.95	0.993
4	357.00	5.33	0.995
5	370.37	5.51	0.995

The maximum adsorption capacity (q_m) of GE/AC beads for Rhodamine B and Pb²⁺ ions determined from the Langmuir model were 256.41 and 370.37 mg g⁻¹, respectively. The GE/AC beads was better than that the other granular activated carbon from literature data displayed in Table 6 (**Paper I and II**).

Table 6 The maximum adsorption capacities (q_m , mg g⁻¹) of Rhodamine B and Pb²⁺ ions by granular adsorbents reported in prior literature.

s/No	Granular activated carbon	pH	* t_{eq} (min)	q_m (mg g ⁻¹)	Ref.
<i>Rhodamine B adsorption</i>					
1.	Cationic surfactant (Hexadecyltrimethylammonium chloride) modified bentonite clay	6.8	250	155.20	Anirudhan, et al. 2015
2.	Oil palm empty fruit bunch activated carbon	9.0	240	69.86	Manase, et al. 2012
3.	Granular activated carbon from Black tea leaves	2.0	300	53.2	Hussain, et al. 2012
4.	Formaldehyde treated parthenium carbon (WC) and phosphoric acid treated parthenium carbon (PWC)	7.0	120	WC = 28.82 PWC = 59.17	Hem, et al. 2009
5.	Gelatin/activated carbon composite bead form (GE/AC beads)	4.0	1,620	256.41	This study
<i>Pb²⁺ ions adsorption</i>					
6.	Nanocomposite of hydroxyapatite with GAC	6.0	2.5	83.33	Fernando, et al. 2015
7.	GAC prepared from peanut shells	4.8	24	198.72	Wilson, et al., 2006
8.	GAC prepared from coconut shell	5.0	20	21.88	Jyotsna, et al., 2004
9.	Gelatin/activated carbon composite bead form (GE/AC beads)	5.0	1	370.37	This study

* t_{eq} is the equilibration time for adsorption

4.2 Freundlich adsorption isotherm

Freundlich proposed another adsorption isotherm known as Freundlich adsorption isotherm or Freundlich adsorption equation or simple Freundlich isotherm. The Freundlich adsorption equation (Freundlich, 1907) is perhaps the most widely used for the description of adsorption in aqueous systems. The Freundlich equation is of the form

$$q_e = K_F C_e^{1/n} \quad (\text{Non-Linear form}) \quad (3)$$

Where q_e and C_e have definition as previously presented for the Langmuir isotherm. K_F is the so-called unit capacity factor that shows adsorption capacity and n is the empirical parameter that represents the heterogeneity of the site energies and also is indicative of the intensity of adsorption.

The logarithm of equation (3) given below is usually used to fit data as

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (\text{Linear form}) \quad (4)$$

The above equation is comparable with equation of straight line, $y = mx + c$ where, m represents slope of the line and c represents intercept on y axis.

Plotting a graph between $\log q_e$ and $\log C_e$, we will get a straight line for Rhodamine B and Pb^{2+} ions adsorption with value of slope equal to n and $\log K_F$ is y -axis intercept (Arivoli et al., 2009) as shown in Figure 14 (**Paper I and II**). Moreover, Table 7 and 8 shows the parameter values of Freundlich equations of Rhodamine B and Pb^{2+} ions, respectively.

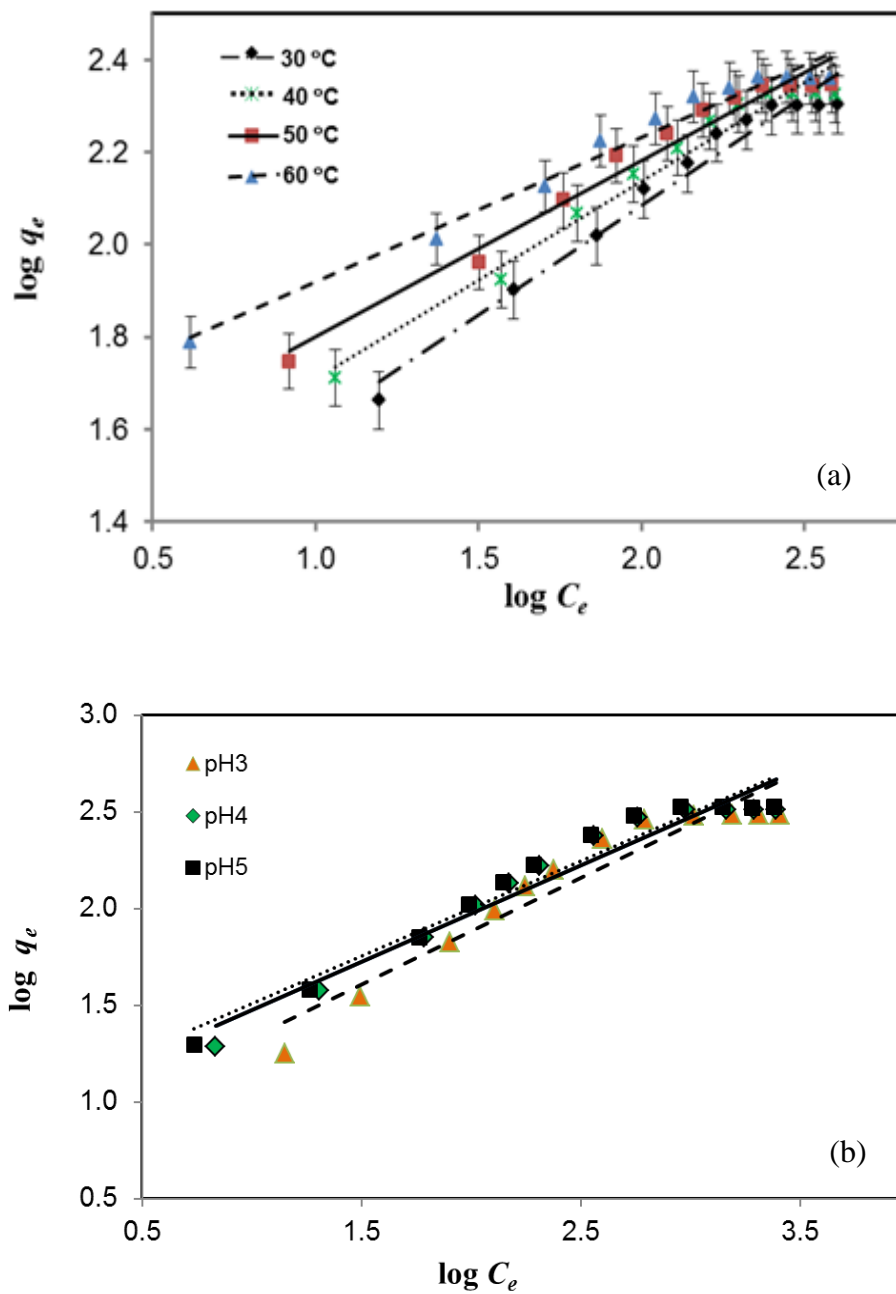


Figure 14 Freundlich adsorption isotherms for (a) Rhodamine B at 30, 40, 50 and 60 °C and (b) Pb^{2+} ions at pH 3, 4 and 5 onto GE/AC beads, GE/AC dose 0.15 g.

Table 7 Fitted parameters in the Freundlich model for Rhodamine B adsorption by GE/AC beads at 30, 40, 50 and 60 °C, GE/AC dose 0.15 g.

Temp (°C)	Rhodamine B adsorption		
	K_F (mg g ⁻¹)	n	R^2
30	13.74	2.11	0.970
40	19.08	2.33	0.970
50	26.24	2.62	0.971
60	40.39	3.20	0.974

Table 8 Fitted parameters in the Freundlich model for Pb²⁺ ions adsorption by GE/AC beads at pH 3, 4 and 5, GE/AC dose 0.15 g.

pH	Pb ²⁺ ions adsorption		
	K_F (mg g ⁻¹)	n	R^2
3	6.02	1.81	0.923
4	9.45	2.00	0.946
5	10.33	2.03	0.953

The Rhodamine B (Table 4 and 7) and Pb²⁺ ions (Table 5 and 8) adsorption by GE/AC beads were well fitted by the Langmuir better than the Freundlich models due to the higher values of correlation coefficient, R^2 indicating the adsorption was monolayer adsorption mechanism.

5. Kinetic models of adsorption

Kinetic studies of adsorption processes have found that adsorption occurs in three distinct phases (Bouchenafa-saib, et al., 2007):

Phase 1: Fast adsorption; which occurs when all of the active sites are free and fixing anions to the material is easy.

Phase 2: Slow adsorption; which occurs after main adsorption sites have been occupied and repulsive force start acting between adsorbed ions and ions in the surrounding solution. This results in further adsorption interactions requiring more energy in order to force the process to continue.

Phase 3: Equilibrium; which occurs when all of the available adsorption sites have been filled and equilibrium has been established between the adsorbed ions and ions in solution.

The adsorption kinetics was analyzed by the use of pseudo-first-order, pseudo-second-order kinetics models and an intra-particle diffusion model.

5.1 Pseudo-First-Order model

The adsorption kinetic data were described by the Lagergren model which is the pseudo first-order model (Lagergren, 1898) which the earliest known equation is describing the adsorption rate based on the adsorption capacity. The pseudo first-order equation is commonly expressed as follows:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (5)$$

By applying the boundary condition $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$ equation 5 become

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (6)$$

where k_1 (min^{-1}) is the rate constant of the pseudo-first order model, where q_t (mg g^{-1}) and q_e (mg g^{-1}) denote the amount of adsorbent adsorbed at time t (min) and equilibrium, respectively.

The slope of linear equation between $\ln (q_e - q_t)$ and t plot gives the adsorption rate constant, k_1 . A linear fit of $\ln (q_e - q_t)$ by t , for pseudo-first-order adsorption kinetics, is displayed in Figure 15 (Paper I and II). The values of k_1 for Rhodamine B and Pb^{2+} ions adsorption were shown in Table 9 and 10, respectively. (Paper I and II)

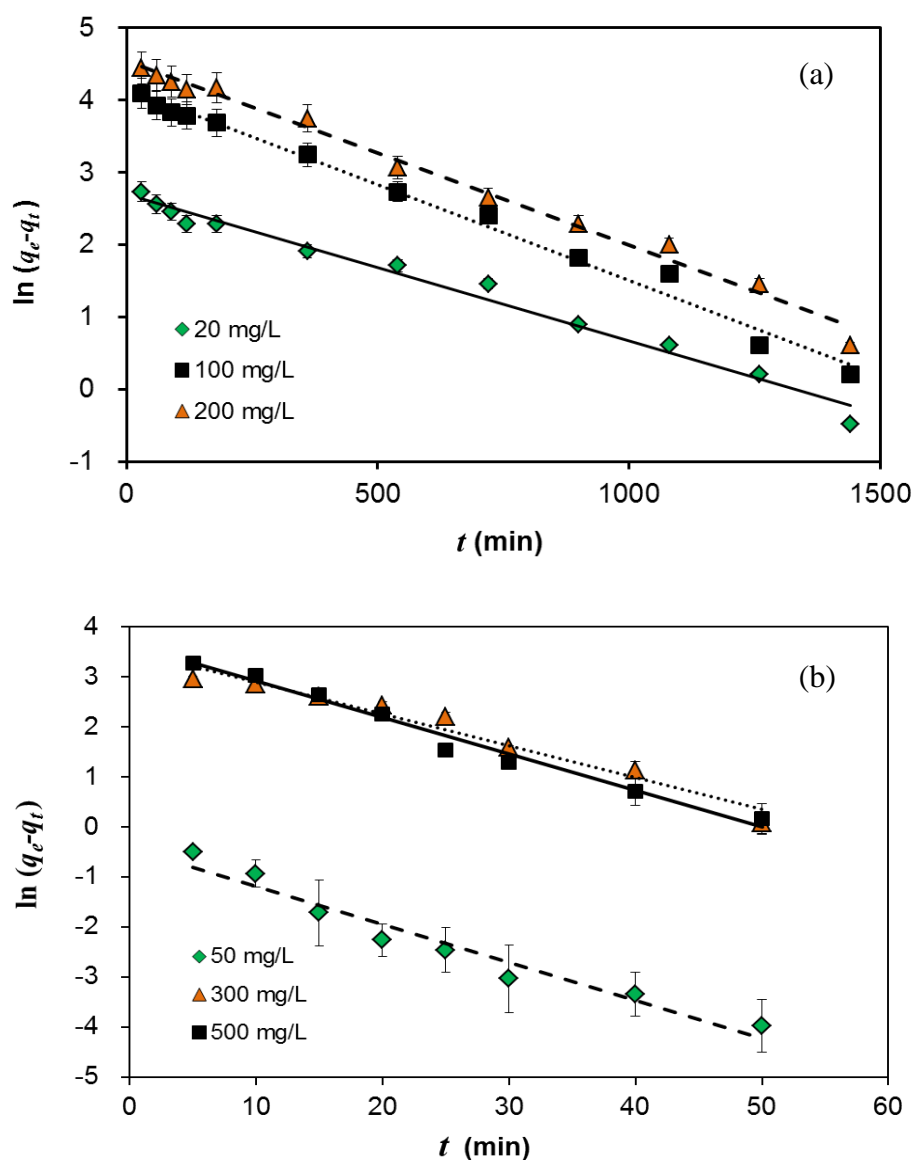


Figure 15 Linearized plots of the pseudo-first-order model for (a) Rhodamine B and (b) Pb^{2+} ions onto GE/AC beads, GE/AC dose 0.15 g.

5.2 Pseudo-Second-Order model

In addition, a pseudo-second-order (Ho, et al., 1999) can be written as in equation 7.

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (7)$$

Integrating equation (7) with the conditions of $q_t = 0$ at $t = 0$ and $q_t = q_t$ at time t and rearranging into a linear form gives equation (8)

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (8)$$

where k_2 is the rate constant of pseudo-second-order adsorption ($\text{g mg}^{-1} \text{min}^{-1}$), q_e is the amount of adsorbent adsorbed at equilibrium (mg g^{-1}) and q_t is the amount of adsorbent on the surface of the sorbent (mg g^{-1}) at any time t (min).

The values of k_2 and q_e were calculated from the intercept and slope of the plot of t / q_t versus t , respectively which are shown in Figure 16 (**Paper I and II**) for Rhodamine B and Pb^{2+} ions adsorption. Table 9 and 10 were presented the values of k_2 for Rhodamine B and Pb^{2+} ions adsorption (**Paper I and II**).

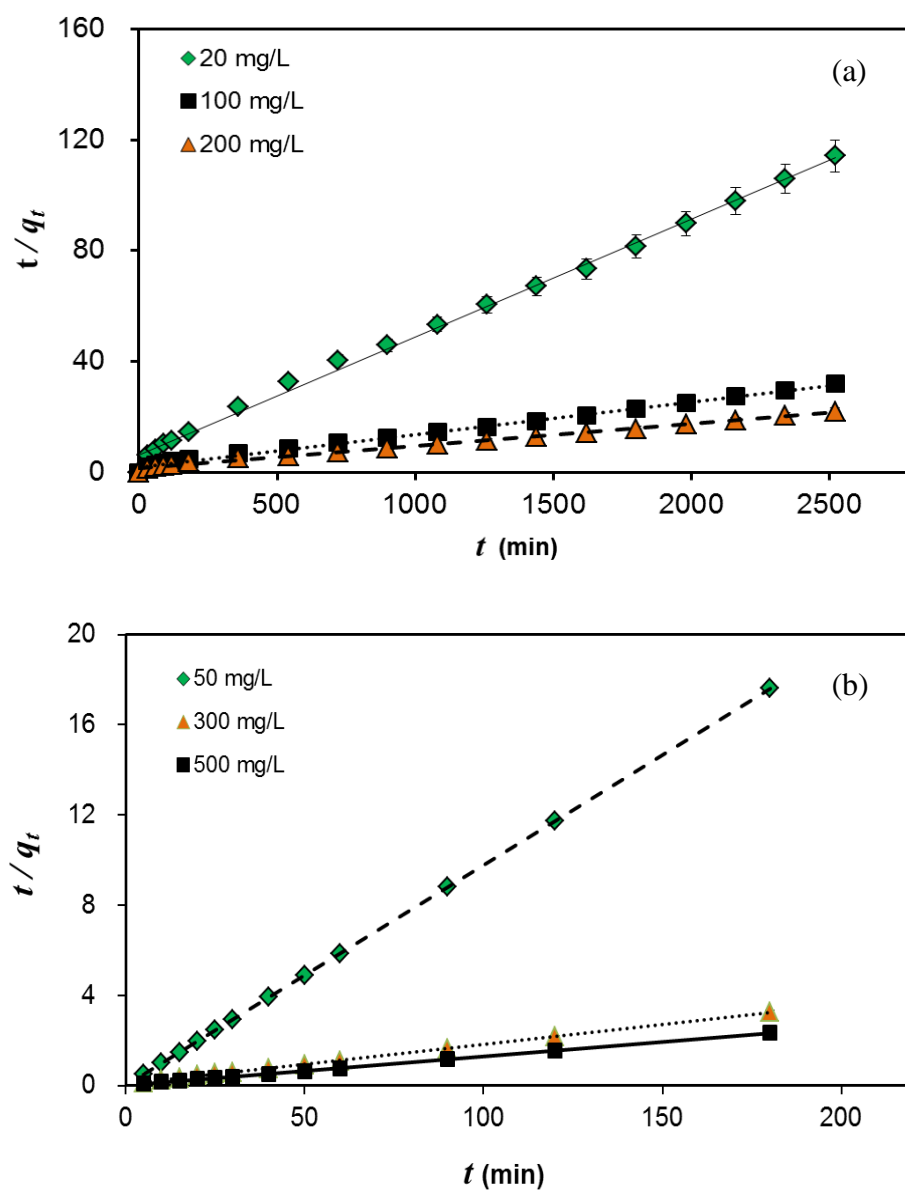


Figure 16 Linearized plots of the pseudo-second-order model for (a) Rhodamine B and (b) Pb^{2+} ions onto GE/AC beads, GE/AC dose 0.15 g.

The values of kinetic parameters of pseudo-first-order and pseudo-second-order model of Rhodamine B (**Paper I**) and Pb^{2+} ions (**Paper II**) at different initial concentrations were indicated in Table 9 and Table 10, respectively.

Table 9 Kinetic parameters of pseudo-first-order and pseudo-second-order model of Rhodamine B adsorption at different initial concentrations.

C_0 (mg L ⁻¹)	q_e (exp) (mg g ⁻¹)	Pseudo-first-order			Pseudo-second-order		
		q_e (mg g ⁻¹)	k_1 (×10 ⁻³)	R ²	q_e (mg g ⁻¹)	k_2 (×10 ⁻⁵)	R ²
20	22.08	14.83	2.00	0.984	23.47	2.90	0.997
100	79.12	63.88	2.60	0.990	84.75	7.50	0.997
200	114.69	93.33	2.50	0.990	114.94	5.40	0.996

Table 10 Kinetic parameters of pseudo-first-order and pseudo-second-order model of Pb^{2+} ions adsorption at different initial concentrations.

C_0 (mg L ⁻¹)	q_e (exp) (mg g ⁻¹)	Pseudo-first-order			Pseudo-second-order		
		q_e (mg g ⁻¹)	k_1 (×10 ⁻²)	R ²	q_e (mg g ⁻¹)	k_2 (×10 ⁻³)	R ²
50	10.21	0.65	7.62	0.9510	10.24	36.85	1.000
300	54.86	34.25	6.37	0.9615	56.50	4.21	0.999
500	76.71	38.16	7.29	0.9808	78.13	4.91	0.999

5.3 Intraparticle diffusion model

The intraparticle diffusion model (IPD) proposed by Weber and Morris (Weber, et al. 1963), as shown in equation (9).

$$q_t = k_p t^{1/2} + C \quad (9)$$

where q_e and q_t are the amount of dye adsorbed (mg g^{-1}) at equilibrium and at any time, k_p is the rate constant of intra-particle diffusion ($\text{mg g}^{-1} \text{min}^{-1/2}$).

In generally, the adsorption by a porous solid tends to occur in three stages, namely (1) external surface adsorption, (2) gradual adsorption with intra-particle diffusion being the rate limiting phenomenon, and (3) interior surface adsorption near complete equilibration (Senthilkumaar, et al. 2011). The role of intraparticle diffusion is here explored by fitting the experimental data to intraparticle diffusion model. The intraparticle diffusion rate constant, k_p , would be obtained from the slope of the linear plot between q_t vs. $t^{1/2}$, as shown in Figure 17 and Table 11.

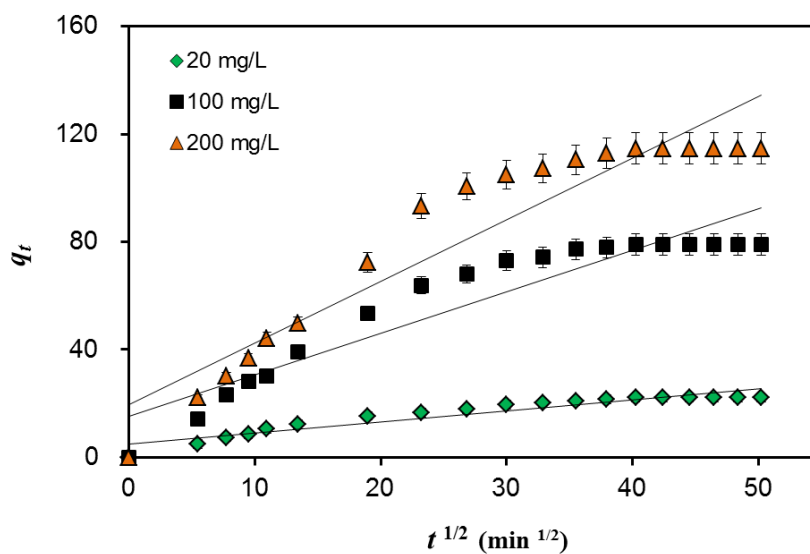


Figure 17 Linearized plots of the intraparticle diffusion model for Rhodamine B onto GE/AC beads, GE/AC dose 0.15 g.

Table 11 The intraparticle diffusion parameter of Rhodamine B adsorption at different initial concentrations.

C_0 (mg L ⁻¹)	q_e (exp) (mg g ⁻¹)	Intraparticle diffusion	
		k_p (mg g ⁻¹ min ^{-1/2})	R ²
20	22.08	0.41	0.901
100	79.12	1.54	0.890
200	114.69	2.28	0.897

6. Thermodynamic studies

The thermodynamic studies of Rhodamine B adsorption by GE/AC beads were determined from experiments at various temperatures. The results showed that the adsorption capacity (q_e) increased with increasing temperature. It is indicating that the adsorption is endothermic process (**Paper I**).

Thermodynamic parameters for the adsorption as the enthalpy (ΔH°) and the entropy (ΔS°) were calculated using the van't Hoff equation in equation 10 and Gibb's free energy (ΔG°) in equation (11) (Hamdi, et al., 2008).

$$\ln K_c = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (10)$$

$$\Delta G^\circ = -RT \ln K_c \quad (11)$$

where K_c is the ratio of C_A , the solid-phase concentration of Rhodamine B at equilibrium (mg L^{-1}), to C_e , the equilibrium concentration of Rhodamine B in solution (mg L^{-1}), R is the universal gas constant ($8.314 \text{ J K}^{-1} \text{ mol}^{-1}$), and T is the absolute temperature (K).

The values of enthalpy (ΔH°) and the entropy (ΔS°) were obtained from the slope and intercept of the van't Hoff plot and the Gibb's free energy (ΔG°) was calculated from equation (11). The results are listed in Table 12. The negative value of ΔG° shows that Rhodamine B sorption by GE/AC beads is a spontaneous process. The positive values of ΔH° and ΔS° indicated the endothermic nature and increased randomness in the solid solution at interfaces during adsorption of Rhodamine B by GE/AC beads (**Paper I**).

Table 12 The thermodynamic parameters for Rhodamine B sorption by GE/AC beads

T(K)	$-\Delta G^\circ$ (kJ mol ⁻¹)	ΔS° (kJ mol ⁻¹ K ⁻¹)	ΔH° (kJ mol ⁻¹)
303	0.98		
313	1.37	0.051	21.94
323	2.07		
333	3.29		

7. Concluding remarks

The high surface areas of powder AC combined with gelatin to form GE/AC beads form as an effective granular adsorbent have been successfully. The characterizations of GE/AC beads were studied by scanning electron microscopy (SEM), the BET surface area and the point of zero charge (pH_{pzc}).

In addition, Batch adsorption method has been used for study effect of contact time, pH, GE/AC dosage and temperature for Rhodamine B and Pb²⁺ ions adsorption. the high performance GE/AC beads for kinetics, thermodynamics and adsorption study of Rhodamine B adsorption have been studied. **(Paper I)**. Moreover, GE/AC beads have been further studied on kinetics and adsorption of Pb²⁺ ions **(Paper II)**.

The results from the Langmuir adsorption isotherm found that the maximum adsorption capacities (q_m) are 256.34 mg g⁻¹ and 370.37 mg g⁻¹ as a high effective GE/AC beads for Rhodamine B and Pb²⁺ ions, respectively. The GE/AC beads would be the excellent granular adsorbent for industrial adsorption.

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Paper I

Kinetics and thermodynamics of Rhodamine B adsorption by gelatin/activated carbon composite beads

Hayeeye, F., Sattar, M., Chinpa, W. and Sirichote, O.

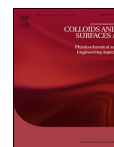
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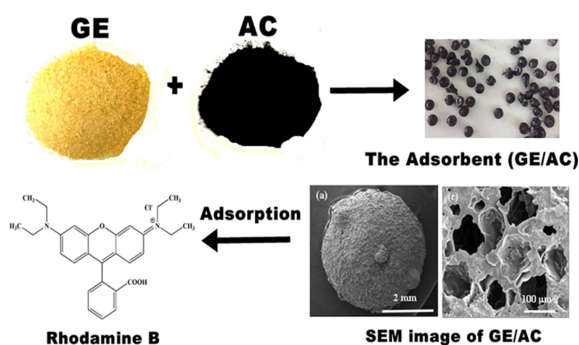
Kinetics and thermodynamics of Rhodamine B adsorption by gelatin/activated carbon composite beads

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HIGHLIGHTS

- The GE/AC adsorbent beads were prepared by compacting AC and gelatin by facile method.
- The practical potential of GE/AC adsorbent beads can remove Rhodamine B from an aqueous solution.
- The sorption isotherm of Rhodamine B by GE/AC was well fit by the Langmuir model.
- The kinetic of adsorption data of Rhodamine B by GE/AC was best fit with the pseudo-second-order model.
- The equilibrium adsorption at different time by GE/AC indicating an endothermic process.

GRAPHICAL ABSTRACT



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ABSTRACT

The Gelatin/Activated Carbon Composite (GE/AC) adsorbent in bead form was prepared and used to adsorb Rhodamine B from an aqueous solution. Gelatin and activated carbon were combined to an eco-friendly, non-toxic, non-carcinogenic, biocompatible and inexpensive biosorbent. Dependence of sorption performance on key factors, such as contact time, adsorbent dosage, pH, and temperature, were experimentally examined. The effects of initial Rhodamine B concentration were also evaluated, and the response followed Langmuir adsorption isotherm, with the maximum adsorption capacity of 256.41 mg g^{-1} at pH 4 and 30°C . The results indicate that the GE/AC adsorbent has potential to serve in wastewater treatment applications, especially in batch removal of Rhodamine B from an aqueous solution.

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1. Introduction

Various dyes are currently widely used in textiles, leather, papermaking, plastics, food, rubber, and cosmetics industries. They are stable resisting light, heat, and oxidizing agents, and are usually

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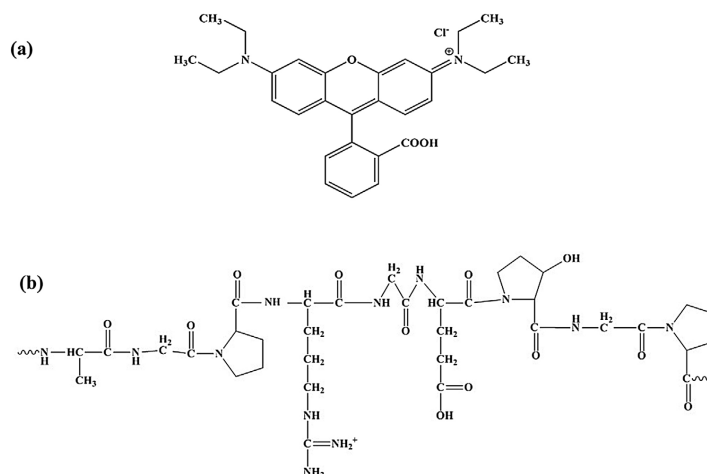


Fig. 1. The chemical structures of Rhodamine B (a), and gelatin (b) [19].

non-biodegradable [1]. Several dyes make their presence strikingly visible by discoloration of water bodies, and more importantly they affect aquatic diversity by blocking sunlight [2]. In addition, discharges of Rhodamine B in natural waters may be harmful to human health. In California, Rhodamine B is suspected to be carcinogenic, so products containing it must present a warning on the label [3]. Practical treatments are necessary to remove this contaminant from wastewater, to avoid emissions. Several such wastewater treatment methods are reported in prior literatures [4–10]. Among the numerous methods, adsorption is the typical mechanism by which toxic organic [11,12] and inorganic pollutants [13], heavy metals [14,15], and dyes [16–18] are removed in these treatments. Activated carbon (AC) powder is the most widely used as adsorbent due to its tremendous surface area available for adsorption. However, AC in powder form is inconvenient in practical use. To overcome this limitations, the effective, eco-friendly and handy granular adsorbent was prepared from biodegradable polymer combined with activated carbon powder. Such adsorbent is expected to be highly effective in terms of adsorption, and simple to use. Gelatin (GE) was chosen because it is a biodegradable polymer, inexpensive, abundant and renewable. A commercial gelatin made from peptone primagen of animal tissue was used, and a basic easy method was selected to make the new adsorbent beads. The chemical structure of GE has amino groups, $-\text{NH}_2$, and carboxylic acid groups, $-\text{COOH}$, as display in Fig. 1(b) [19].

In this work we develop adsorbent beads by compacting AC with gelatin and use these to study adsorption of Rhodamine B dye, which was selected as a representative of the common cationic dyes in effluents from textile and food industries, from wastewater. The structure of Rhodamine B is shown in Fig. 1(a). The aim of this work was to prepare more convenient, effective and low cost adsorbent from gelatin and activated carbon powder. Several studies have reported on kinetics, equilibrium and thermodynamics of adsorption, across various classes of dyes, with activated carbon and other biomaterials as adsorbents. However, to the best of our knowledge, there was a few study of Rhodamine B adsorption by composite beads. Thus, this study explores the development and the practical potential of GE/AC adsorbents to remove Rhodamine B from an aqueous solution. Experimental evaluation and optimization of the key factors affecting performance, namely GE/AC dose, contact

time, pH, and temperature, in terms of the adsorption isotherm of Rhodamine B by the GE/AC composite beads, are pursued and discussed in this study.

2. Materials and methods

2.1. Materials and reagents

The adsorbate Rhodamine B, with molecular weight of $479.02 \text{ g mol}^{-1}$, was procured from Fluka, UK. Gelatin powder (GE) and activated carbon (AC) were obtained from Ajax Finechem Pty. Ltd. and Sigma–Aldrich, respectively. Glutaraldehyde, which is a crosslinking reagent, was supplied by Fluka Analytical. NaOH and HCl were purchased from Merck, Germany, for use in adjusting the pH.

2.2. Methods

2.2.1. Preparation of gelatin/activated carbon composite beads (GE/AC)

The GE/AC beads were prepared following the procedure described by Hayeeye et al., 2015 [20]. The AC was sieved to 200–270 mesh size [21] and dried at 110°C for 24 h before use. A homogeneous solution with GE 30% wt. was prepared by dissolving GE powder of 30 g in distilled water of 70 g. To obtain AC of 10% wt., 10 g of AC was added in to the GE solution of 90 g. The mixture suspension was stirred at room temperature for 30 min, and added dropwise to cold water, causing gelling of the GE. The formed GE/AC beads were filtered and immersed in 1% v/v of glutaraldehyde aqueous solution for overnight, to induce crosslinking in the gel and stabilize it. Finally, the obtained GE/AC beads were dried at 60°C for 6 h.

2.2.2. Characterization of the GE/AC

Scanning electron microscopy (SEM, Quanta 400) was performed by the Scientific Equipment Center, Prince of Songkla University, to characterize the morphology and the functional groups in GE/AC, respectively.

The adsorbent, GE/AC 10% wt., was characterized in terms of Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda (BJH)

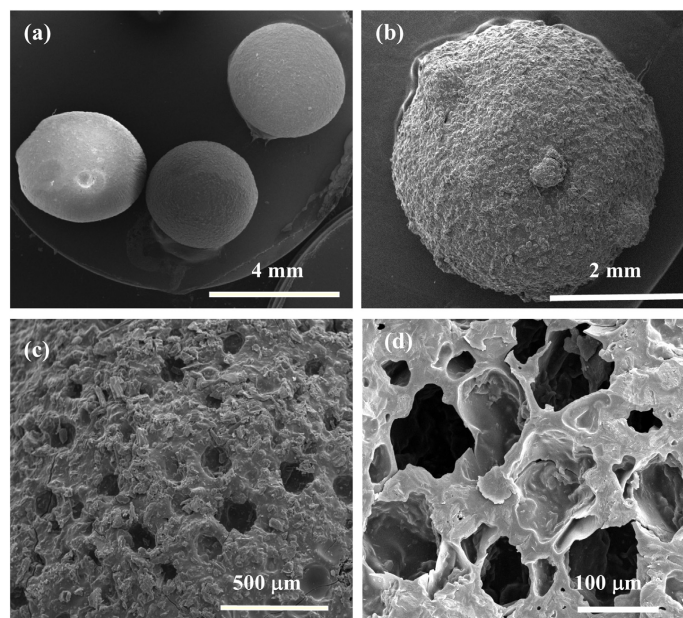


Fig. 2. SEM images of GE/AC 10% wt. beads in magnitude $\times 12$ (a), $\times 25$ (b) and surface (c) and a cross-section (d).

models [22], using the Quanta Chrome Autosorb automated gas sorption test, at the Institute for Scientific and Technological Research and Services, King Mongkut's University of Technology Thonburi, to estimate the surface area and the pore size distribution, respectively.

The point of zero charge (pH_{PZC}) was determined by using the pH drift method [23,24]. Briefly, the procedure described by Hayeeye et al., 2014 [25], is as follows. A series of 50 mL of 0.1 M NaCl solution was adjusted to desire from 2 to 12, by using 0.01 M HCl or NaOH. GE/AC of 0.15 g was added into each of this series, which was then sealed and kept overnight at ambient temperature. The relation of final pH (pH_f) to initial pH (pH_0) was used to determine the pH_{PZC} value of the adsorbent beads. At this point the initial and final pH values do not differ, and the surface of GE/AC is neutral.

2.2.3. Batch adsorption

The adsorption of Rhodamine B by GE/AC 10% wt. was studied by a batch adsorption method [26]. The effects of various parameters, namely the amount of GE/AC (0.03–0.21 g), contact time (0–42 h), pH (2–11) and temperature (30, 40, 50 and 60 °C) were experimentally explored. In all adsorption experiments 50 mL of 100 mg L⁻¹ Rhodamine B solution was used at pH 4, which is the natural pH of this dye solution. Moreover, each experimental case was conducted in triplicate. To assess effects of pH, the initial pH of the dye solution was adjusted to desired value between 2 and 11 by using HCl or NaOH solution. In the adsorption experiments, 0.15 g of GE/AC was added into 50 mL sample of 50–550 mg L⁻¹ of dissolved Rhodamine B, and the mixture was agitated in a thermostat shaker bath at 30 °C. The Rhodamine B concentration, before and after adsorption, was determined by a UV–vis spectrophotometer (UV 2600, Shimadzu) at 554 nm.

The equilibrium data was used to evaluate the kinetic adsorption, adsorption isotherm and thermodynamics. The adsorption capacity, q_e (mg g⁻¹), of the adsorbent was calculated as follows [27]:

$$q_e = \frac{V(C_0 - C_e)}{W} \quad (1)$$

where q_e is the adsorption capacity (mg g⁻¹), V is the volume of the solution (L), C_0 is the initial concentration of Rhodamine B (mg L⁻¹), C_e is the final equilibrium concentration of Rhodamine B (mg L⁻¹), and W is the mass of adsorbent (g).

3. Results and discussion

3.1. Characterization of GE/AC

3.1.1. Scanning electron microscopy (SEM)

Fig. 2 shows the morphology of the GE/AC 10% wt. bead using SEM. The result in Fig. 2(a) presented that the GE/AC beads are spherical with nearly equal size (diameter of 4 mm). It was also found that the adsorbent bead has a rough surface (Fig. 2(b)). At higher magnification of GE/AC bead as shown in Fig. 2(c) and (d), respectively, it can be seen clearly that there are many pores on the surface and internal cross-section of bead. This porous structure may affect the Rhodamine B sorption efficiency.

3.1.2. Specific surface area

Specific surface area of the GE/AC 10% wt. bead is summarized in Table 1. It was found that the GE/AC bead has a relatively narrow pore size distribution and its average pore diameter was 3.25 nm being in mesoporous scale (2–50 nm). The BET surface areas of the current study can be compared with granular AC in prior work, in Table 1, showing that the BET surface area of GE/AC10% was

Table 1
Characteristics of GE/AC 10% wt. bead and BET surface area of granular adsorbent from literature data.

Sample	BET surface area (m ² g ⁻¹)	Total pore volume (cm ³ g ⁻¹)	Average pore diameter (nm)	pH _{pzc}
GE/AC 10% wt. [This study]	34.75	0.028	3.25	4.5
AC from granular red mud [28]	15.28	–	–	–
AC from calcined alunite [29]	26.40	–	–	–

Table 2
Kinetic parameters for the pseudo-first-order, the pseudo-second-order, and the intra- particle diffusion model, for experimental cases with various initial concentrations of Rhodamine B at 30 °C, GE/AC dose 0.15 mg, and pH = 4.0.

C ₀ (mg L ⁻¹)	q _e (exp) (mg g ⁻¹)	pseudo-first-order			pseudo-second-order			intra-particle diffusion	
		q _e (mg g ⁻¹)	k ₁ (×10 ⁻³) (min ⁻¹)	R ²	q _e (mg g ⁻¹)	k ₂ (×10 ⁻⁵) (g mg ⁻¹ min ⁻¹)	R ²	k _p (mg g ⁻¹ min ^{-1/2})	R ²
20	22.08	14.83	2.00	0.984	23.47	2.90	0.997	0.41	0.901
100	79.12	63.88	2.60	0.990	84.75	7.50	0.997	1.54	0.890
200	114.69	93.33	2.50	0.990	114.94	5.40	0.996	2.28	0.897

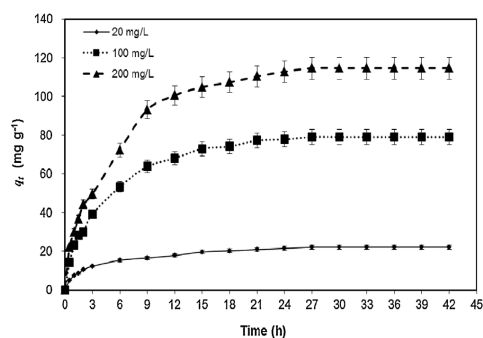


Fig. 3. Effect of contact time and initial dye concentration (20, 100 or 200 mg L⁻¹) of Rhodamine B adsorbed by GE/AC 10% wt. (0.15 g) at 30 °C and pH = 4.0.

higher than those of granular activated carbon from granular red mud [28], and of calcined alunite [29]. This indicates that the GE/AC 10% wt. should have better adsorption capacity relative to granular activated carbon, based on its high specific surface.

3.2. Adsorption studies

3.2.1. Effect of contact time and initial dye concentration

For study of kinetic adsorption, it is necessary to know the time of adsorption to reach the equilibrium [30–34]. Fig. 3 shows the dye adsorption by GE/AC bead at different contact time and initial dye concentration. The result shows that the equilibration times for adsorption are approximately 27 h at 30 °C, with pH 4 and 100 mg L⁻¹ of initial dye concentration, and 0.15 g of GE/AC dose. However, in the kinetic studies, determining the adsorption isotherms, and thermodynamic studies, 30 h was allowed to ensure the equilibrium was complete. As expected, the adsorbed amount increased with initial dye concentration.

In this study, three kinetic models were fitted to the experimental data, namely the Lagergren model, which is pseudo-first-order [35,36], a pseudo-second-order model [37], and an intra-particle diffusion model [38]. These models are given in Eqs. (2)–(4), in the same order.

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (2)$$

Table 3
Fitted parameters in the Langmuir and the Freundlich models for Rhodamine B adsorption by GE/AC 10% wt. at various temperatures, GE/AC dose 0.15 g, pH 4.0.

Temp (°C)	Langmuir			Freundlich		
	q _m (mg g ⁻¹)	b (L mg ⁻¹)	R ²	K _F (mg g ⁻¹)	n	R ²
30	243.90	0.013	0.990	13.74	2.11	0.970
40	250.00	0.016	0.991	19.08	2.33	0.970
50	256.41	0.019	0.994	26.24	2.62	0.971
60	256.41	0.032	0.995	40.39	3.20	0.974

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (3)$$

$$q_t = k_p t^{1/2} + C \quad (4)$$

where q_t are the amounts of dye adsorbed (mg g⁻¹) at a given time t , k_1 is the pseudo-first-order rate constant (min⁻¹), k_2 is the pseudo-second-order rate constant (g mg⁻¹ min⁻¹), and k_p is the intra-particle diffusion rate constant (mg g⁻¹ min^{-1/2}). Corresponding plots of Rhodamine B adsorption on GE/AC 10% wt. are shown in Fig. 4(a–c).

A linear fit of $\ln(q_e - q_t)$ by t , for pseudo-first-order adsorption kinetics, is displayed in Fig. 4(a). The value of k_1 is the slope of the straight line. Moreover, the value of k_2 in the pseudo-second-order adsorption kinetic model was calculated from the slope of linearly fitting t/q_t by t (Fig. 4(b)).

In generally, the adsorption by a porous solid tends to occur in three stages, namely (1) external surface adsorption, (2) gradual adsorption with intra-particle diffusion being the rate limiting phenomenon, and (3) interior surface adsorption near complete equilibration [39]. The role of intra-particle diffusion is here explored by fitting the experimental data to intra-particle diffusion model (Eq. (4)). The intra-particle diffusion rate, k_p , would be obtained from the slope of the linear plot between q_t vs. t , as shown in Fig. 4(c). The model fits are summarized in Table 2. By considering correlation coefficient, R², the kinetics of adsorption data of Rhodamine B by GE/AC was best fit with the pseudo-second-order model.

In this model, the removal Rhodamine B from a solution is due to physicochemical interactions between the two phases [37].

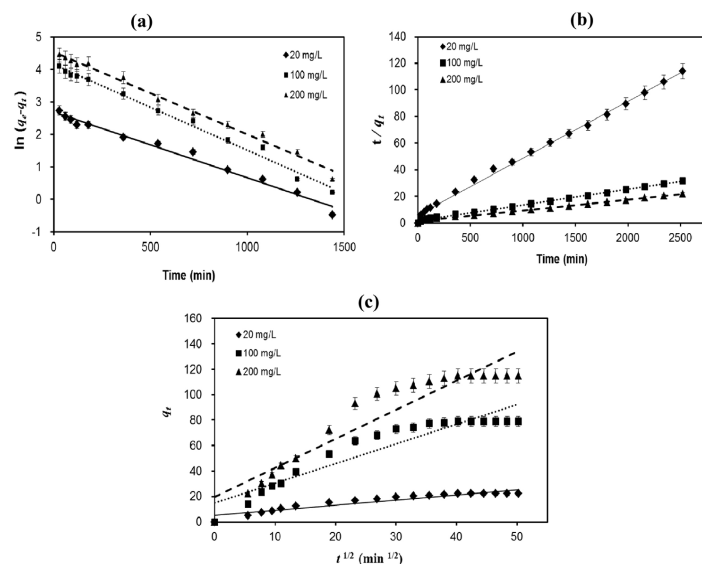


Fig. 4. Fitting of adsorption kinetics by (a) pseudo-first-order model, (b) pseudo-second-order model, and (c) an intra-particle diffusion model, for the adsorption of Rhodamine B by GE/AC 10% wt., with 0.15 g dosage at 30 °C and pH = 4.0.

3.2.2. Effect of GE/AC dosage

The GE/AC dosage is another important parameter which influences the extent of Rhodamine B uptake from the solution. The dosage of GE/AC 10% wt. was varied from 0.03 g to 0.21 g in 100 mg L⁻¹ of Rhodamine B. As shown in Fig. 5, the equilibrium adsorption of Rhodamine B increased with the dosage of GE/AC. In the case of q_e value, the result was consistent with the works of Bozorgpour et al. [40], Najua et al. [41] and Charles et al. [42], were reported effect of adsorbent dosage. The percent dye adsorbed and q_e value increased with an increase of GE/AC 10% wt. weight, and reached a maximum value when the weight of GE/AC bead was 0.15 g. An increment of q_e value may be due to adsorbent having tremendous surface area and adsorption sites; therefore an increase in small amount of adsorbent provides much greater surface areas to adsorb large number of Rhodamine B molecule [40,41]. However, after 0.15 g, the adsorption capacity decreased with the increasing of GE/AC 10% wt. This result may be because after the certain dose of GE/AC 10% wt., the maximum adsorption is reached and the amount of Rhodamine B molecule bound to the adsorbent and the amount of free dye molecule remains constant even with further addition of the dose of adsorbent [42,43]. The maximum amount adsorbed at equilibrium (q_e) was 79.73 mg g⁻¹ obtained from 0.15 g of GE/AC 10% wt. This dosage is here considered to be the optimum level, as also the time to reach equilibrium was short, which is desirable in industrial applications [44].

3.2.3. Effect of pH

It is well known that the pH affects the surface charge on the adsorbent as well as on the adsorbate species in the solution. Fig. 6 depicts the effects of pH on Rhodamine B adsorption by GE/AC 10% wt. adsorbent, across the pH range 2–11. As the pH increased from 2 to 6, the Rhodamine B adsorption capacity increased. At low pH values, the high concentration of H⁺ ion promotes the protonation of functional groups such as carboxylic, amide and hydroxyl groups in the adsorbent, which makes to become positive charges

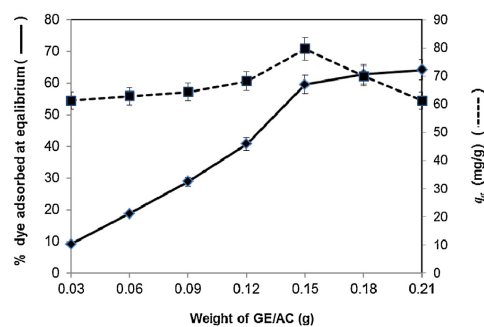


Fig. 5. Effect of GE/AC 10% wt. dosage in the range 0.03–0.21 g/50 mL, for 100 mg L⁻¹ of Rhodamine B, on equilibrium sorption at 30 °C, pH = 4.0, with 30 h of equilibration.

and repel with the positive charges of the cationic dye molecules: so lowering an acidic pH should reduce adsorption, as was observed. An alternative view is that at such low pH values the H⁺ cations compete with Rhodamine B cations for the adsorption sites. A decrease in adsorption around pH 6–8 is due to the hydration of Rhodamine B ions, increasing the effective molecular size and hindering entry of the dye into the pores of the adsorbent. The similar result about decreasing trend in adsorption capacity with pH has been reported by Hema et al. [45]. At pH values exceeding 8, the GE/AC surfaces tend to become negative charge due to deprotonation of carboxylic and hydroxyl groups by OH⁻, thus the adsorption of cationic dye like Rhodamine B was improved by electrostatic attraction [46].

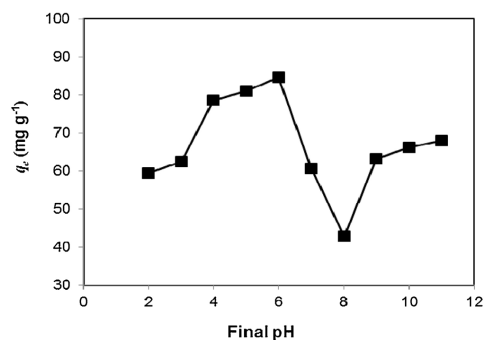


Fig. 6. Effect of pH (2–11) on Rhodamine B sorption by GE/AC 10% wt. adsorbent (0.15 g), at 30 °C, over 30 h duration, with 100 mg L⁻¹ dye concentration.

3.2.4. Adsorption isotherm

To identify the mechanisms of adsorption process, two types of isotherm model were tested for fitting the adsorption data, namely the Langmuir isotherm [47] and the Freundlich isotherm [48]. These models are shown in Eqs. (5) and (6), in the same order.

$$\frac{C_e}{q_e} = \frac{1}{q_m b} + \frac{C_e}{q_m} \quad (5)$$

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (6)$$

where q_m and b are the Langmuir constants representing the maximum adsorption capacity (mg g^{-1}) and adsorption equilibrium (L mg^{-1}), K_F and n are the Freundlich constants representing the adsorption capacity (L g^{-1}) and the adsorption intensity, respectively. Plots of the Langmuir and Freundlich adsorption isotherm are shown in Fig. 7 (a) and (b), respectively, and the model fits are summarized in Table 3. The favorability of adsorption is indicated by the dimensionless separation factor (R_L) [49], calculated from Eq. (7):

$$R_L = \frac{1}{1 + bC_0} \quad (7)$$

R_L value indicates the adsorption nature to be unfavourable ($R_L > 1$), linear ($R_L = 1$), favourable ($0 < R_L < 1$) or irreversible ($R_L = 0$). From the data calculated, the R_L values was 0.06–0.64 at 30–60 °C in the range of initial dye concentration of 50–500 mg L⁻¹ which is indicated that Langmuir isotherm is favorable.

Fig. 7 shows the Langmuir (a) and the Freundlich (b) adsorption isotherms of Rhodamine B on GE/AC 10% wt. at 30 °C, 40 °C, 50 °C, and 60 °C, from initial dye concentrations of 50–550 mg L⁻¹ and pH 4.0. The results indicate that biosorption by GE/AC is well fitted by the Langmuir and the Freundlich models. Of these two models, the Langmuir model performed better with higher correlation coefficient, R^2 (Table 3), indicating monolayer adsorption mechanism. The maximum adsorption capacity (q_m) of GE/AC 10% wt. for Rhodamine B, determined from the Langmuir model, is 256.41 mg g⁻¹, which is better than that of granules prepared from oil palm empty fruit bunch ($q_m = 69.86 \text{ mg g}^{-1}$) [50], black tea leaves ($q_m = 53.12 \text{ mg g}^{-1}$) [51], modified bentonite clay ($q_m = 155.10 \text{ mg g}^{-1}$) [2], and phosphoric acid treated parthenium carbon ($q_m = 59.17 \text{ mg g}^{-1}$) [52].

3.2.5. Effect of temperature

The thermodynamic parameters of Rhodamine B adsorption by GE/AC 10% wt. were determined from experiments at various temperatures. The results in Fig. 8 showed that the adsorption capacity

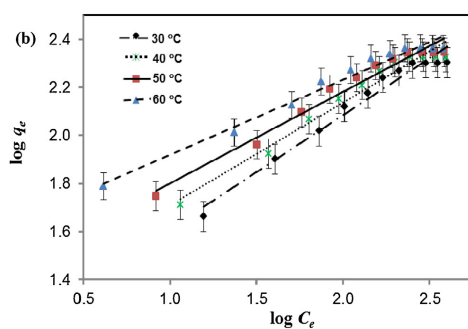
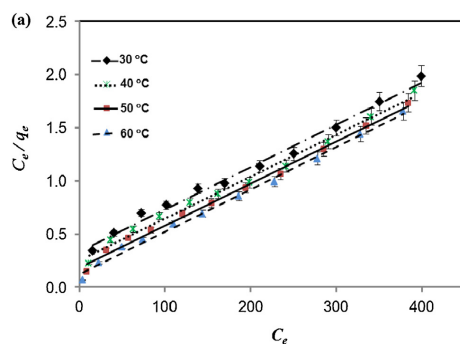


Fig. 7. Langmuir (a) and Freundlich (b) adsorption isotherms of Rhodamine B adsorption by GE/AC 10% wt. at various temperatures, with initial dye concentration in the range 50–550 mg L⁻¹, equilibration time 30 h, and pH=4.0.

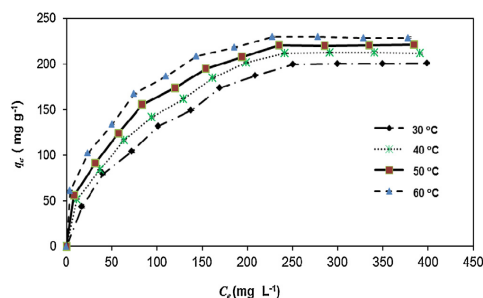


Fig. 8. Adsorption isotherms of Rhodamine B on GE/AC 10% wt. at various temperatures, from initial dye concentration of 50–550 mg L⁻¹, equilibration time 30 h, and pH=4.0.

q_e increased with temperature in the range of 30–60 °C indicating endothermic adsorption process.

The temperature affects through the enthalpy (ΔH°) and the entropy (ΔS°), in accordance with the van't Hoff Eq. (8) [53] and the Gibb's free energy ΔG° in Eq. (9):

$$\ln K_c = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (8)$$

$$\Delta G^\circ = -RT \ln K_c \quad (9)$$

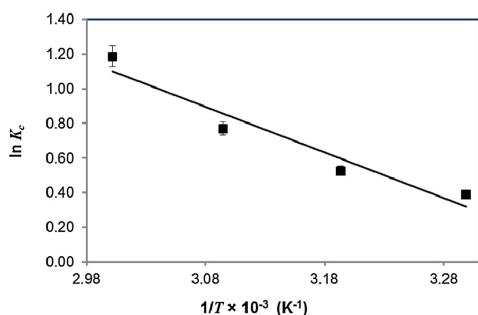


Fig. 9. The van't Hoff plots for Rhodamine B sorption by GE/AC 10% wt. at 30 °C, 40 °C, 50 °C and 60 °C, from initial dye concentrations 100 mg L⁻¹, GE/AC dose 0.15 g, at 30 h equilibration and pH = 4.0.

where K_c is the ratio of C_A , the solid-phase concentration of Rhodamine B at equilibrium (mg L⁻¹), to C_e , the equilibrium concentration of Rhodamine B in solution (mg L⁻¹), R is the universal gas constant (8.314 J K⁻¹ mol⁻¹), and T is the absolute temperature (K). The values of enthalpy (ΔH°) and the entropy (ΔS°) were obtained from the slope and intercept of the van't Hoff plot shown in Fig. 9, and the Gibbs's free energy (ΔG°) was calculated from equation (9). The results are listed in Table 4. The negative sign of ΔG° shows that Rhodamine B sorption by GE/AC 10% wt. is a spontaneous and feasible process. The positive values of ΔH° and ΔS° indicate the endothermic nature and increased randomness in the solid solution at interfaces during adsorption of Rhodamine B by GE/AC 10% wt.

A comparison of the maximum Rhodamine B dye uptake capacities (q_m , mg g⁻¹) by GE/AC to those of other adsorbents reported in the literature is given in Table 5. Many of these powder and granular adsorbents have been used to remove Rhodamine B. Despite the

Table 4

The thermodynamic parameters from van't Hoff equation for Rhodamine B sorption by GE/AC 10% wt., from initial dye concentration 100 mg L⁻¹, 0.15 g of GE/AC 10% wt. and pH = 4.0.

T(K)	$-\Delta G^\circ$ (kJ mol ⁻¹)	ΔS° (kJ mol ⁻¹ K ⁻¹)	ΔH° (kJ mol ⁻¹)
303	0.98	0.051	21.94
313	1.37		
323	2.07		
333	3.29		

gel component in the beads employed in this study far exceeded a particular adsorption capacity than activated carbon powder, and is comparable to that of granular activated carbon. Moreover, the GE/AC 10% wt. adsorbent is easy to prepare in bead form, which is handier to manage for adsorption than activated carbon powder.

4. Conclusions

The results indicate that the GE/AC 10% wt. adsorbent beads synthesized in the current study provide an efficient and eco-friendly biosorbent, for the removal, extraction and treatment of Rhodamine B in aqueous solution. High Rhodamine B biosorption capacity was obtained in acidic conditions at pH 4, at which the surfaces of the AC in GE/AC 10% wt. beads get negatively charged, which attracts the positive dye cations. The sorption isotherm of Rhodamine B by GE/AC 10% wt. had the best fit by the Langmuir model, which predicted the adsorption capacity $q_{max} = 256.41$ mg g⁻¹. The equilibrium adsorption q_e and the percentage of adsorption by GE/AC 10% wt. increased with temperature in the range 30–60 °C, indicating an endothermic process. The developed granular bio-sorbent GE/AC 10% wt. is more convenient to use than activated carbon powder and has higher adsorption capacity than typical granular activated carbon, in the removal of dyes from wastewater. This interesting granular adsorbent tends to have potential for commercial and industrial adoption.

Table 5

Comparison of maximum Rhodamine B dye adsorption capacities (q_m , mg g⁻¹) by powder and granular adsorbents reported in prior literature.

s/No	Adsorbent	pH	t_{eq}^a (min)	q_m (mg g ⁻¹)	Refs.
<i>Powder activated carbons</i>					
1.	Activated carbon prepared from the steel and fertilizer industries	5.5	30	91.1	[21]
2.	Activated carbon prepared from pericarp of rubber fruit	4.0	1440	110.46	[25]
3.	Activated carbon prepared from Thespusia populina bark	7.0	90	77.18	[45]
4.	Activated carbon prepared from walnut shell	9.0	300	18.70	[49]
5.	Activated carbon prepared from bagasse pith	5.7	1440	98.23	[53]
6.	Activated carbon prepared from an indigenous waste	7.1	100	51.55	[54]
7.	Activated carbon prepared from tamarind fruit shells	7.0	100	4.57	[55]
<i>Granular activated carbons</i>					
8.	Cationic surfactant(Hexadecyltrimethylammonium chloride) modified bentonite clay	6.8	250	155.20	[2]
9.	Oil palm empty fruit brunch activated carbon	9.0	240	69.86	[50]
10.	Granular activated carbon from Black tea leaves	2.0	300	53.2	[51]
11.	Formaldehyde treated parthenium carbon(WC) and phosphoric acid treated parthenium carbon(PWC)	7.0	120	WC = 28.82 PWC = 59.17	[52]
12.	Gelatin/activated carbon composite bead form (GE/AC10%wt.)	4.0	1620	256.41	This study

^a t_{eq} is the equilibration time for Rhodamine B adsorption.

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Paper II

Adsorption of Pb²⁺ ions from aqueous solutions by gelatin/ activated carbon composite bead form.

Hayeeye, F., Yu, Q.J., Sattar, M., Chinpa, W. and Sirichote, O.

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Abstract

Gelatin and activated carbon materials have been combined together to obtain a gelatin/activated carbon composite bead form which is ecofriendly, nontoxic, biocompatible, and inexpensive material. In this paper, gelatin/activated carbon adsorption for Pb²⁺ ions from aqueous solutions was studied experimentally under various conditions. The experimental conditions such as contact time, solution pH, and gelatin/activated carbon dosage were examined and evaluated by using batch adsorption experiments. The maximum adsorption capacity of gelatin/activated carbon for Pb²⁺ ions was obtained to be 370.37 mg g⁻¹. This maximum capacity was comparable with that of commercial ion exchange resins and it was much higher than those of natural zeolites. The uptake process for Pb²⁺ ions was found to be relatively fast with 92.15% of the adsorption completed in about 5 min in batch conditions. The adsorption capacity was also strongly solution pH dependent. Adsorption was observed at pH value as low as 2.0 and maximum adsorption was achieved at a pH of approximately 5. The results indicated that the gelatin/activated carbon was effective to be used as an adsorbent for Pb²⁺ ions removal in wastewater treatment.

Keywords

Lead(II) ions, activated carbon, gelatin, gelatin/activated carbon composite bead, kinetic

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Introduction

The excess of Pb^{2+} ions released in environment from many activities such as agriculture and chemical industry, mining, and metal processing is very harmful to human and animal health. A low lead concentration of 0.006 mg l^{-1} in blood can damage fetal brain causing diseases of kidney, circulatory system, and nervous system (Barakat, 2011). Therefore, it is necessary to treat lead-containing wastewater prior to its discharge to the environment.

There are various methods for heavy metal removal in industrial wastewater treatment such as ultrafiltration (Majewska-Nowak, 1989), coagulation–flocculation (Prashant, 2012), adsorption (Bansode et al., 2003; Chuenchom, 2004; Dogan et al., 2007; Jiang et al., 2014; Ma et al., 2016; Suna et al., 2010), precipitation (Yüzera et al., 2008), electroplating (Fabiola et al., 2016), evaporation (Zeng et al., 2008), ion exchange (Li et al., 2014), and membrane processes (Lina et al., 2007). Many of these processes when applied to dilute systems with heavy metal ion concentrations of less than 100 mg l^{-1} are less effective or cost restrictive (Jose and Qiming, 1999). Thus, adsorption technology for the removal of trace amounts of heavy metals from dilute aqueous solutions attends to a growing interest.

Adsorption of heavy metal ions by activated carbon (AC) has been widely utilized as AC is one of the most effective adsorbent because AC has a porous structure with very high surface area, high capacity, and high rate of adsorption (Sirichote et al., 2008) for organic substances (Geçgel et al., 2016) and heavy metal ions (Gupta and Maheshwari, 2014). There have been several reports that AC can be used to adsorb Pb^{2+} ions. These include AC prepared from sugarcane bagasse (Tran et al., 2016), apricot stone (Kobya et al., 2005), date stones (Jamal et al., 2013), coconut shell (Jyotsna et al., 2004), and walnut wood (Ghaedi et al., 2015). However, AC in fine powder form limits its usage (Ninan et al., 2014). Therefore, studies on the adsorption of Pb^{2+} ions by granular AC have also been reported. Granular ACs prepared from various low-cost materials such as walnut shell (Kima et al., 2001), pecan shell (Bansode et al., 2003), peanut shell (Wilson et al., 2006), coconut shell (Jyotsna et al., 2005), red mud (Zhua et al., 2007), and cherry stones (Jaramillo et al., 2009) have been studied for heavy metal ion adsorption. However, generally the maximum adsorption capacities of granular AC are lower than those of powdered AC.

The combination of gelatin (GE) and powdered AC in the form of GE/AC bead for the adsorption of pollutants from aqueous solutions as well as actual wastewater samples has been reported (Hayeeye et al., 2015). GE is a biodegradable polymer derived from collagen from various animal by-products. It is an excellent material for the formation of bead forms of powdered materials. Recently, a commercially available GE made from peptone primagen of animal tissue was used to prepare adsorbent bead of GE and powdered AC (2 wt%). It was used for the adsorption of a cationic dye (Rhodamine B) with a maximum adsorption capacity of 13.12 mg g^{-1} (Hayeeye et al., 2015).

In this work, we developed adsorbent beads by increasing the amount of AC with GE ratio 10% w/w (GE/AC) to study adsorption of Pb^{2+} ions, which was selected as a representative of the heavy metal ions in effluents from wastewater. Batch equilibrium and kinetics experiments were carried out under various conditions to evaluate and optimize the adsorption efficiencies. Moreover, the adsorption behavior of the GE/AC for the removal of Pb^{2+} ions from aqueous solutions was investigated.

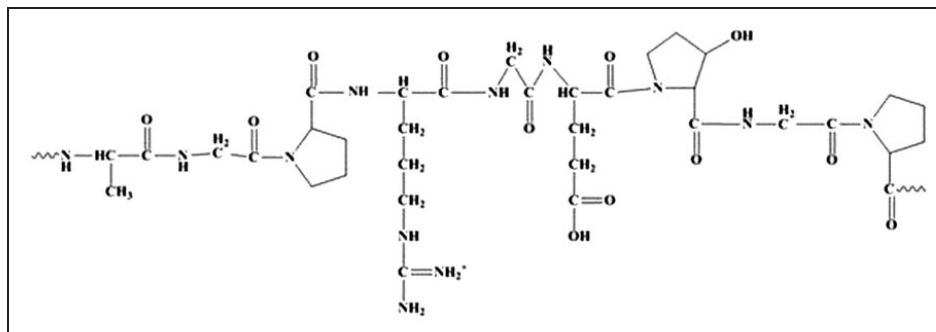


Figure 1. Chemical structure of gelatin.

Materials and methods

Materials and analytical methods

The GE/AC composite bead was prepared by the facile method as follows: a homogeneous solution of GE of 30 wt% was prepared by dissolving GE powder in distilled water. An amount of powdered AC of 10 wt% was added in the GE solution and stirred at room temperature for 30 min. The mixture was then added dropwise into cold water by using a syringe to form the bead form. The GE/AC beads were filtrated out and immersed in 1 wt% of glutaraldehyde solution for overnight. The GE/AC beads were then dried in an oven at 60 °C for 6 h. Further details of the preparation methods have been reported elsewhere (Hayeeye et al., 2015). The chemical structure of the GE used is given in Figure 1 (Martin, 1975).

Compound Pb(NO₃)₂ was procured from UNILAB, UK and used to prepare aqueous solutions of Pb²⁺ ions. The concentrations of Pb²⁺ ions were determined by using an atomic adsorption spectrophotometer (GBC SDS-270) (Martin, 1975).

Characterization of GE/AC

The specific surface area measurements for GE/AC were obtained from nitrogen adsorption isotherms at 77 K using a Quanta Chrome Autosorb automated gas sorption test, at the Institute for Scientific and Technological Research and Services, King Mongkut's University of Technology Thonburi.

The point of zero charge (pH_{pzc}) was determined by using the pH drift method (Jia et al., 1998, 2002). In brief, a series of 50 ml of 0.1 M NaCl solution was adjusted to desired pH from 2 to 12, by using 0.01 M HCl or NaOH. GE/AC of 0.15 g was added into each of this series and then sealed and kept overnight at ambient temperature. The relation of final pH (pH_f) to initial pH (pH₀) was used to determine the pH_{pzc} value of the adsorbent beads. At this point the initial and final pH values do not differ, and the surface of GE/AC is neutral (Hayeeye et al., 2014).

The exterior surface of GE/AC was obtained by scanning electron microscopy (SEM). The distribution of elemental component for GE/AC can be analyzed using the mapping

analysis of scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM/EDX) using a SEM, Quanta 400 at the Scientific Equipment Center, Prince of Songkla University, to characterize the morphology and the elemental components in GE/AC, respectively.

Batch kinetic experiments

Kinetic experiments were conducted at different initial Pb^{2+} concentrations of 50, 300, and 500 mg l^{-1} . The initial pH of the lead solution was adjusted to 5.5 by using 0.1 M HCl and NaOH solutions. An amount of 0.15 g of GE/AC was added to a continuously shaken container containing 50 ml of Pb^{2+} ions solution. Samples of 1 ml solution were withdrawn at predetermined time intervals by using a syringe and analyzed for Pb^{2+} concentration by atomic adsorption spectrophotometry. The amount of adsorption for Pb^{2+} onto the adsorbent was calculated by using equation (1) as follows (Hayeeye et al., 2014)

$$q_e = \frac{V(C_0 - C_e)}{W} \quad (1)$$

where q_e is the concentration of Pb^{2+} ions (mg g^{-1}) in solid phase at equilibrium, V is the volume of the solution (l), C_0 is the initial concentration of Pb^{2+} ions (mg l^{-1}), C_e is the equilibrium concentration of Pb^{2+} ions (mg l^{-1}), and W is the mass of adsorbent (g).

All experiments were carried out in triplicates and mean values including standard deviations were reported.

Batch equilibrium experiments

Batch equilibrium experiments were carried out to obtain the equilibrium isotherms and study the effects of contact time (5 min–24 h), initial concentration of Pb^{2+} ions (50, 300, and 500 mg l^{-1}), dosage of GE/AC (0.03–0.21 g), and solution pH (Jyotsna et al., 2005). Amounts of 0.15 g of GE/AC were added into 50 ml Pb^{2+} ions solutions and the mixtures were placed in a rotary shaker for 24 h. Then the supernatant solutions were analyzed for Pb^{2+} ions concentrations. All the experiments were carried out in triplicates and mean values were reported. For studying the effect of pH, both the initial pH and the final pH of the solutions were adjusted to a value between 1.5 and 5.5 by using 0.1 M HCl and NaOH solutions. Pb^{2+} ions concentrations were analyzed by atomic adsorption spectrophotometry. The amount of adsorbed Pb^{2+} ions was calculated by using equation (1).

Mathematical models for data analysis

The adsorption kinetics of Pb^{2+} ions was analyzed by the use of pseudo-first-order and pseudo-second-order kinetic models. The pseudo-first-order kinetic model can be written as shown in equation (2) (Lagergren, 1898)

$$\frac{dq}{dt} = k_1(q_e - q_t) \quad (2)$$

where q is the adsorbent phase concentration, t is the time, and k_1 is the first-order kinetics constant. Integrating equation (2) with the initial condition of $q_t=0$ at $t=0$ and the final condition of $q_t=q_t$ at time t and rearrange into a linear form to obtain equation (3)

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (3)$$

The pseudo second-order kinetic model can be written as in equation (4) (Ho and McKay, 1999; Umar et al., 2015)

$$\frac{dq}{dt} = k_2(q_e - q_t)^2 \quad (4)$$

where k_2 is the second-order kinetics constant. Integrating equation (4) with the conditions of $q_t=0$ at $t=0$ and $q_t=q_t$ at time t and rearrange into a linear form as shown in equation (5)

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (5)$$

For the evaluation of the equilibrium data, the commonly used Langmuir and Freundlich isotherm equations were used. The Langmuir equation (Langmuir, 1916, 1918) is often used to describe the adsorption on homogeneous surfaces based on the assumptions of monolayer adsorption. The Langmuir equation and its linearized form can be expressed as equations (6) and (7)

$$q_e = \frac{q_m b C_e}{1 + b C_e} \quad (6)$$

$$\frac{C_e}{q_e} = \frac{1}{q_m b} + \frac{C_e}{q_m} \quad (7)$$

where C_e is the equilibrium concentration of adsorbate in solution (mg l^{-1}), q_e is the equilibrium concentration of adsorbate in adsorbent (mg g^{-1}), and q_m and b are Langmuir constants which are related to the maximum adsorption capacity (mg g^{-1}) and the adsorption equilibrium constant (l mg^{-1}), respectively.

The Freundlich isotherm (Freundlich, 1907) is used for nonideal adsorption, which involves systems with heterogeneous surface energy. It assumes that the adsorption occurs at sites of different energy. The Freundlich equation and its linearized form are given in equations (8) and (9) as follows

$$q_e = K_F C_e^{1/n} \quad (8)$$

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (9)$$

where K_F and n are Freundlich constants related to the adsorption capacity and the adsorption intensity, respectively.

Results and discussion

Characterization of GE/AC

By BET surface area measurement, the narrow pore size distribution and its average pore diameter of 3.25 nm were found for GE/AC bead. This result indicated that this bead

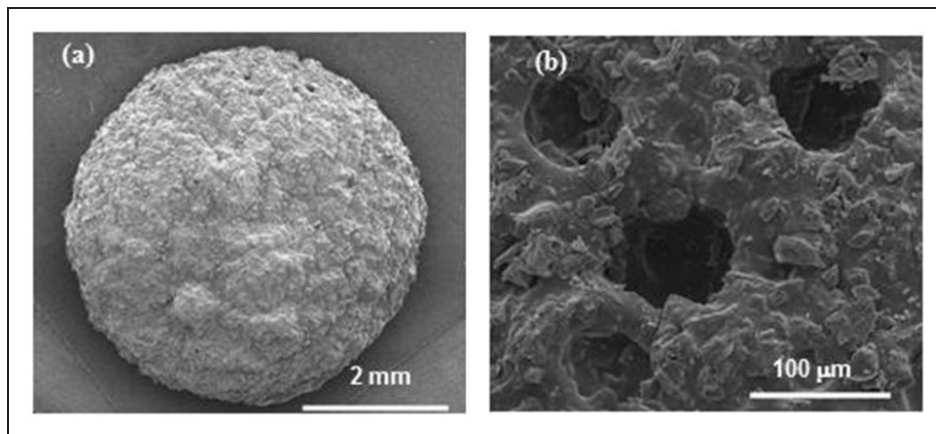


Figure 2. The SEM photographs of (a) bead size and (b) external surface of GE/AC. GE/AC: gelatin/activated carbon; SEM: scanning electron microscopy.

adsorbed was in mesoporous scale (2–50 nm). The specific surface area for GE/AC is $34.75 \text{ m}^2 \text{ g}^{-1}$. The point of zero charge of GE/AC is 4.5 indicated that the surface nature of GE/AC is acidic.

The SEM photographs in Figure 2(a) and (b) were taken at $20\times$ and $200\times$ magnification to observe the shape and surface morphology, respectively. SEM image presented the spherical bead with diameter about 4 mm (Figure 2(a)). At higher magnification, the rough surface showing many pores was also observed.

The elemental components for GE/AC before and after adsorption of Pb^{2+} ions were detected by SEM/EDX using a standardless qualitative EDX analytical technique. The peak heights in the EDX spectra are proportional to the elemental concentrations. The qualitative spectra for GE/AC before and after Pb^{2+} ions adsorbed are shown in Figure 3(a) and (b), respectively, and indicated that C, N, and O are the main constituents. In addition, the EDX spectrum of GE/AC after Pb^{2+} ions adsorbed was illustrated in Figure 3(b). The presence of Pb^{2+} ion in the spectrum revealed that Pb^{2+} ions were adsorbed on GE/AC.

Figure 4 shows EDX dot mapping of GE/AC (a) before and (b) after Pb^{2+} ions adsorbed. It can provide indication of the elemental distribution mapping. The blue bright points represented the Pb^{2+} ions adsorbed on GE/AC which are clearly shown in Figure 4(b). The high density of blue dot distributed on the surface of GE/AC indicated the abundant Pb^{2+} ions. These results confirmed that Pb^{2+} ions of 7.7 wt% adsorbed on GE/AC surface.

Kinetics of adsorption

The adsorption kinetics were studied at three different initial concentrations of 50, 300, and 500 mg l^{-1} and the respective kinetic profiles obtained are shown in Figure 5. The results indicated that the rate of Pb^{2+} ions uptake was rather fast with 90% of the total uptake occurred in about 5 min. However, after that, there was a slower process of uptake to about 1 h, after which no significant further adsorption was observed. Thus, the equilibrium time for Pb^{2+} ions adsorption was determined to be around 60 min at $23 \pm 2^\circ\text{C}$, pH 3–5, and

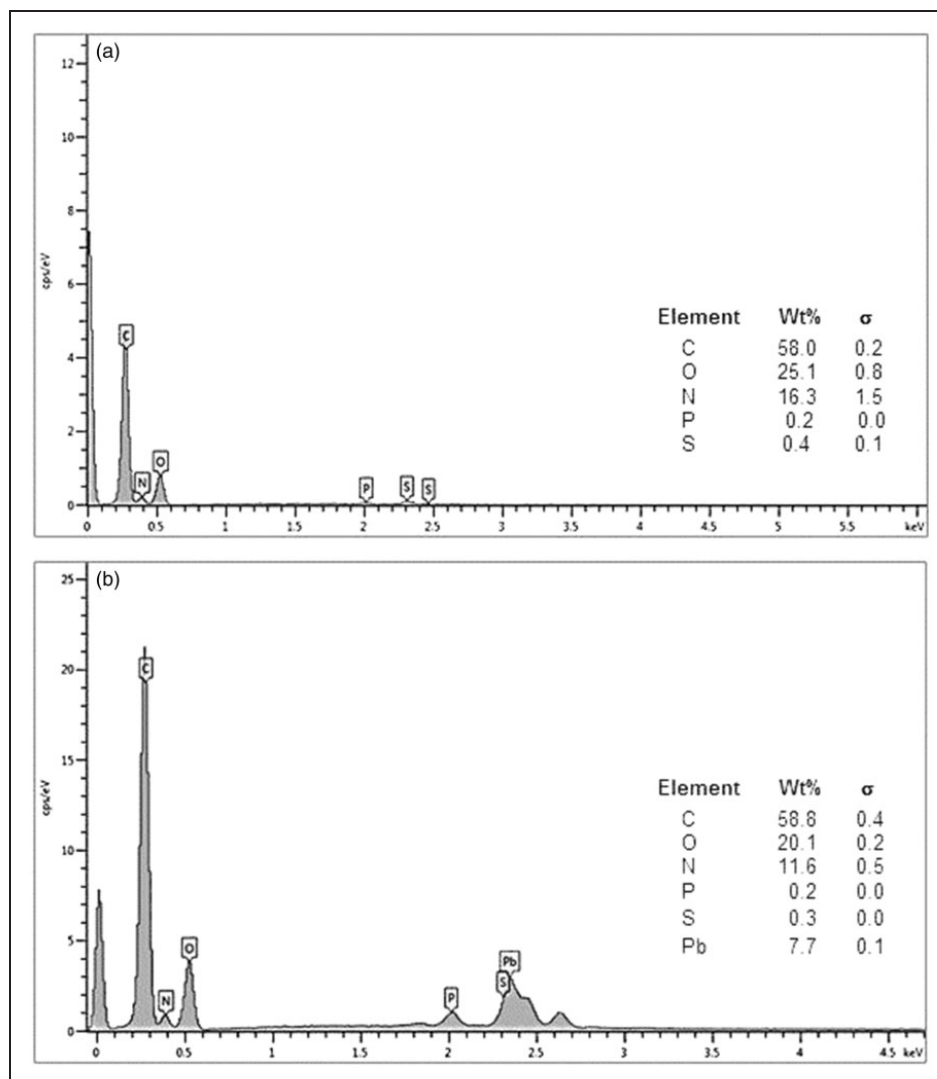


Figure 3. EDX spectra of GE/AC (a) before and (b) after adsorption of Pb^{2+} ions. EDX: energy dispersive X-ray spectroscopy; GE/AC: gelatin/activated carbon.

dosage of GE/AC of 0.15 g. Moreover, the results show that different initial concentrations were not effect to equilibrium time.

The evaluations of the kinetic profiles with the use of linearized forms of the pseudo kinetic models are shown in Figure 6 and the associated parameter values listed in Table 1. The values of kinetic parameter k_1 and k_2 were obtained from the slopes of the linear plots and those for q_e from the intercepts.

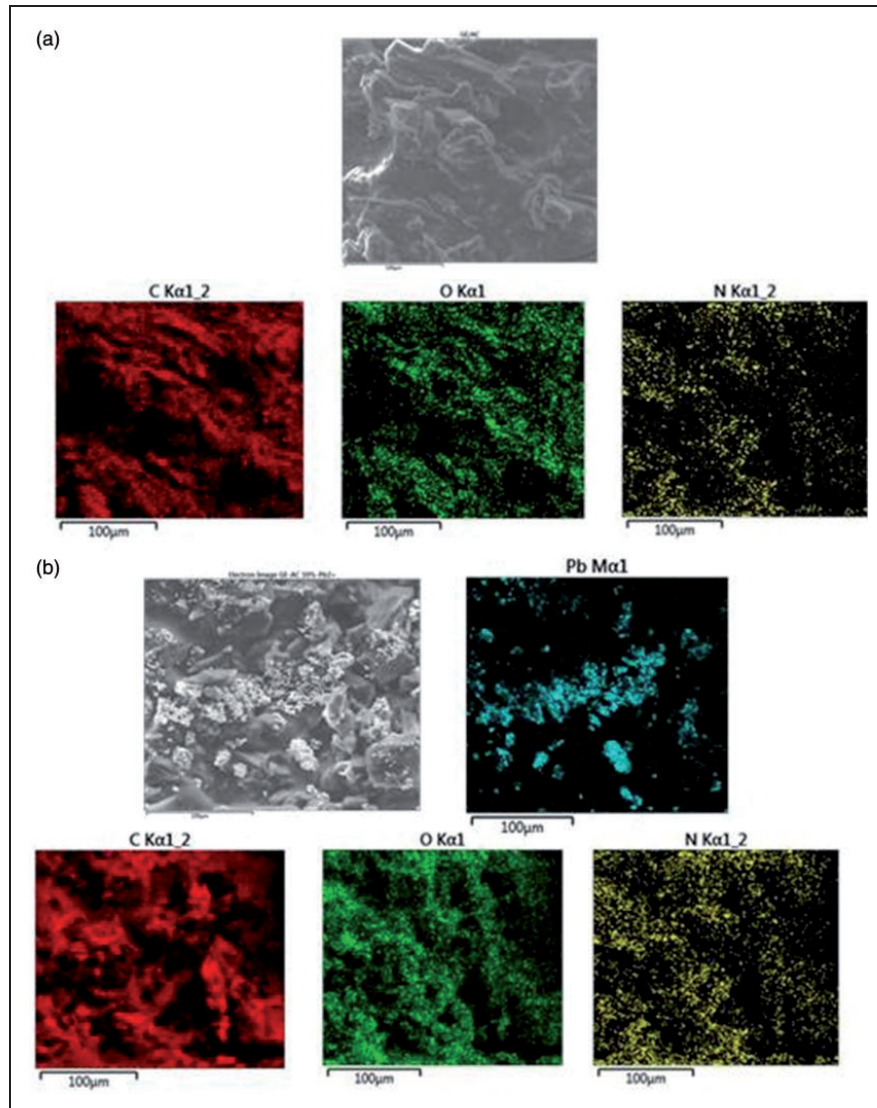


Figure 4. EDX dot mapping of GE/AC (a) before and (b) after adsorption of Pb^{2+} ions. EDX: energy dispersive X-ray spectroscopy; GE/AC: gelatin/activated carbon.

The plots in Figure 6 show that both the first- and the second-order pseudo kinetic models can fit the concentration profiles, but a better fit with a higher correlation coefficient ($R^2 > 0.99$). The q_e values obtained from the model were also in close agreement with those obtained experimentally. The pseudo-second-order rate constants were in the range of 4.19×10^{-3} to $36.85 \times 10^{-3} \text{ g mg}^{-1} \text{ min}^{-1}$.

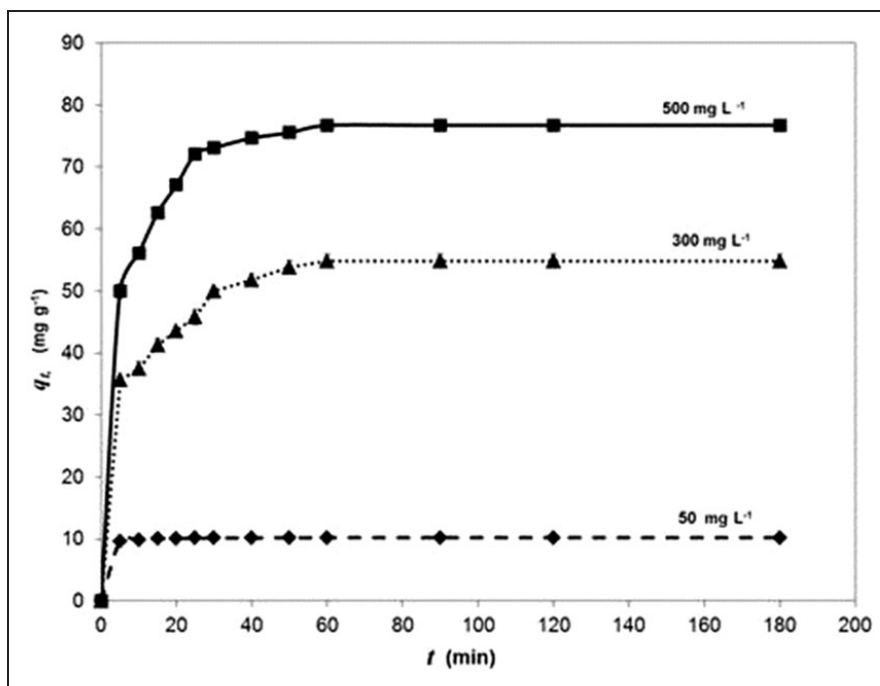


Figure 5. Kinetic profiles of Pb^{2+} ions adsorption onto GE/AC at different initial Pb^{2+} concentrations ((a) 50 mg l^{-1} , (b) 300 mg l^{-1} , and (c) 500 mg l^{-1}). GE/AC dose $0.15 \text{ g}/50 \text{ ml}$, temperature $23 \pm 2 \text{ }^\circ\text{C}$ and $\text{pH} = 5$. GE/AC: gelatin/activated carbon.

Effect of pH on Pb^{2+} ions uptake by GE/AC adsorbent

Solution pH affects the ionic states of functional groups on the adsorbent surface, such it is expected the adsorption is solution pH dependent. This effect was studied by evaluating the adsorption capacities at different solution pH in the range of 1.5–5 and the results are shown in Figure 7. Experiments beyond an initial pH value 5.5 were not conducted to avoid Pb^{2+} ions precipitation. It can be seen from Figure 4 that the adsorption capacity (q_e) of the GE/AC adsorbent increased with the pH of solution. The sharpest increase in q_e was observed between pH 2 and 3, while around pH 4 a plateau was reached. These results showed the suitability of the GE/AC adsorbent for the treatment of acidic wastewater. At a low pH range, the concentration of H^+ is high which promotes the protonation of the functional groups of the adsorbent, resulting it to be more positively charged, which in turn leads to the electrostatic repulsion of the positive charged Pb^{2+} ions. Moreover, at low pH values, the H^+ ions compete with Pb^{2+} ions for the adsorption sites (Kobyta et al., 2005).

Adsorption equilibrium isotherms

The adsorption isotherms for GE/AC adsorbent for Pb^{2+} ions presented in the aqueous phase at the solution pH range of 3–5 are shown in Figure 8. The adsorption isotherm has

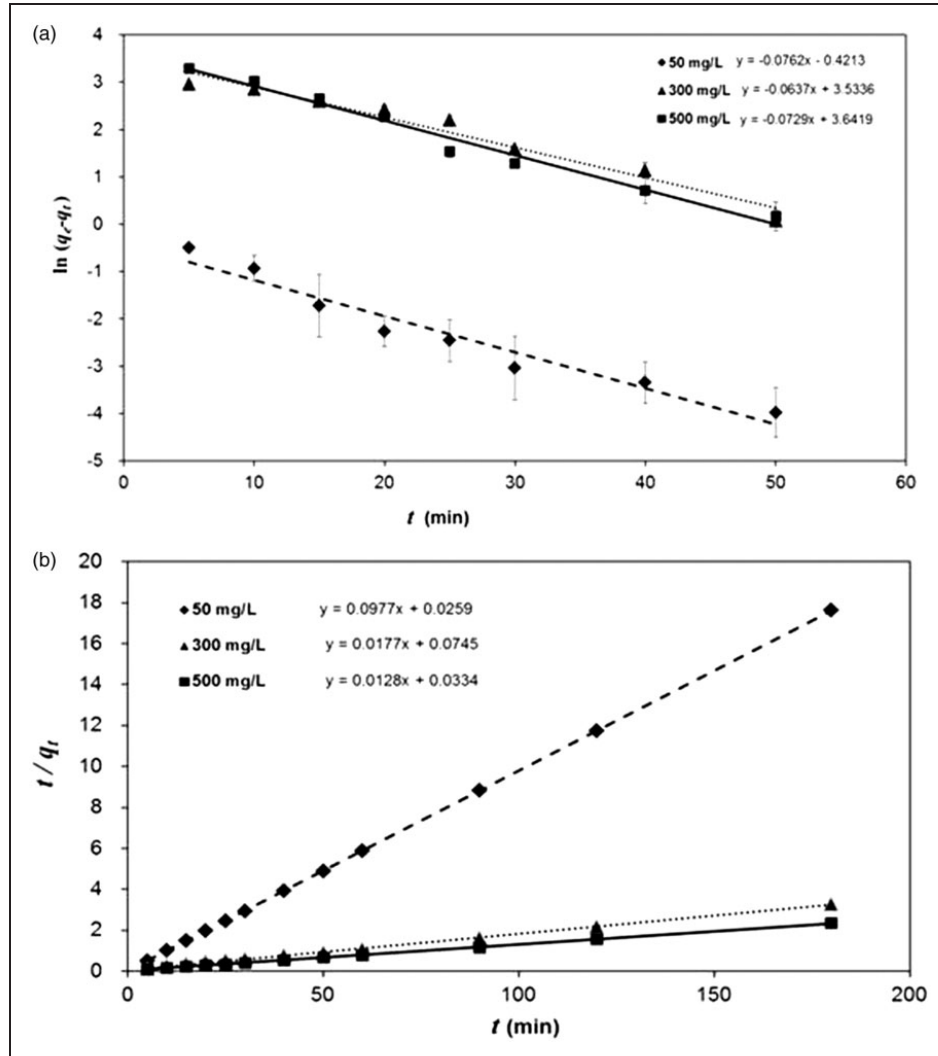


Figure 6. Linearized plots of the pseudo-first-order model (a) and pseudo-second order model (b) for Pb²⁺ ions adsorption onto GE/AC. GE/AC dose 0.15 g/50 ml, temperature 23 ± 2 °C, and pH = 5. GE/AC: gelatin/activated carbon.

Table 1. Kinetic parameters of pseudo-first-order and pseudo-second-order model at different initial concentrations.

C_0 (mg l ⁻¹)	q_e (exp) (mg g ⁻¹)	Pseudo-first-order			Pseudo-second-order		
		q_e (mg g ⁻¹)	k_1 ($\times 10^{-2}$)	R^2	q_e (mg g ⁻¹)	k_2 ($\times 10^{-3}$)	R^2
50	10.21	0.65	7.62	0.9510	10.24	36.85	1.0000
300	54.86	34.25	6.37	0.9615	56.50	4.21	0.9993
500	76.71	38.16	7.29	0.9808	78.13	4.91	0.9997

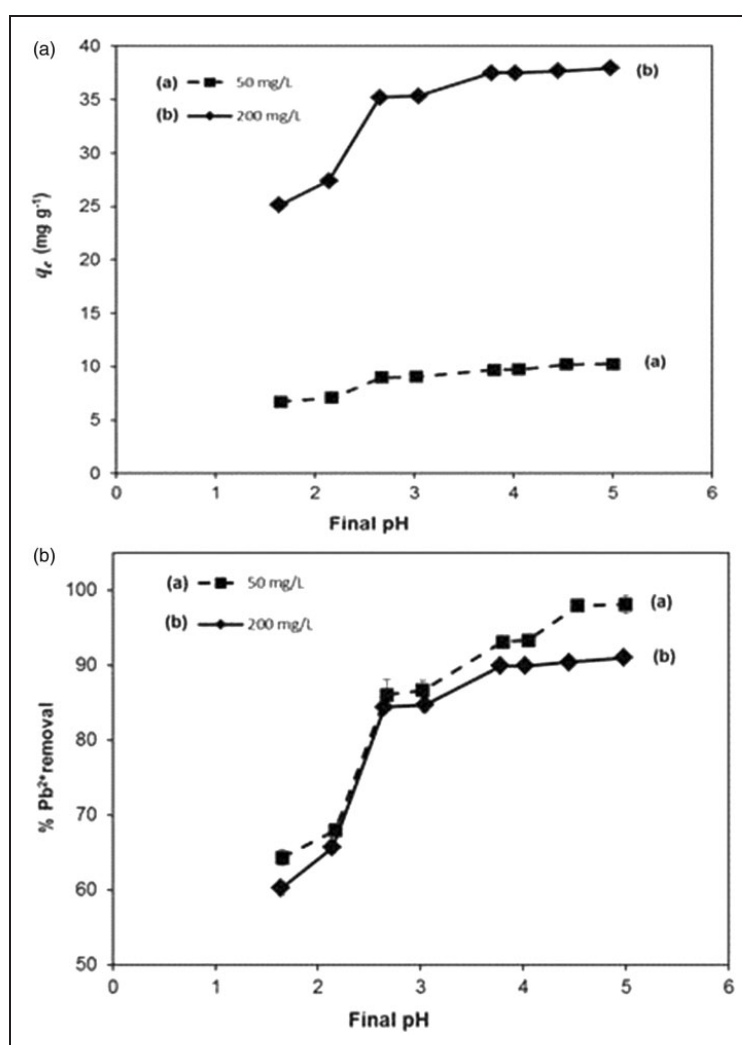


Figure 7. Effect of pH on GE/AC for Pb²⁺ ions adsorption. GE/AC dose 0.15 g/50 ml, temperature $23 \pm 2^\circ\text{C}$, Pb²⁺ concentration of (a) 50 mg l⁻¹ and (b) 200 mg l⁻¹. GE/AC: gelatin/activated carbon.

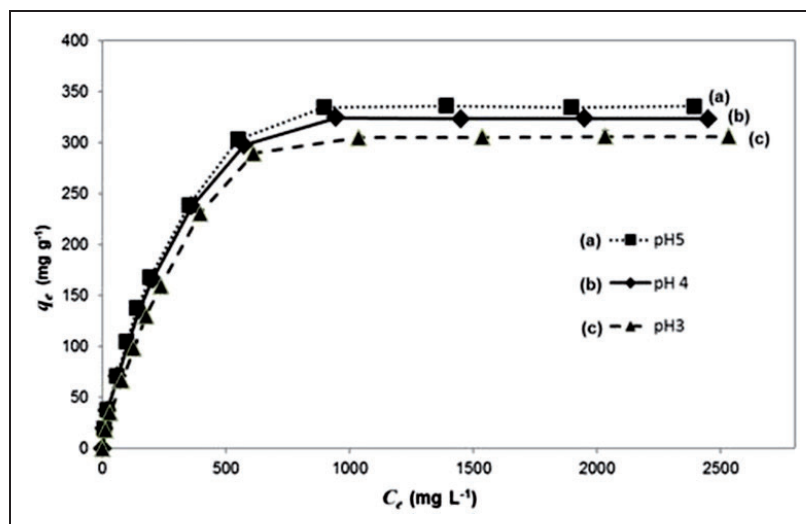


Figure 8. Adsorption equilibrium isotherms of Pb^{2+} ions onto GE/AC, GE/AC dose 0.15 g/50 ml, temperature $23 \pm 2^\circ C$, pH (3, 4, and 5), and equilibrium time 24 h. GE/AC: gelatin/activated carbon.

a typical shape of the L-2 type isotherms (Limousin et al., 2005). This indicated that there was a reduction in the number of active sites on the adsorbent surface at a high Pb^{2+} concentration in the solution phase.

The equilibrium isotherms in Figure 8 were fitted with the linearized forms of the both the Langmuir and the Freundlich equations as shown in Figure 9. The isotherm equation parameters are given in Table 2.

Figure 9 shows that the equilibrium isotherms are well correlated with the Langmuir model, with the R^2 values > 0.99 observed. On the other hand, the correlation with the Freundlich model was less satisfactory, particularly in the higher concentration ranges. The highest maximum adsorption capacity (q_m) of GE/AC for Pb^{2+} ions determined from the Langmuir model as 370 mg g^{-1} , which was higher than those of some granular AC. Table 3 show a comparison of the maximum adsorption capacities of Pb^{2+} ions (q_m , mg g^{-1}) by GE/AC to those of other adsorbents reported in the literature. The GE/AC bead was employed to increase a particular adsorption capacity of granular activated carbon. Moreover, the GE/AC bead adsorbent is easier to use for adsorption than activated carbon powder.

Effect of GE/AC dosage on Pb^{2+} ions removal

Experiments with the use of different dosages of GE/AC from 0.03 to 0.21 g per 50 ml of solutions were carried out to evaluate the effect of dose on Pb^{2+} ions removal at the initial concentrations of 100, 200, and 300 mg l^{-1} . The results are shown in Figure 10. An increase in adsorbent dosage increased percentage of Pb^{2+} ions adsorbed at equilibrium due to the surface area and availability of adsorption sites (Namasivayam and Kadirvelu, 1999), thus increased the removal efficiency. On the other hand, the adsorption capacity decreased with the increasing

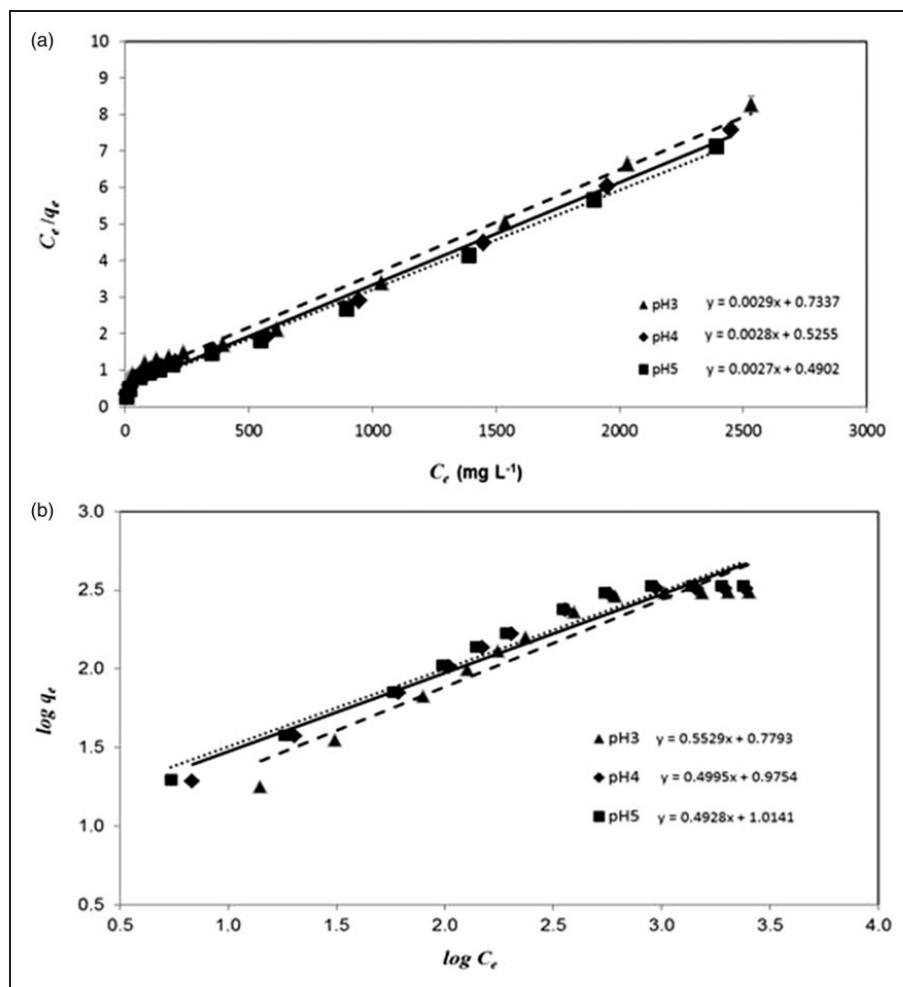


Figure 9. (a) Langmuir and (b) Freundlich adsorption isotherms for Pb²⁺ ions adsorption onto GE/AC. pH (3, 4, and 5), equilibrium time 24 h, temperature 23 ± 2 °C, GE/AC dose 0.15 g. GE/AC: gelatin/activated carbon.

Table 2. Parameter values of Langmuir and Freundlich equations of Pb²⁺ ions sorption on GE/AC at different solution pH at 23 ± 2 °C.

pH	Langmuir equation			Freundlich equation		
	q_m (mg g ⁻¹)	b ($\times 10^{-3}$) (l mg ⁻¹)	R^2	K_F (mg g ⁻¹)	n	R^2
3	345	3.95	0.993	6.02	1.81	0.923
4	357	5.33	0.995	9.45	2.00	0.946
5	370	5.51	0.995	10.33	2.03	0.953

GE/AC: gelatin/activated carbon.

Table 3. Comparison of the adsorption capacities (q_m , mg g^{-1}) of Pb^{2+} ions by powder, modified, and granular activated carbon reported in prior literature.

S. no.	Adsorbent	pH	t_{eq} (h)	q_m (mg g^{-1})	Reference
Powder activated carbons (PAC)					
1.	PAC prepared from sugarcane bagasse	5.0	24	19.30	Tran et al. (2016)
2.	PAC prepared from walnut wood	7.0	1.5	58.82	Ghaedi et al. (2015)
3.	PAC prepared from apricot stone	5.0	48	22.84	Kobyas et al. (2005)
4.	PAC prepared from coconut shell	4.5	24	26.50	Sekar et al. (2004)
Modified activated carbons					
5.	Alkali-modified biochar from hickory chips	5.0	24	53.60	Ding et al. (2015)
6.	AC with chelating polymer	5.0	1	20.00	Aroua et al. (2009)
7.	Coconut shell-based granulated modified AC	5.0	20	29.44	Jyotsna et al. (2004)
Granular activated carbons (GAC)					
8.	Nanocomposite of hydroxyapatite with GAC	6.0	2.5	83.33	Fernando et al. (2015)
9.	GAC prepared from peanut shells	4.8	24	198.72	Wilson et al. (2006)
10.	GAC prepared from coconut shell	5.0	20	21.88	Jyotsna et al. (2004)
11.	Gelatin/activated carbon composite bead form (GE/AC)	4.0	1	370.37	This study

GE/AC: gelatin/activated carbon.

^a t_{eq} is time at equilibrium.

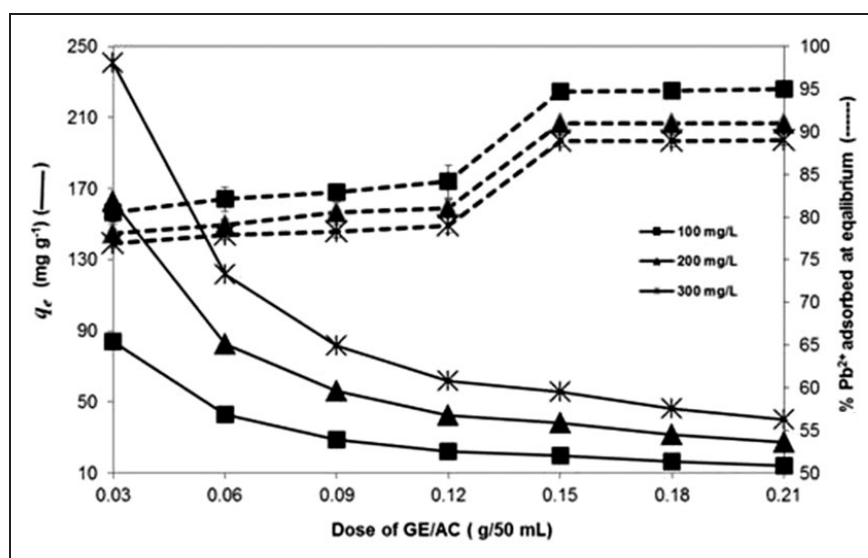


Figure 10. Effect of dosage on GE/AC for Pb^{2+} ions adsorption. GE/AC dose 0.03–0.21 g/50 ml, temperature $23 \pm 2^\circ\text{C}$, and $\text{pH} = 5$ and initial Pb^{2+} concentration of 100, 200, and 300 mg l^{-1} . GE/AC: gelatin/activated carbon.

of GE/AC. This result may be because after a certain dose of GE/AC, the maximum adsorption is reached due to both of amount of Pb^{2+} ions bound to the adsorbent and the amount of free ions remaining constant even with further addition of the dose of adsorbent (Charles and Odoemelam, 2010). A higher initial concentration of Pb^{2+} resulted in lower removal efficiency, as the number of active sites of GE/AC adsorbent is limited (Jamal et al., 2013).

Conclusions

Adsorption results obtained in this study indicated that the adsorbent obtained from the combination of GE and powdered AC in bead form could be used as practical adsorbent for the recovery of Pb^{2+} ions from wastewater. The GE/AC was an efficient and eco-friendly adsorbent. Batch kinetic studies showed that the rate of lead ion uptake by GE/AC adsorbent was high even at low initial concentrations and the concentration profiles followed the pseudo-second-order kinetic model. The adsorption capacity was found to be solution pH dependent with a higher capacity obtained at the higher pH ranges. Batch equilibrium studies showed that the equilibrium isotherms were well described by the Langmuir isotherm model and the highest maximum adsorption capacity was found to be 370 mg g^{-1} at pH 5. The highest adsorption efficiency observed was about 90%. Therefore, the GE/AC appears to be well suited for removal of Pb^{2+} ions from wastewater streams.

Declaration of Conflicting Interests

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List of Publication and Proceeding

1. Fareeda Hayeeye, Memoon Sattar, Watchanida Chinpa, and Orawan Sirichote, “Kinetics and thermodynamics of Rhodamine B adsorption by gelatin/activated carbon composite beads”. (2017). *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 513: 259–266.
2. Fareeda Hayeeye, Qiming Jimmy Yu, Memoon Sattar, Watchanida Chinpa, and Orawan Sirichote, “Adsorption of Pb²⁺ ions from aqueous solutions by gelatin/activated carbon composite bead form”. (2017). *Adsorption Science & Technology*, 0(0), 1–17 (First online: 1 Jan 2017).
3. Memoon Sattar, Fareeda Hayeeye, Watchanida Chinpa, and Orawan Sirichote, “Preparation and characterization of poly (lactic acid)/activated Carbon composite bead via phase inversion method and its use as adsorbent for

Rhodamine B in aqueous solution”. (2017). *Journal of Environmental Chemical Engineering*

4. Fareeda Hayeeye, Maimoon Sattar, Watchanida Chinpa, and Orawan Sirichote, “Preparation and adsorption study of gelatin/activated carbon composite bead form”. (2015). *Advanced Materials Research*, 1077: 18 - 22.
5. Fareeda Hayeeye, Maimoon Sattar, Surajit Tekasakul and Orawan Sirichote. “Adsorption of Rhodamine B on activated carbon obtained from pericarp of rubber fruit in comparison with the commercial activated carbon”. (2014). *Songklanakarin Journal of Science and Technology*, 36 (2): 177-187.
6. Maimoon Sattar, Fareeda Hayeeye, Watchanida Chinpa, and Orawan Sirichote. “Preparation and characterization of polysulfone/activated carbon composite bead form”. (2014). *Applied Mechanics and Materials*, 625: 106 – 109.

Oral presentation

Fareeda Hayeeye, Maimoon Sattar, Watchanida Chinpa, and Orawan Sirichote, “Preparation and adsorption study of gelatin/activated carbon composite bead form”. (2015). 3rd International Conference on Mechanical Engineering and Materials (ICMEM 2014), November 5 – 6, 2014, Singapore.

Abstract presentation

Fareeda Hayeeye, Maimoon Sattar, Watchanida Chinpa, and Orawan Sirichote, “The novel biosorbent for adsorption study of Rhodamine B” Advance Composite Innovation Conference 2016, April 13 – 14, 2016, Melbourne, Australia.