

# Synthesis and Utilization of Composite Beads of Activated Carbon-Phosphate-Chitosan as Adsorbent of $Mg^{2+}$ and $Pb^{2+}$ Metal Ions

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## ABSTRACT

We report a new modification of composite beads to absorb metal ions. The phosphate insertion into the activated carbon coated with chitosan is expected to have a higher adsorption capacity and the better mechanical properties than activated carbon and chitosan respectively. The identification of the adsorption ability of the composite beads was carried out at various contact times between the adsorbent and metal ions ( $Mg^{2+}$  and  $Pb^{2+}$ ) using a batch system. Furthermore, the beads are regenerated using  $Na_2EDTA$ . Characterization of beads is carried out using a Surface Area Analyzer (SAA), Fourier Transform Infrared (FTIR) and Transmission Electron Microscope (TEM). Concentration of metal ions was determined using Atomic Absorption Spectroscopy (AAS). The characterization of composite beads of activated carbon-phosphate-chitosan showed that the beads had a spherical morphology with a measure of activated carbon on a nano scale ( $<100$  nm) and a surface area of  $0.01176$   $m^2/g$ . The composition of chitosan and phosphate in adsorbent is supported by FTIR spectrum absorption peaks, namely N-H, -OH and P-O bonds. The composite beads have adsorption capacity for both  $Mg^{2+}$  and  $Pb^{2+}$  ions which is almost the same, which is  $\sim 11$   $mg/g$  with the contact time to the analyte relatively constant of  $\sim 150$  minutes. The identification of regeneration beads with  $Na_2EDTA$  shows that the adsorbent has been potential to be reused.

**Keywords:** Adsorbent, Composite beads, Activated carbon, Phosphate, Chitosan

## 1. INTRODUCTION

Activated carbon is a carbon material that has porosity and a broad surface, which is  $500$ - $2,000$   $m^2/g$  [1]. Therefore, activated carbon has a high absorption and is widely used as an adsorbent, especially metal ions [2]. Nevertheless, modification of activated carbon as an adsorbent continues to be done, in order to increase the capacity of the adsorbent, selectivity, or mechanical strength [3].

Materials that can be used to modify activated carbon include chitosan and phosphate. Adsorption of  $Cu^{2+}$  ions by phosphate modified zeolites, the effectiveness of adsorption increased by  $67\%$ , while the  $Pb^{2+}$  ions increased by  $99.67\%$  for Z-PN $a_2$ -S and  $99.29\%$  for Z-PN $a_2$ -L [3,4]. Another material

commonly used as an adsorbent is chitosan. Chitosan is commonly synthesized from chitin, which can be found in crustaceans, shrimp shells, crab shells, snail shells, and green mussel shells [5-8]. Chitosan has a free amino group and a high degree of deacetylation, so it has the ability to bind metals, proteins and dyes [5,9]. However, the use of chitosan directly as an adsorbent is less effective, because chitosan is easily soluble in acids which can interfere with the adsorption process. One of the Technique that can be done to overcome these problems is chitosan compiled to a stronger material, such as carbon [6].

In this study composite materials were made consisting of activated carbon-phosphate-chitosan in the form of beads. The composite beads is expected to have a large adsorption capability on metal ions.

The function of adding phosphate and chitosan to activated carbon is to increase the number of active groups thereby increasing its adsorption power. In addition, activated carbon has resistance to high temperatures. Temperature greatly affects the mechanical properties of a polymer, so that the form of the composite produces better mechanical properties than chitosan without any addition. The metal ions that were tested in this study are  $Mg^{2+}$  and  $Pb^{2+}$  ions. Furthermore, the composite beads in the adsorption process will be identified the ability of adsorption at various contact times between the adsorbent and the analyte also the ability to regenerate using  $Na_2EDTA$ . Regeneration using  $Na_2EDTA$  is better than  $H_2SO_4$ , therefore in this study  $Na_2EDTA$  will be used for regenerating composite beads [5].

## 2. EXPERIMENT SECTION

**Chemicals.** The materials required are carbon (technical), chitosan (technical), HCl (pa E Merck),  $Pb(NO_3)_2$  (pa E Merck),  $MgCl_2$  (pa E Merck), phosphoric acid (pa E Merck), acetic acid (pa E Merck), NaOH solution (pa E Merck), formaldehyde (pa E Merck), 99% ethanol (pa E Merck),  $Na_2EDTA$  (pa E Merck), and distilled water. Chemicals used without further purification.

**Instruments.** The tools used are the Atomic Absorption Spectrophotometer type AA-7000 Shimadzu, Fourier Transform Infrared Spectrophotometer Shimadzu type Prestige-21, Surface Area Analyzer type St 2 on NOVA touch 4LX, Transmission Electron Microscope type JEOL JEM-1400, magnetic stirrer plus electric heater, oven, vacuum pump, analytical balance, pH meter, shaker, 100 mesh sieve, mortar and pestle, and glassware.

### 2.1. Activated Carbon Preparation

Commercial activated carbon is crushed using a mortar until smooth, and sieved at 100 mesh. After that, activated carbon is washed with distilled water and dried to dry. Then, the carbon was reactivated by immersing 60 g of carbon in a 2 M HCl activator reagent for 10 hours while in a shaker. After that, activated carbon is filtered and washed with distilled water to a neutral pH. Activated carbon is dried in an oven at 110 °C for 3 hours.

### 2.2. Inserting Phosphate to Activated Carbon

As much as 50 grams of activated carbon plus 1000 mL of distilled water and 13 grams of phosphoric acid, stirred at 60 °C for 3 hours and dried

at 110 °C for 3 hours [4].

### 2.3. Chitosan Preparation

As much as 1 gram of chitosan powder was dissolved in 1% (v/v) acetic acid solution. Furthermore, the mixture was added with 60 mL of distilled water in beaker glass while stirring for 2 hours to form a yellowish-colored gel. Chitosan gel formed was left at room temperature for 24 hours.

### 2.4. Synthesis of Composite Beads of Activated Carbon-Phosphate-Chitosan

One gram of activated carbon-phosphate is mixed in chitosan gel while stirred for 1 hour. The mixture is then pipetted and dropped into 0.5% (w/v) NaOH solution and a few drops of 99% ethanol, to form black beads. Beads in the NaOH and ethanol solution were shaken for 15 minutes and allowed to stand for 30 minutes. After that, the beads are filtered and washed with distilled water. Then the beads are immersed in 0.1 M formaldehyde solution for 2 days which functions as a crosslinking agent. Beads are filtered and washed again with distilled water to a neutral pH and dried at room temperature (constant weight). The dried dots are then called the composite beads of activated carbon-phosphate-chitosan.

### 2.5. Characterization of Composite Beads of Activated Carbon-Phosphate-Chitosan

Characterization of composite bead includes surface area, functional groups, and morphology. The surface area of the composite adsorbent was analyzed using a Surface Area Analyzer (SAA). Analysis of the adsorbent functional groups using Fourier Transform Infrared Spectroscopy (FTIR). The morphology of the beads was identified using Transmission Electron Microscopy (TEM).

The concentration of metal ion solution was determined using Atomic Absorption Spectroscopy (AAS). The adsorbed metal ion is calculated by the difference between the initial concentration of the metal ion solution and final concentration of the metal ion solution, i.e. after interacting with the adsorbent.

### 2.6. Adsorption Process

The adsorption process includes identification of the adsorption ability of many adsorbents, including activated carbon, activated carbon-phosphate, chitosan, and composite beads of activated carbon-phosphate-chitosan. In addition, identification of the

ability of adsorption of activated carbon-phosphate-chitosan beads was carried out at various contact times between the adsorbent and the analyte, i.e.  $\text{Mg}^{2+}$  and  $\text{Pb}^{2+}$  ions. Identification of the adsorption ability is done by 0.2 g of each adsorbent (composite beads of activated carbon-phosphate-chitosan, activated carbon, activated carbon-phosphate, and chitosan) contacted with 10 mL of metal ion solution (10 ppm for  $\text{Mg}^{2+}$  ion and 300 ppm for  $\text{Pb}^{2+}$  ion) for 16 hours. Next, the number of particles absorbed by adsorbent is analyzed, i.e. the difference between the initial concentration and the final concentration after the adsorption process. While identification of the effect of contact time on the adsorption ability is done by immersing 0.2 g of composite beads of activated carbon-phosphate-chitosan into 10 mL of metal ion solution (300 ppm  $\text{Mg}^{2+}$  ion and 200 ppm  $\text{Pb}^{2+}$  ion) for 50, 100, 150, 200, 720 and 1440 minutes.

### 2.7. Regeneration Process

One gram of composite beads of activated carbon-phosphate-chitosan has been used for adsorption of metal ions is immersed in 10 mL of 0.5 M  $\text{Na}_2\text{EDTA}$  solution for 30 minutes. After filtering, the beads are soaked in NaOH solution for 2.5 hours. Then, the beads are filtered, washed with distilled water to a neutral pH, and dried at room temperature. Then, 0.2 grams of dried regenerated beads were contacted again in 10 mL a solution of metal ions (300 ppm  $\text{Mg}^{2+}$  ions and 200 ppm  $\text{Pb}^{2+}$  ions) and placed in a shaker for 150 minutes.

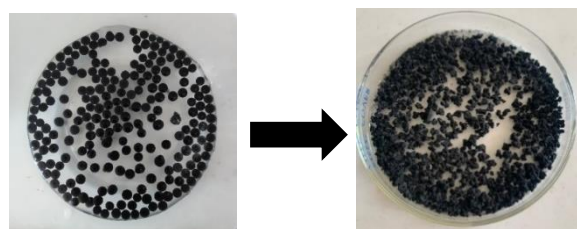
## 3. DISCUSSION

Composite beads of activated carbon-phosphate-chitosan have been successfully synthesized. First, composites are made by inserting phosphoric acid into the pores of activated carbon. The use of phosphoric acid refers to the previous research, which states that phosphate has four oxygen atoms which can increase the total negative charge on the zeolite adsorbent, thereby increasing the adsorption capacity of  $\text{Pb}(\text{II})$  ions [4]. Visually, activated carbon before and after modification with phosphate, both of which have no physical changes. Second, activated carbon-phosphate is mixed with chitosan gel. The function of adding chitosan gel to carbon is to increase the number of active groups thus increasing its adsorption power. In addition, activated carbon composites also have high temperature resistance. Temperature greatly affects the mechanical properties of a polymer, so that chitosan in the form of

composites produces better mechanical properties than chitosan without any addition.

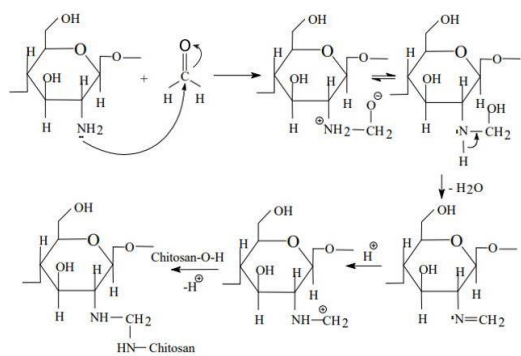
Further the composite is formed into beads by dripping a mixture of chitosan-activated carbon-phosphate gel into a solution of NaOH containing ethanol. NaOH solution hardens the beads and does not break when dried. In addition, the alkaline nature of NaOH is intended to neutralize the acetic acid contained in the chitosan gel. The presence of ethanol serves to help reduce surface tension so that the beads can be spherical. After the composite beads are formed, they are immersed with a crosslinking agent, formaldehyde which is used to increase the chemical stability of the adsorbent in the acid. The mechanical properties of composite beads before and after crosslinking have changed. Composite beads before crosslinking have a fragile structure, whereas beads after crosslinking have a harder structure and are not easily damaged.

The synthesized composite beads can be seen in Figure 1. The composite beads of activated carbon-phosphate-chitosan that have been dried are irregularly spherical in shape, different from before being drained which tends to be perfectly round in shape. Beads are black, a little hard, not sticky and have a diameter of about 1 mm. The smaller the shape of the beads produced, the greater the surface area, means it has a large adsorption ability.



**Figure 1.** The composite beads of activated carbon-phosphate-chitosan before drying (left) and after drying (right).

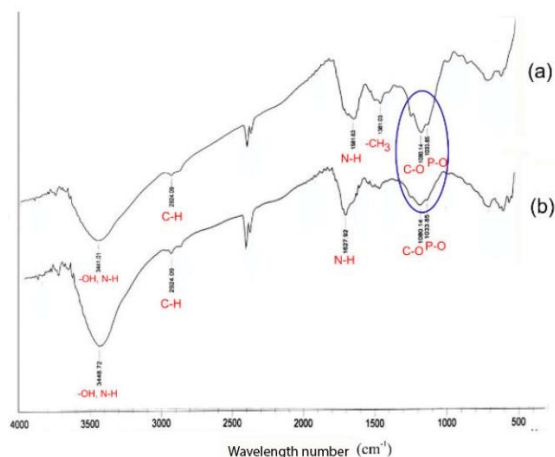
The reaction between chitosan and formaldehyde involves an amine group of chitosan that is cross-linked with a carbonyl acetaldehyde group. The formation of these follows the mechanism of forming Schiff bases through an elimination-addition reaction. The mechanism is shown in Figure 2.



**Figure 2.** Mechanisms of cross-link reaction between chitosan and formaldehyde [10].

### 3.1. Characterization of Composite Beads of Activated Carbon-Phosphate-Chitosan

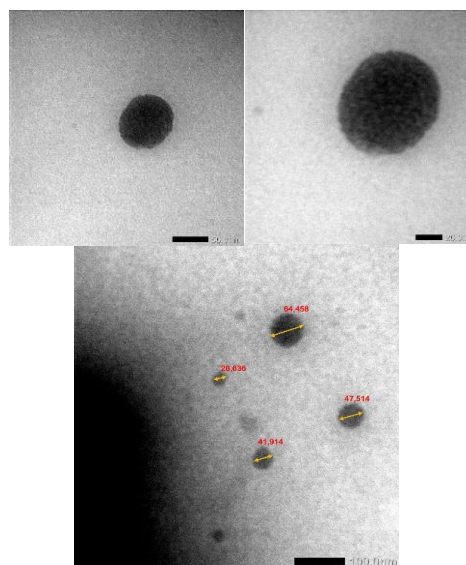
Characterization with Surface Area Analyzer (SAA) showed composite beads had a pore surface area of 0.01176 m<sup>2</sup>/g, a pore volume of 0.000488948 cc/g and a pore diameter of 83.1546 nm. The value of the pore of beads is close to zero means the surface of activated carbon is almost entirely enveloped in chitosan.



**Figure 3.** FTIR spectrum of composite beads of activated carbon-phosphate-chitosan (a) before adsorption; (b) after regeneration.

Characterization of composite beads using FTIR was done just before adsorption and after regeneration. The FTIR spectrum produced is shown in Figure 3. The spectrum shows the overlapping vibrations of the -OH group with N-H stretching in the wavelength number 3441.01 cm<sup>-1</sup> for composite beads before adsorption and 3448.72 cm<sup>-1</sup> for composite beads after regeneration. Absorption at 2924.09 cm<sup>-1</sup> of both spectra shows aliphatic C-H stretching vibrations. Wavelength number 1581.63 cm<sup>-1</sup> in composite beads spectrum before adsorption

and 1627.92 cm<sup>-1</sup> in composite beads spectrum after regeneration showed bending vibrations of amine (N-H). The bending absorption of -CH<sub>3</sub> in the adsorbent before adsorption was seen in the area of 1381.09 cm<sup>-1</sup>. The vibration of the C-O group was identified at the wavelength number 1080.14 cm<sup>-1</sup>. Peak appears in the wavelength number 1033.85 cm<sup>-1</sup> which is likely a P-O vibration. Absorption at these wavelength number shows the decrease absorption intensity of C-O and P-O, probably due to the regeneration process. Generally, spectrum FTIR of composite beads before adsorption and after regeneration do not change.

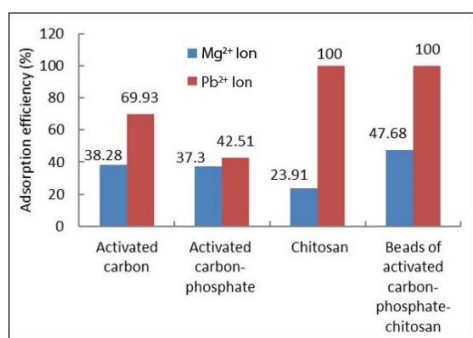


**Figure 4.** Results of TEM analysis of composite beads of activated carbon-phosphate-chitosan.

Identification the surface of composite beads of activated carbon-phosphate-chitosan was using TEM which can be seen in Figure 4. In the figure it appears that activated carbon (black colour) was successfully coated by chitosan (grey), forming a sphere that called a grain (bead). Based on these images, it can be observed that the morphology of particles that are spherical in a ball shape with a slightly rough surface. Each of these circles has different sizes, ranging from the largest to the smallest at 64.458 nm; 47.514 nm; 41.914 nm, and 28.636 nm. So, the composite beads of activated carbon-phosphate-chitosan are composed of nano-sized particles.

### 3.2. Identification of The Adsorption Ability of Composite Beads of Activated Carbon-Phosphate-Chitosan Towards $Mg^{2+}$ and $Pb^{2+}$ Metal Ions

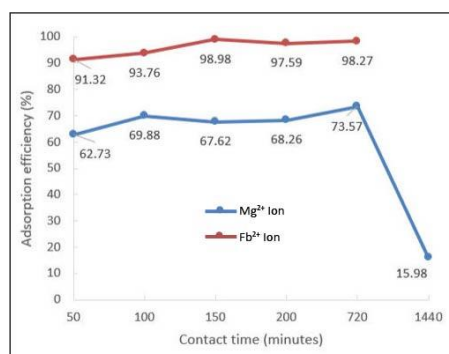
The adsorption ability of composite beads of activated carbon-phosphate-chitosan beads to metal ions has been compared with the adsorption ability of activated carbon, activated carbon-phosphate, and chitosan. The comparison of the adsorption efficiency values of these adsorbents towards  $Mg^{2+}$  and  $Pb^{2+}$  ions can be seen in Figure 5.



**Figure 5.** The adsorption efficiency towards  $Mg^{2+}$  and  $Pb^{2+}$  ions at various adsorbents. As much as 0.2 g adsorbent were immersed in each solution, which is 10 mL soluble  $Mg^{2+}$  300 ppm and 10 mL soluble  $Pb^{2+}$  200 ppm.

Composite beads of activated carbon-phosphate-chitosan have the highest adsorption efficiency of  $Mg^{2+}$  ion and  $Pb^{2+}$  ion than the adsorption efficiency of activated carbon, activated-phosphate carbon, and chitosan. Apparently, the adsorption ability of composite beads seems to be dominated by the adsorption ability of chitosan which coats the surface of beads is almost non-porous. Interactions between composite beads with the metal ions tend to be chemical interactions on the surface, i.e. the amine and hydroxyl groups of chitosan with metal ions ( $Mg^{2+}$  and  $Pb^{2+}$  ions). Amino and hydroxyl groups of chitosan with metal ions can form covalent bonds, hydrogen bonds or electrostatic forces such as van der Waals [11]. The advantage of activated carbon as composite of chitosan is to increase the mechanical strength of the adsorbent to be more resistant to acidic condition, temperature and pressure. In addition, oxygen atoms from phosphate in activated carbon are useful to improve the electronegativity of chitosan so that metal ions ( $Mg^{2+}$  and  $Pb^{2+}$  ions) are increasingly attracted towards composite beads.

Based on Figure 6, identification the adsorption efficiency of composite beads of activated carbon-phosphate-chitosan towards metal ion solution by contact time 100 minutes to 720 minutes shows the graph values tend to be relatively constant. A significant increase in the efficiency value (~ 5%) occurs in  $Mg^{2+}$  ion by the contact time of 100 minutes to 150 minutes. Based on the analysis in this study it can be said that the recommended contact time between the composite beads and the analyte is 150 minutes.



**Figure 6.** Identification contact time to adsorption efficiency of composite beads of activated carbon-phosphate-chitosan in each metal ion solution, i.e. 10 mL  $Mg^{2+}$  300 ppm and 10 mL  $Pb^{2+}$  200 ppm.

**Table 1.** Adsorption power of composite beads of activated carbon-phosphate-chitosan towards  $Mg^{2+}$  and  $Pb^{2+}$  ions at various contact times

Metal Ion		$Mg^{2+}$		$Pb^{2+}$
Concentration Metal Ion at Various of Contact times	50'	$C_x$ (ppm)	184.72	203.15
		Q (mg/g)	9.24	10.16
	100'	$C_x$ (ppm)	205.78	208.57
		Q (mg/g)	10.29	10.43
	150'	$C_x$ (ppm)	199.12	220.18
		Q (mg/g)	9.96	<b>11.01</b>
	200'	$C_x$ (ppm)	201.00	217.09
		Q (mg/g)	10.05	10.85
	720'	$C_x$ (ppm)	216.65	218.61
		Q (mg/g)	<b>10.83</b>	10.93

Note:  $C_x$  = adsorbed analytes concentration (ppm or mg/L); Q = adsorption power (mg/g).

When the contact time between the analyte and the adsorbent is too long (> 360 minutes or 6 hours), the adsorption efficiency is less effective in terms of time efficiency. Even more, when the contact time is more than 24 hours, the analyte tends to be easily separated from the adsorbent as shown in the contact time analysis of  $Pb^{2+}$  ion, i.e. 1440 minutes or 24 hours. It is possible that the interaction between both the adsorbent and the metal ions with water

molecules weakens the interaction of the metal ions with the adsorbent. Furthermore, the highest adsorption power in this research can be determined, which is 10.83 mg/g for  $Mg^{2+}$  and 11.01 mg/g for  $Pb^{2+}$  ion (see Table 1). The adsorption power of composite beads is almost the same as the value of chitosan adsorption power in previous studies, which is 13.25 mg/g [5]. This supports that the composite beads adsorption ability is dominated by the chitosan adsorption power.

### 3.3. Identification of Adsorption Efficiency of Composite Beads of Activated Carbon-Phosphate-Chitosan after Regeneration Process

Regeneration aims to restore the function of the active site on chitosan so that the adsorbent can bind again to metal ions. Regeneration was done by immersing composite beads that have been used in  $Na_2EDTA$  solution. It is called desorption process, which is the process of releasing metal ions absorbed in the adsorbent.  $Na_2EDTA$  is used as desorption agent because EDTA is a chelating agent that can form complexes with metal ions. The chelate complex is more stable than the non-chelate, so EDTA has the good ability to bind  $Mg^{2+}$  ions and  $Pb^{2+}$  ions. Thus, the metal ions can be separated from the adsorbent so that the adsorbent has the potential to be reused.

The composite beads that have been regeneration are re-contacted with each a solution of metal ion, i.e.  $Pb^{2+}$  ion and  $Mg^{2+}$  ion. In this study obtained that the regenerated composite beads activated carbon-phosphate-chitosan has an adsorption efficiency of  $Mg^{2+}$  ion and  $Pb^{2+}$  ion, respectively 13.47% and 59.30%. Decreasing of adsorption efficiency can be possible because the concentration of EDTA solution and contact time are not yet optimum. It can also be possible due to chitosan is slightly soluble during regeneration. Although the efficiency of adsorption has not been satisfactory, these results indicate that regenerated adsorbents have potential for reuse as adsorbents. This leads to a deeper study of about concentration of desorption agent, contact time between adsorbent with desorption agent, up to the kind of absorption agent so that the regenerated composite performance can return of 100%.

## 4. CONCLUSION

Composite beads of activated carbon-phosphate-chitosan have been successfully synthesized. Morphologically, the beads are almost spherical in

shape, black in color and are composed of particles that are nano-sized. The composite beads performed the ability for adsorption of metal ions such as  $Mg^{2+}$  and  $Pb^{2+}$  ions with an adsorption power almost the same, which is ~11 mg/g. By this study, the recommended contact time in the adsorption process of composite beads of activated carbon-phosphate-chitosan is ~150 minutes. In addition, the adsorbent has the potential to be regenerated with complexing agents such as EDTA so that it can be reused.

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