

Applicability of reused industrial dry sanding powder for adsorption of arsenic

Y. J. Park, J. K. Yang and S. I. Choi

ABSTRACT

This study examined the potential reuse of powdered wastes (PW) generated during the sanding and sawing process in a local chemical company in Korea with the viewpoint of the recycling these wastes and minimizing the level of contamination. As the aluminium hydroxide inside the PW could be thermally converted to various types of aluminium oxides depending on the calcination temperature, the adsorptive properties could be changed and it may affect on adsorption ability. Calcination of the PW was performed for 3 h at 550°C, 750°C, and 950°C. From the results, amorphous aluminium oxide was thermally generated by calcinating the PW at 550°C and with further increase of temperature to 950°C, the crystallinity of amorphous aluminium oxide was gradually increased. The physicochemical analysis of calcined powdered wastes (CPW) at various temperatures showed that more developed porosity was noted in the CPW as the calcinations temperature increased, whereas surface area was significantly decreased from $175.5\text{ m}^2\text{ g}^{-1}$ to $46.5\text{ m}^2\text{ g}^{-1}$. The removal efficiency of arsenate on the CPW decreased as the calcinations temperature increased from 550°C to 950°C. The CPW₅₅₀ exhibited the highest adsorption capacities toward arsenate over pH range of 2–8 and showed a complete removal of the arsenate (10.0 mg L^{-1}) within the first 10 min. Adsorption kinetic studies showed that the rate of arsenic adsorption on the CPW decreased with the increase of the calcination temperature. When the maximum adsorption capacity of arsenic onto the CPW was calculated by Langmuir equation, the CPW₅₅₀ has the highest value as 43.9 mg g^{-1} .

Key words | aluminium oxide, arsenate, calcination, powdered wastes

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INTRODUCTION

Arsenic contamination of portable ground water is a world-wide concern where prolonged exposure might have adverse health effects on humans. Based on human health data, the World Health Organization (WHO) drinking water guidelines for arsenic was reduced from 50 to $10\text{ }\mu\text{g L}^{-1}$ in 1993 and several countries have adopted this new value as a drinking water standard. According to recent studies arsenic concentration in surface and subsurface water is high, particularly in tropical regions, which include Argentina, Chile, southwestern Taiwan, northern Mexico, southern Thailand, Inner Mongolia, China, Vietnam, West Bengal in India, and

Bangladesh (Smedley & Kinniburgh 2002). Therefore, removal of arsenic from drinking water is extremely important and had been given much consideration the world over. For the removal of arsenic from water, adsorption has been found to be the most effective process at lower cost and aluminium oxide including activated alumina is suggested to be an economical adsorbent with a higher efficiency among various adsorbents (Modal *et al.* 2006). In recent years, several efforts have been directed to improve the efficiency and cost effectiveness for arsenic removal from the viewpoint of waste recycling and re-utilization which have gained popularity

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due to their environmental friendliness and cost reductive advantages (Namasivayam & Senthilkumar 1998).

A chemical company in Korea, which manufactures decorative interior products, produces significant amounts of dry sanding powdered wastes (PW) as a by-product. As PW have a high percentage of impurities, they are generally disposed of in landfills or are incinerated. The PW, however, compose of high percentage of aluminium hydroxide and many attempts are carried out to recycle them. As the aluminium hydroxide inside the PW could be easily converted to aluminium oxide by thermal treatment, the PW has been considered to have a potential for the removal of arsenic from wastewater.

As aluminium hydroxide is transformed thermally to various types of aluminium oxides from amorphous alumina to α -alumina (Trimm & Stanislaus 1986), the adsorptive properties could be changed depending on thermal formation of aluminium oxide and it may affect on adsorption ability.

In this study, the adsorption of arsenate was studied to evaluate the use of the PW as a potential adsorbent from aqueous solutions. To examine the characteristics of arsenate on the PW, kinetic batch experiments were performed with aluminium oxides prepared at different calcination temperature, followed by physical properties analysis.

METHODS

Adsorbents

The PW were obtained from a local chemical company in Korea. During sanding and sawing process in the company, the PW were generated 29,000 kg d⁻¹ on average and stored temporarily at its own waste storage facilities. The raw PW basically contained aluminum hydroxide and matrix organic resins, which were found to be 40–60% and 30–45%, respectively, depending on manufacturing schedule of the company. Calcination of the PW was performed for 3 h at different temperature between 550°C and 950°C to eliminate impurities and to activate the PW for adsorbents and then stored in a desiccator to be used later in the experiments. Table 1 shows the properties of the PW.

Table 1 | Main characteristics of dry sanding powdered wastes

Properties	Unit	Raw PW
Average particle size	μm	112.18
Organic carbon	%	61.9
Moisture	%	0.72
Specific gravity		1.7
Bulk density	g mL^{-1}	1.65
Al	%	20.46

Characterization of adsorbents

In order to characterize the calcined powdered wastes (CPW), thermo-gravimetric analysis/differential scanning calorimetry (TGA/DSC) was conducted using SDT Q600 Thermal Analyzer (TA Instruments, USA) from 30 to 1,200°C at a heating rate of 10°C min⁻¹. The elemental information and structure of the CPW calcined between 550°C and 950°C were determined by X-ray fluorescence (XRF, PW1480 Philips Analytical B.V.) and X-ray diffractometer (XRD, MAC M03HF) at ambient temperature. The XRD was equipped with a copper anode generating Cu K α radiation, 40 kV and 30 mA. The sample was scanned from 10° to 80° 2 θ , and the scanning rate was fixed at 4.0° 2 θ min⁻¹. Brunauer-Emmett-Teller (BET) surface area, porosity, and pore size were determined using computer-controlled nitrogen gas adsorption analyzer (ASAP 2010, Micrometrics). A scanning electron microscope (SEM) JEOL JSM-5410LV, operated at 15 kV was used to study the surface of the CPW calcined at different temperature.

Adsorption experiments

All the chemicals used in the study were of high purity analytical grades and double distilled/de-ionized water was used in the preparation of all solutions. All the experiments were carried out at room temperature (25 \pm 1°C) and atmospheric pressure. Arsenate stock solution (1,000 mg L⁻¹) was prepared by dissolving sodium arsenate (Na₂HAsO₄·7H₂O 98%+, Sigma-Aldrich Co.) in the de-ionized water. The pH-edge adsorption experiments were conducted by mixing 0.1 g CPW with 50 ml arsenic solution in 250 ml conical flasks. The concentration of arsenic was controlled at 1 mg L⁻¹, 10 mg L⁻¹, 100 mg L⁻¹, 200 mg L⁻¹, 300 mg L⁻¹, 400 mg L⁻¹, respectively. At a fixed ionic strength of 0.01 M using NaNO₃,

the pH of the solutions was adjusted to the desired values between 2 and 8, using either 0.1 M HNO₃ or 0.1 M NaOH, and equilibrated for an additional 24 hrs. After equilibration, the suspension pH was measured. The effect of contact time was studied with an initial arsenic concentration of 10 mg L⁻¹ and adsorbent dose of 2 g L⁻¹. The pH of the slurry was kept constantly at 5.0. After adsorption time of 10 min, 20 min, 40 min, 60 min, 120 min, and 180 min, aliquot portions were taken out, centrifuged at 4,000 rpm for 30 min. The pH of the zero point charge (pH_{pzc}) was determined using the method suggested by Stumm & Morgan (1996). Briefly, 1.0 g of the CPW was suspended in 500 ml of a solution with a given ionic strength at 25°C. The suspension was then titrated with 0.1 M HNO₃ and pH was recorded after stabilization. After titration with HNO₃, 0.1 M NaOH was used to bring the pH to 10 and pH was measured. Quantitative determination of the residual aqueous concentration of arsenic was done by inductively coupled plasma (ICP) emission spectrometry (Optima 3000XL, Perkin Elmer) after being filtered through a 0.45 μm membrane filter within 24 hrs. The data from the analysis is presented as the average of duplicate experiments.

RESULTS AND DISCUSSIONS

Adsorbent characterization

Figure 1 shows the XRD patterns of raw PW and the PW calcined at 550°C, 750°C, and 950°C, respectively. The XRD

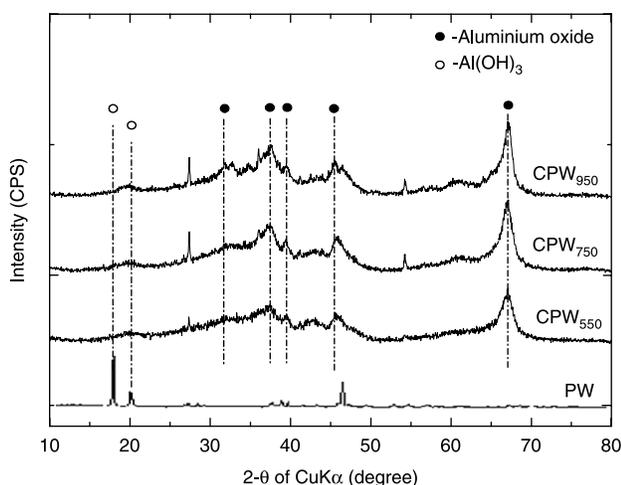


Figure 1 | XRD patterns for powdered wastes at different temperature.

data was analyzed using the Joint Committee on Powder Diffractions Standards (JCPDS) diffraction files. It can be seen that the diffraction peaks of the raw PW indexed with the crystalline Al(OH)₃, whereas XRD peaks of the CPW at 550°C showed no diffraction peaks, indicating poor crystallinity. The amorphous aluminium oxide was thermally generated from Al(OH)₃ by heating the PW up to 550°C. With further increasing calcination temperature from 550°C to 950°C, the crystallinity of amorphous aluminium oxide was gradually increased.

The TGA/DSC analysis of the raw PW was performed at temperature ranging from 30 to 1,200°C at an air-flow of 100 mL min⁻¹. After calcination, organic material and other impurities were effectively removed and the fraction of the aluminium oxide was observed approximately 40% of the raw PW. In addition, the thermal profile indicates that the decrease of weight remained constant after 550°C. The DSC curve also indicated that the decomposition processes proceed with several endothermic and exothermic peaks. It is well known that reaction of melting, dehydration, vaporization, and glass transition were described by location of the endothermic peaks, while crystallization, decomposition, and transition appeared at the location of exothermic peaks (Pradyot 2004). The endothermic peaks appeared in the range of 220–350°C suggested that the dehydration of aluminium hydroxide was occurred. When the calcination is continuously performed over 350°C, the weight loss is stabilized, indicating the beginning of phase transformation of amorphous aluminium oxide. In addition, the exothermic peaks between 750°C and 810°C could be attributed probably to a result of the crystallization of amorphous aluminium oxide.

The BET surface area (S_{BET}), average pore size, and pore volume of the CPW is presented in Table 2. Because of the low reproducibility, information about physical properties of the raw PW was not available in this study. With increasing calcination temperature, the raw PW create a considerable amount of pores and internal surface area. Similar results were found by Hitetale *et al.* (1989). They hypothesized that low surface area material possesses a fraction of pores that are partially closed at low temperature but with heating up high temperature these pores open and their surface area becomes measurable. Sun *et al.* (2008) reported that the release of structure water, free water, and

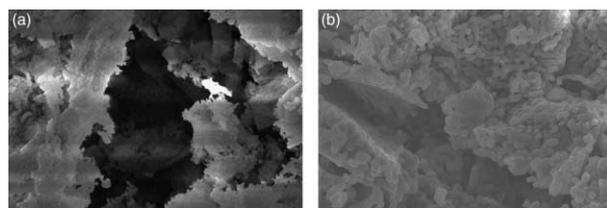
Table 2 | Properties of the calcined powdered wastes

Sample	S_{BET} ($\text{m}^2 \text{g}^{-1}$)	Average pore size (nm)	Pore volume ($\text{cm}^3 \text{g}^{-1}$)
PW	NA*	NA	NA
CPW ₅₅₀	175.5	5.8	0.271
CPW ₇₅₀	113.7	8.7	0.138
CPW ₉₅₀	46.5	13.2	0.256

*Not available.

water in layers and the removal of polyethylene glycol induced the mesostructured aluminium hydroxide to an amorphous structure with increasing temperature, which attributed a large amount of pores and surface area. The same as results were observed in this study. The CPW₅₅₀ possesses a high mesoporous area of $0.271 \text{ cm}^3 \text{ g}^{-1}$ and S_{BET} was as high as $175.5 \text{ m}^2 \text{ g}^{-1}$. Meanwhile, it can be seen that with increase of calcination temperature from 550°C to 950°C , there was a significant decrease for S_{BET} from 175.5 to $46.5 \text{ m}^2 \text{ g}^{-1}$. It has been reported that decrease of specific surface area caused by of noncrystalline aluminium oxide is attributed to formation of thermodynamically stable structure (Goldberg *et al.* 2001). Ogata & Kawasaki (2006) reported that specific surface area decreased when amorphous aluminium oxide became aluminium oxide with crystal structure by raising calcination temperature. From XRD results in this study, the aluminium phase of CPW₅₅₀ was transitioned from poorly crystallized aluminium oxide to crystallized phase and the S_{BET} considerably reduced during the crystallization. On the other hand, the average pore size gradually increased from 5.8 to 13.2 nm with increasing temperature from 550 to 950°C , while the pore volume of the CPW was lowest at 750°C and became higher at 550°C and 950°C (Figure 2).

The morphology of CPW at different temperature was studied by SEM. Figure 3(a) indicates that the CPW₅₅₀ showed essentially amorphous, narrow cracks, and irregular dense

**Figure 2** | SEM images of calcined powdered wastes: (a) micrographs at 550°C at $5,500\times$ magnification, (b) micrographs at 950°C at $5,500\times$ magnification.

structures. As the calcination temperature increased to 950°C , the microstructure of the CPW₉₅₀ became more smooth and regular. This is probably due to the changes of crystallinity.

Arsenic adsorption

Figure 3 shows the adsorption of arsenate onto the CPW at various temperatures as a function of the final solution pH. As a result, the pH showed relatively significant effect for the CPW calcined at 750°C and 950°C , especially at higher pH, compared to the CPW at 550°C . The complete removal of arsenate was observed with the CPW₅₅₀ in the pH range of 2.0–8.0. For the CPW at higher calcination temperature, adsorption exhibited anionic-type behaviour. It can be seen that the adsorption of arsenate was relatively constant when the equilibrium solution pH ranged from 2.0 to 6.0, while adsorption was decreased with increasing the pH over 6. These results can be related to the surface charge of the adsorbents and the speciation of arsenate. The point of zero charge (pH_{pzc}) of the CPW measured from acid–base titrations is presented in Table 3. Since pH_{pzc} for the CPW was decreased when the calcination temperature increased, the point of positively charged surface of the CPW would be shifted to lower pH. This is normally malignant for the adsorption of the negatively charged anionic species as competitive effect with hydroxide ion occurs for higher pH. The arsenate occurs mainly in the form of H_2AsO_4^- in the pH range between 3.0 and 6.0. It can thus be said that

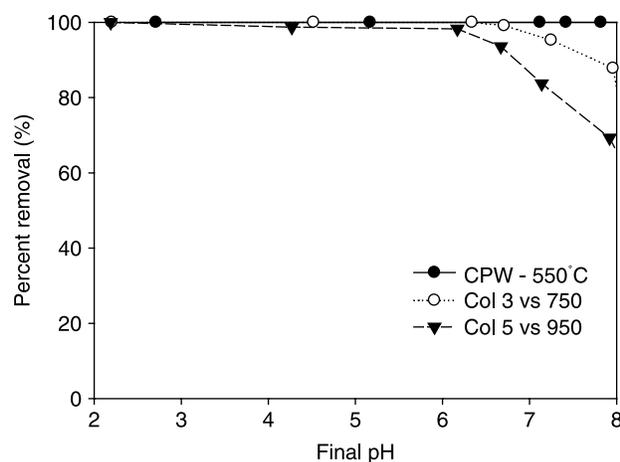
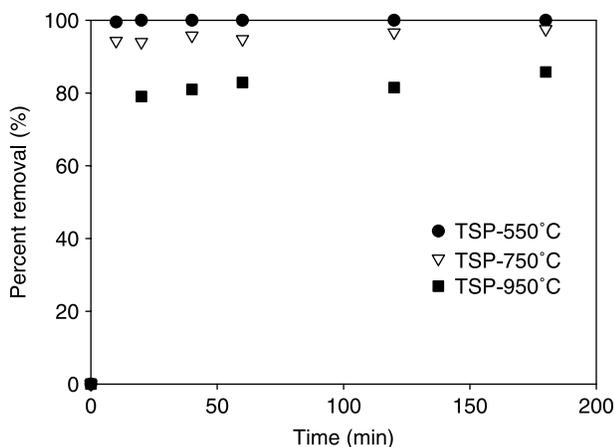
**Figure 3** | Arsenate adsorption onto CPW as a function of equilibrium pH (As(V): 12.8 mg L^{-1} ; CPW: 2 g L^{-1} ; 0.01 M NaNO_3).

Table 3 | Point of zero charge for calcined powdered wastes

Sample	pK _{a1}	pK _{a2}	pH _{pzc}	N _T (mole L ⁻¹)
CPW ₅₅₀	6.3	10.4	8.4	7.84 × 10 ⁻⁴
CPW ₇₅₀	6.3	9.7	8.0	1.52 × 10 ⁻⁴
CPW ₉₅₀	6.9	9.2	8.1	6.05 × 10 ⁻⁵

arsenate in the pH range between 3.0 and 6.0 are easily adsorbed on the CPW₅₅₀ compared to others.

The adsorption of arsenate onto the CPW at various temperatures as a function of time was carried out. Figure 4 shows the adsorption kinetic results. For all samples, the arsenate was adsorbed generally within 10 min and the removal becomes constant, indicating an equilibrium condition for a longer period of time. For the CPW₅₅₀, more than 99% of the adsorption occurred rapidly within the first 10 min and the kinetic rate constant was found to be 0.54 mg min⁻¹. For higher calcination temperature at 750°C, the removal of arsenate reached about 97% after 180 min. The CPW₉₅₀ was the lowest value of adsorption and arsenate was found not to be eliminated over 90% under conditions of 180 min. The kinetic rate constants for the CPW at 750°C and 950°C were 0.48 and 0.14 mg min⁻¹, respectively. This is also in agreement with the decrease in percent removal observed with the increase in calcination temperature. These results were probably due to the surface area of the CPW calcined at different temperature. The CPW which have the lowest surface area exhibited the lowest site concentration on surface area basis. A surface

**Figure 4** | Adsorption of arsenate onto CPW as a function of contact time (pH: 5.0; As(V): 10 mg L⁻¹; CPW: 2 g L⁻¹; 0.01 M NaNO₃).

site concentration, N_T, presented in Table 3 was highest value for CPW₅₅₀ as 7.84 × 10⁻⁴ mole L⁻¹ and N_T became lower as calcination temperature increased. It can be clarified that the adsorption of arsenate would be dependent on surface area of the CPW.

The adsorption isotherm of arsenate onto the CPW at various temperatures is shown in Figure 5. The amount of arsenate onto the CPW was higher as the calcination temperature decreased in agreement with kinetic experimental results. Meanwhile, the experimental isotherm data were analyzed by Langmuir and by Freundlich equations. The Langmuir adsorption isotherm was expressed as

$$\frac{1}{q_e} = \frac{1}{aQC_e} + \frac{1}{Q} \quad (1)$$

where q_e is the amount of arsenate adsorbed at equilibrium (mg g⁻¹), C_e is the equilibrium concentration of arsenate in solution (mg L⁻¹), Q is the saturated monolayer adsorption capacity (mg g⁻¹), and a is the binding energy of the sorption system. Meanwhile, the linear form of Freundlich equation is expressed as

$$\log q_e = \log K + \frac{1}{n} \log C_e \quad (2)$$

where q_e is the amount of arsenate adsorbed at equilibrium (mg g⁻¹), C_e is the equilibrium concentration of the arsenate in solution (mg L⁻¹), K and $1/n$ are Freundlich constant. The constants of regression equations and parameters of the adsorption isotherm for arsenate are presented in Table 4.

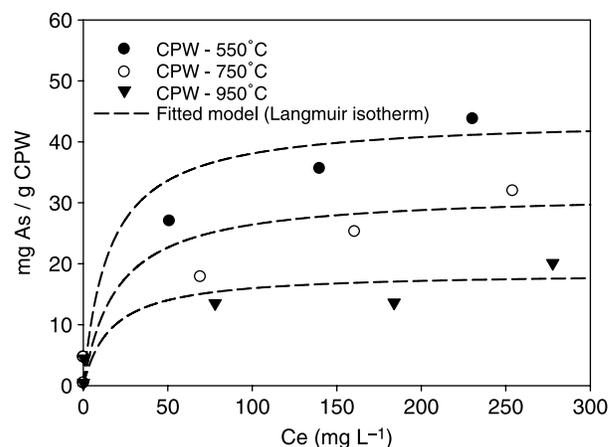
**Figure 5** | Adsorption isotherm of arsenate onto CPW (pH: 5.0; CPW: 2 g L⁻¹; 0.01 M NaNO₃).

Table 4 | Adsorption isotherm constants calculated for arsenate adsorption by TSP

	Langmuir adsorption isotherm			Freundlich adsorption isotherm		
	Q (mg g ⁻¹)	logK	R ²	LogK	1/n	R ²
CPW ₅₅₀	43.9	0.6584	0.9746	0.6584	0.4169	0.7645
CPW ₇₅₀	31.7	0.5381	0.949	0.5381	0.3963	0.7856
CPW ₉₅₀	18.6	0.3411	0.9284	0.3411	0.3990	0.8547

As shown in Table 3, the Langmuir adsorption plot showed a linear line with correlation coefficient of 0.928–0.975, indicating that Langmuir isotherm equation was very suitable for the experimental isotherm data. A basic assumption in the Langmuir theory is that sorption takes place at specific homogenous sites within the adsorbent (Seader & Henley 1998). Kim *et al.* (2004) reported that the surface coverage is correlated with the Langmuir isotherm. With measuring distribution coefficient (Q/C_e in mL g⁻¹), arsenic does not completely cover the surface sites at conditions of saturation adsorption due to a reduction in the affinity between arsenic ions and alumina surface site. Therefore, Langmuir adsorption isotherm could be successfully applied to sorption processes. Results of adsorption experiments in this study showed that the maximum adsorption capacity of arsenate onto CPW at 550°C would be highest as 43.9 mg g⁻¹.

CONCLUSIONS

CPW calined with various temperatures possess different physical properties, which have effect on adsorption of arsenate in aqueous solution. CPW showed amorphous aluminium oxide at 550°C and with increasing temperature up to 950°C, the crystallinity was gradually increased. The CPW₅₅₀ exhibited the highest adsorption capacities and the removal efficiency of arsenate was decreased, proportion to the surface area, as the calcination temperature increased from 550°C to 950°C. It can be seen that surface area of

CPW has significant effect on the adsorption of arsenate due to different surface site concentration on surface area basis. Adsorption isotherm of arsenate onto the CPW indicated that Langmuir isotherm equation was very suitable and the maximum adsorption capacity of arsenate onto the CPW at 550°C was 43.9 mg g⁻¹.

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