Preparation and characterization compatible pellets for immobilization of colloidal sulphur nanoparticles

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Abstract. Mercury pollution in atmosphere is dominated by mercury vapour release from coal burning and gold-amalgam separation in gold mining. The initial steps in formulating a compatible mercury absorbent for mercury stabilization was fabrication of pellet supported colloidal sulphur. Sulphur is used to stabilize mercury vapour by formation of metacinnabar that has much lower toxicity. The sulphur reactivity toward mercury vapour can be enhanced by using colloidal sulphur nanoparticles immobilized on compatible pellets. Clay pellets would have heat resistance but in fact, they were less stable in aqueous solution although their stability increased with inclusion of rice husk ash and sawdust or pineapple leaf fibre in the composite. Pellets made of rice husk ash and polyvinyl acetate were stable in water at least for 24 hours. Sulphur from thiosulfate precursor that immobilized onto surface of pellet using chitosan as the stabilizer and the binding agent gave lower sulphur content compared to sulphur from other precursors (sulphur powder and sulphur-CS\textsubscript{2}). Sulphur from thiosulfate precursor was in form of colloid, has nanosize, and disperse particles on the surface of rice husk ash pellets. Sulphur immobilization methods affect on sulphur particles exposure on the pellet surface.

1. Introduction
Elemental mercury and the compounds are among the most toxic heavy metal groups [1-2]. The main source of mercury pollution was from burning coal and burning amalgam in gold mining [3]. Mercury vapour backs to the earth and forms some water-soluble compound that eventually pollutes food chain [4].

Sulphur powder was commonly used to stabilize mercury vapour pollution since it will form meta cinnabar that is much lower toxicity [5-7]. Sulphur powder has large particle size and it is ineffective to stabilize mercury vapour in continuous gas reactor since the sulphur particles will block the vapour stream. To overcome this issue, sulphur powder was immobilized in a solid support such as granular carbon and coal [8-9]. Reactivity of impregnated sulphur toward mercury vapour was considered low especially operated at low temperature as reported previously. Mullett and co-workers used sulphur immobilized on granular carbon to stabilize mercury vapour 25°C for 8 weeks exposing and found low mercury uptake [10]. Mercury uptake was much higher at higher temperature (140°C) as reported by Reddy and colleagues [11]. Operating condition at above sulphur melting point will cause sulphur melt out from the support, aggregated, block the vapour steam and finally reduce the reactivity. Thereby finding more reactive sulphur that feasible operated at moderate temperature is preferable.

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Attempting to improve sulphur reactivity is by reducing the particle size into nanometer scale. This can be prepared in colloidal form by using a stabilizer [12]. The colloidal sulphur requires stabilizer and a support to disperse the particles and to avoid particle aggregation. Since colloidal sulphur was usually prepared from sodium thiosulfate-HCl, which is polar [13-14], then it needs compatible pellets to immobilize the sulphur particles. Screening the best material and the formula for preparation of compatible pellets, the effect of sulphur precursors and the immobilization colloidal sulphur technique toward the characteristic of sulphur particles are the main discussion in this papers.

2. Material and Methods

2.1. Materials

Rice husk ash, dried clay, sawdust, sago starch that pass through 200-mesh sifter. Banana leaf and pineapple leaf fibres. Na2S2O5.5H2O (p.a, Merck), Na2S.9H2O (ACS, Fischer, 98%), Chitosan medium molecular weight (Fluka), CS2 (ACS, Merck), mercury metal (>99.6%, Merck), acetic acid glacial (CH3COOH), sodium cyanide (KCN), iron (III) chloride (FeCl3.6H2O), methanol (CH3OH, Pure Analysis), hydrochloric acid (HCl), and acetone, sulphur powder purified (Merck) were purchased without further purification.

2.2. Equipment

Several analytical instrumentations were used for collecting data. Light microscope (optilab). UV-Vis Spectrophotometer. Hitachi SU-3500 SEM and Horiba EDX equipment were used for pellet surface analysis. The measurement was at Vacc 20 kV and spot intensity of 50. The test was based on point analysis in four points for inorganic element searching using Back Scatter Electron (BSE) with 500-2500 times magnification. Torontech TT-EDXPRT. XRF was used to analyse the chemical content of the samples. Philip CM 12 Electron Microscope was used for TEM micrograph to measure particle size.

2.3. Methods

2.3.1. Screening for pellet formula

(a) Pellet made of rice husk ash (RHA) and sago starch as the adhesive

Dried RHA and sago starch that pass through 200 mesh particles were blended and water was added carefully until with weight proportion of 70 g (RHA): 30 g (SS): 70 mL (water) as shown in Table 1. While mixing, the mixture was heated 80°C and a few drops of water were added until the mixture rigid. The mixture was inserted into pellet dies hole (4 mm length and 3 cm diameter) and pressed at 100 Nm² to fabricate the pellets. Pellets were dried in oven at 105°C until constant weight.

(b) Pellet made of clay and natural fibre composite

The dried clay (earthenware type) in form of powder, rice husk ash (RHA) powder and pineapple leaf chopped fibres (2 mm length) that all pass through 200 mesh sieve were mixed using mixer and water was added drop wise until from a sticky and coagulated mixture as shown in Table 1. The weight proportion was 90% (clay): 10% (RHA) with and without additional 5% of natural fibres. The mixture was inserted into pellet dies hole (4 mm length & 3 mm diameter) and pressed with hydraulic press at 100 Nm². Dried pellets were soaked for 48 hours in 200 mL distilled water to test the decomposition resistance in water.

Each type of pellet was divided into two porcelain crucibles, one was heated in a furnace at 200°C, and the other was heated up 400°C for 2 hours. The sulphur immobilization described in procedure point (a) was repeated for these pellets. Dried pellets were soaked for 48 hours in 200 mL distilled water to test the decomposition resistance in water.

(c) Pallets made of RHA with Polyvinyl Acetate as Adhesive
RHA as described above was mixed with polyvinyl acetate (PVAc) as the adhesive material using a blender with weight ratio of RHA:PVA:H₂O was 7:2:1. The mixture then inserted into holes of pellet dies (3 mm diameter holes, 4 mm height). It was pressed with a hydraulic press machine at 0.5 tones before heating at 50°C and dried for 24 h. Dried pellets were soaked for 48 hours in 200 mL distilled water to test the decomposition resistance in water.

Dried pellets were dipped in chitosan solution made of (2% wt chitosan in 5% of aqueous-acetic acid) for 2 minutes until all pellets were covered with chitosan solution. The pellets were separated and dried with hot air using hair drier for 2 minutes. The hair dryer was placed 30 cm from the sample to avoid excessive heating.

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| Pellet | Clay (g, %) | RHA, (g) | (PF, g) | Sawdust (g) | H₂O (mL) | SS (g) | PVAc | Temp. (°C) |
|--------|-------------|----------|---------|-------------|----------|--------|------|------------|
| A      | -           | 140 (70%)| -       | -           | 140      | 60 (30%)| 100  |            |
| B1     | 150 (100%)  | -        | -       | -           | 35       | -      | 200  |            |
| B2     | 225 (90%)   | 25 (10%) | -       | -           | 63.5     | -      | 200  |            |
| B3     | 112.5 (90%) | 12.5 (10%)| -       | -           | 35.5     | -      | 200  |            |
| B4     | 135 (90%)   | 15 (10%) | -       | -           | 35       | -      | 200  |            |
| C1     | 150 (100%)  | -        | -       | -           | 35       | -      | 400  |            |
| C2     | 225 (90%)   | 25 (10%) | -       | -           | 63.5     | -      | 400  |            |
| C3     | 112.5 (90%) | 12.5 (10%)| -       | -           | 63.5     | -      | 400  |            |
| D1     | 112.5 (88%) | 12.5 (11%)| 2.5 (2%)| 63.5        | 400      |        |      |            |
| D2     | 112.5 (88%) | 12.5 (11%)| -       | 63.5        | 200      | 10     | 20 (22%)| 50         |
| D3     | 0           | 70 (77%) | 0       | 0           | 10       | 200    | 10   |            |

**PF** = Pineapple fibre; **RHA** = Rice Husk Ash; **SS** = sago starch

### 2.3.2. Sulphur immobilization and chitosan coating

Chitosan coating and sulphur immobilization was divided into methods that were stepwise and simultaneous methods. Stepwise methods: pellet was coated chitosan film yang dipping chitosan pellets on viscous chitosan solution. Dried chitosan films on surface of pellets were swelled by dipping them into 1.5% aqueous acetic acid solution before sinking into Na₂S₂O₅.5H₂O (2 M) solution and HCl (4 M). The simultaneous methods: 10 mL of Na₂S₂O₅.5H₂O (2 M) was added into 50 mL of chitosan solution and 10 mL of HCl (4 M) was added dropwise until form slurry solution. The pellets were dipped into slurry solution and dried until constant weight. This immobilization method was modified from Chaudhuri and Paria [13]. Finally, the pellets were separated and dried with hot air using a hair drier until constant weight. Dried pellets were soaked for 48 hours in 200 mL distilled water to test the decomposition resistance in water.

### 2.3.3. Effect of sulphur precursor on the RHA-PVAc pellets-immobilized sulphur

Three types of sulphur precursors were used that were sulphur powder, sulphur powder in CS₂ and Na₂S₂O₅·HCl. Pellet surface covered with S from CS₂ solution (P-S₃CS₂): dried pellets (50 g) were dipped 2 minutes in saturated cold solution of sulphur-CS₂ (100 mL) then; the pellets were filtered and air-dried for 2 hours. Pellet covered with S powder (P-Spowde): This chitosan coating techniques was modified from previous methods [12]. Pchitosan (50 g) were placed in a plastic sifter, dipped in 50% methanol-water for one minute, filtered and transferred into a boiling flask containing 100 g sulphur-powder. The flask was rotated with a rotary evaporator until all pellets’ surfaces were covered by sulphur powder. Pellet covered with S from sulphur colloid (P-Scolloid): Another half portion of Pchitosan (50 g) was placed in a plastic sifter and dipped in water-methanol (50:50) before shook gently and sprayed with 2 M of Na₂S₂O₅·5H₂O solution until all part of pellets were wet. These pellets were placed on a plastic strainer then were carefully sprayed with 4 M HCl solution until all were wet and changed to white, then dried.
again with hot air using hair dryer until pellets reached constant weight. The hair dryer was placed 25 cm from the sample to avoid excessive heating. All types of pellets (a, b & c) were sprayed with 1% of Na2S solution (Antony 1962) and dried with a hair dryer before store in oven at 70°C for 24 h.

2.3.4. Sulphur determination on the surface of pellets. Sulphur content within the pellets was determined using XRF, EDX and gravimetric analysis. In gravimetric analysis, the pellets was dried in oven at 105°C until constant weight. Then, 10 gram of the pellets was extracted using acetone. The filtrate was dried in water bath until constant weight. The residue was weight as sulphur content.

3. Result and Discussion

3.1. Screening for pellet formula

A number of pellets with different material and composition was denoted Pellet A up to Pellet D3 in methodology sections (Table 1) were tested on the stability in water by counting the percentage of pellets that crack or decomposed in water for 24 hours soaking and the interaction in in chemical environment as shown in Table 2. The pellet shape was cylindrical with dimension of 4 mm height and 3 cm diameter as displayed in Figure 1 (a-d).

It is found that all pellets made of clay only (B1) and calcinated at 200°C was not stable in water as shown by 100% of pellets decomposed. The stability increase when they were prepared at higher temperature (C1) although these pellets did not last in acid solution. The stability of clay pellets increased if RHA is part of the composite (B3 & B4). The calcination temperature also affect the pellet endurance as shown in case of pellet C2 & C4 that calcinated at 400°C. The addition of pineapple fibre and sawdust in clay composite make even more better stability for the pellets (D1 & D2) in water and chemical environment but they still did not last long in acidic solution. Pellets made of RHA and PVAc (D3) show better characteristic, there were no decomposition in water at least 24 hours and stand for acidic interaction. The further study on these pellets was carried out on immobilization of sulphur from various precursors.

Some explanations for this research funding was deduced from literatures. Since most clay containing kaolinite, reducing temperature would remove water between the particles, shrunk the particles and increase the stiffness a long with the temperature escalation. Elimbi et al reported the best geopolymer cement formation was between 400-700°C [15]. Addition RHA into the clay matrix reduced the water absorption but the revise properties were reported at higher proportion of RHA (> 10%), consequently less recrystallization then subsequently reduced the pellet strength (Fernando, 2017) [16]. The compatible fibres on the composite aimed to improve the flexibility of composite. Husen et al reported the improvement in tensile strength and modulus clay composite by approximately 8 % and 15 % respectively due to inclusion of raw jute fibres [17]. The objective of using clay in this study was to prepare the compatible pellet at high temperature and aqueous solution but in fact it is found the weaknesses, then clay was excluded from pellet matrix and substituted with PVAc as the adhesive agent. The later composition was stable in water solution but it has low heat resistance. It would decompose above PVAc boiling point that 112°C.

Sulphur immobilization was carried out with and without chitosan that function as stabilizer and adhesive to avoid sulphur particle aggregation and to bind sulphur particles on the surface of pellets. In utilizing chitosan, we used two comparative methods that were stepwise or simultaneous sulphur colloid-chitosan immobilization. In stepwise method, pellets were coated with chitosan and subsequently sulphur was impregnated on the surface of chitosan-coated pellets. The chitosan coating on the surface the pellet was displayed in Figure 2. The mean thinness of coating was 26-89 micron. Colloidal sulphur was immobilized on the surface of pellets that previously coated by chitosan. Chitosan function as binding agent for sulphur particles onto pellet surface and also functioned as stabilizer to disperse sulphur particles and to avoid sulphur particle aggregation. Using chitosan as stabilizer and binding agents has been reported previously in preparation of colloidal Nobel metal nanoparticles [18-20].
Table 2. Pellets made of various compositions and the stability in water and in chemical environment

| Pellets | Number of pellets decomposed (%) | Remarks |
|---------|----------------------------------|---------|
|         | In water | In chitosan solution | In Na2S2O3 solution | In acid solution | |
| A       | 0        | 0                   | 25                   | 30               | instable |
| B1      | 100      | 0                   | -                    | -                | instable |
| B2      | 0        | 10                  | -                    | -                | instable |
| B3      | 0        | 70                  | -                    | -                | instable |
| B4      | 0        | 25                  | -                    | -                | instable |
| C1      | 0        | 0                   | 0                    | 100              | instable |
| C2      | 0        | 25                  | -                    | -                | instable |
| C3      | 0        | 0                   | 100                  | -                | instable |
| D1      | 0        | 0                   | 0                    | 50               | instable |
| D2      | 0        | 0                   | 0                    | 10               | instable |
| D3      | 0        | 0                   | 0                    | 0                | Stable continued for further study |

Figure 1. Shape and dimension of pellets; (a) & (b) clay pellets, (c) RHA pellet, (d) pellet size.
3.2. Effect of sulphur precursor on the RHA-PVAc pellets-immobilized sulphur.

Pellets made of RHA-PVAc were stable in water at least for 24 hour and relatively stand in chemical environment. The effect of different sulphur precursor on the sulphur characteristics was studied using RHA-PVAc pellets. Sulphur immobilized on the pellet surface were from three precursors that were sulphur powder (P-S\text{powder}), sulphur dissolved in CS$_2$ (P-S\text{CS}_2) and colloidal sulphur from sodium thiosulphate-HCl (P-S\text{colloid}). It is found that different sulphur precursors gave different colour sulphur-immobilized pellets. P-S\text{powder} was yellow, P-S\text{CS}_2 and P-S\text{colloid} were yellowish and grey-white respectively.

XRF displayed the sulphur content that follows the trend of P-S\text{powder} > P-S\text{CS}_2 > P-S\text{colloid} but the weight percentages (wt%) were much lower than found in gravimetric and in EDX methods as shown in Table 3. Probably this is due to sulphur sublimation as reported by Chinchon et al [21]. From the EDX spectrum (Figure 3) randomly scanned on several points, the relative sulphur content was the lowest in P-S\text{colloid}, which was only 2.55 wt% compared to P-S\text{powder} and P-S\text{CS}_2 that were 20.75 and 25.21 wt% respectively. This trend was also consistent with gravimetric data although slightly different in terms of wt% sulphur content. EDX data showed the variance of wt% sulphur content on pellet surface, which was smallest in P-S\text{colloid}(s^2 = 9.5). The larger data variations was found in P-S\text{powder}(s^2 = 1462.7) and smaller variance was in P-S\text{CS}_2(s^2 = 738.8). This suggested that sulphur particles dispersed better on the surface of P-S\text{colloid} compared to the others.

| Table 3. XRF data for pellet and coated pellet chemical composition |
|---------------------------------------------------------------|
| Pellet components    | P-control (%wt) | P-S\text{powder} (%wt) | P-S\text{CS}_2 (%wt) | P-S\text{colloid} (%wt) |
| SiO$_2$              | 96.6            | 10.59               | 90.3                | 91.72                 |
| K$_2$O              | 1.51            | 0.25                | 1.50                | 1.54                 |
| P$_2$O$_5$           | 0.55            | 0.10                | 0.59                | 0.61                 |
| SO$_3$              | 0.10            | 88.44               | 5.67                | 2.93                 |
| CaO                 | 0.39            | 0.06                | 0.34                | 0.37                 |
| MgO                 | 0.29            | 0.06                | 0.25                | 0.29                 |
| Na$_2$O             | 0.19            | 0.41                | 1.56                | 2.14                 |
| Others              | 0.37            | 0.09                | 0.34                | 0.40                 |

The sulphur powder (S-powder) has bulky particles and such characteristics were brought into pellet surface. Dissolved sulphur in CS$_2$ have find particles but they aggregated easily on pellet surface soon after CS$_2$ evaporated. These were different from Na$_2$S:O$_3$ sulphur precursor, sulphur was in aqueous
colloidal form on the pellet surface. The aggregation slowly occurred since water was not as volatile, therefore sulphur particles were finest compare to other preparation.

Having determined that P-S\textsubscript{colloid} gave best characteristic pellets among other sulphur immobilized pellets. Then, the immobilization techniques were compared between simultaneous and stepwise immobilization. The effect of immobilization technique was deduced from the TEM images of sulphur particles in chitosan matrix. To obtain the contrast images of sulphur particles, the mercury vapour was flown through the pellets and it formed black particles of HgS. In TEM sample preparation, the coating layer (chitosan & HgS) was swelled by suspending in 1.5% of aqueous acetic acid to obtain a slurry solution containing those particles. TEM analysis gave different TEM images as displayed in Figure 4. TEM images Figure. 4(a) represents particles in on the surface P\textsubscript{powder}. It showed that the diameter of HgS was around 100 nm on the surface of P\textsubscript{powder} but they were 25 nm and 10 nm on the surface of P-S\textsubscript{colloid-chi-simultaneous} and P-S\textsubscript{colloid-chi-setpwise} respectively.

In P-S\textsubscript{colloid-chi-simultaneous} system, it shows that most of HgS particles were covered by chitosan film. This is different from the stepwise techniques that apparently HgS were smaller and more accessible on the surface. These phenomena confirmed the previous publication that chitosan stabilized palladium catalyst prepared by simultaneous immobilization has lower catalytic activity than the stepwise one due to shielding effect of chitosan layer [20]. Illustration of the immobilization technique that affected on the sulphur particles exposure on pellet surface is presented in Figure 5.
Figure 3. SEM images and EDX spectra for (a) P-S$\text{powder}$; (b) P-S$\text{CS}_2$ and (c) P-S$\text{colloid}$

Figure 4. Representative TEM images comparison of (a) P-S$\text{powder}$, (b) P-S$\text{colloid}$-simultaneous and P-S$\text{colloid}$-stepwise.

(a) Simultaneous immobilization

$\text{Na}_2\text{S}_2\text{O}_3(\text{aq}) + \text{Chi}(\text{aq}) + \text{HCl}(\text{aq}) \rightarrow$ immobilized onto pellet $\rightarrow$
(b) Stepwise immobilization

$$\text{Na}_2\text{S}_2\text{O}_3(aq) + \text{HCl}(aq) \rightarrow \text{immobilized onto chi coated pellet}$$

**Figure 5.** Illustration of immobilization effect on the sulphur particles exposure. (a) simultaneous immobilization led to sulphur particles covered up by chitosan layers, (b) stepwise immobilization made surface of sulphur particles more excessable for further chemical reaction.

4. Conclusion
Calcination temperature and type of the filler affected on the stability of clay pellets. High calcination and the present of sawdust or pineapple leaf fibres as the filler in pellet matrix enhanced the stability pellets in aqueous solution. Pellets made of rice husk ash and sago starch produced more stable pellets but the best composite in this study was rice husk ash-polyvinyl acetate since it gave much more stable pellets. Type of sulphur precursor has correlation with particle size of immobilized sulphur on the surface of pellets. Sulphur fabricated from thiosulfate-HCl formed colloidal nanosize particles. Colloidal sulphur immobilized on the pellets that previously coated by chitosan showed better dispersion of sulphur particles compared to those that prepared by simultaneous immobilization of colloidal sulphur-chitosan onto pellet surface.

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