Removal of Pb, Cd, and Cr in a water purification system using modified mineral waste materials and activated carbon derived from waste materials

H R Lu\textsuperscript{1,2}, L C Su\textsuperscript{1} and H D Ruan\textsuperscript{1}

\textsuperscript{1}28 Jinfeng Road, Tang jia wan, Zhuhai, Guangdong, China

\textsuperscript{2}E-mail:h230400019@mail.uic.edu.hk

Abstract. This study attempts to find out and optimize the removal efficiency of heavy metals in a water purification unit using a low-cost waste material and modified mineral waste materials (MMWM) accompanied with activated carbon (AC) derived from waste materials. The factors of the inner diameter of the purification unit (2.6-7.5cm), the height of the packing materials (10-30cm), and the ratio between AC and MMWM in the packing materials (1:4-4:1) were examined based on a L18 (4) 3 orthogonal array design. In order to achieve an optimally maximum removal efficiency, the factors of the inner diameter of the purification unit (2.6-7.5cm), the height of the packing materials (10-30cm), and the ratio between AC and MMWM in the packing materials (1:4-4:1) were examined based on a L16 (4) 3 orthogonal array design. A height of 25cm, inner diameter of 5cm, ratio between AC and MMWM of 3:2 with size of 60-40mesh and 0.075-0.045mm, respectively, were the best conditions determined by the ICP-OES analysis to perform the adsorption of heavy metals in this study.

1. Introduction

In the past two decades there has been an increasing public awareness of the hazards that exist from the contamination of the environment by toxic substances. Heavy metal pollutions are one of the most significant hazards in our daily life. The term “heavy metal” refers to any metallic element with a high density and toxicity.

Heavy metals exist in the environment naturally, or they can be emitted into an environment through the discharge of domestic and industrial wastes. Some human activities such as mining operations, electronics manufacturing and recycling, are the major causes of heavy metal emission [1]. Heavy metal pollution of surface and underground water sources result in considerable soil pollution. Another cause to soil pollution is when mined ores are dumped on the ground surface for manual dressing [2].

Heavy metals are one of the most significant concerns in water treatment. Heavy metals (e.g. lead (Pb), cadmium (Cd), chromium (Cr)) are of great environmental concern because of their toxicity [3]. A mail challenge remains in dealing with the water safety for local citizens. To date, there are a number of technologies available for the removal of heavy metals from wastewater. For example, chemical precipitation by adding flocculants including those containing OH\textsuperscript{-}, CO\textsubscript{3}\textsuperscript{2-}, and S\textsuperscript{2-}, are commonly employed in industrial water treatment. However, some compounds among them are amphoteric with a point of low solubility [4]. Other more advanced technologies such ion exchange,
ultra-filtration, and reverse osmosis can achieve better removal efficiency of heavy metals, but the high operating costs make them uncompetitive.

Adsorption has served as an economical choice in terms of removing trace metals from water [5]. A lot of research has demonstrated that AC with its high surface area has a high ability of metal ion adsorption due to its micro porous character and chemical nature; therefore it can be utilized to remove the heavy metals from industrial wastewater [6]. In addition to AC, modified mineral waste materials (MMWM), another green and environmentally friendly adsorption material, is proposed and tested in this study. This kind of material is recycled from construction waste materials through physical and chemical treatments. MMWM has been applied not only for the removals of heavy metals and toxic organic compounds in water [7], but has also been using for the remediation of contaminated soils through neutralizing the acidic soil to an appropriate pH due to high pH value of MMWM relative to the contaminated soil, which has been verified in our current experiments. It is a good practice that pollutions can be treated using waste materials without introducing new wastes. Moreover, a possible application of this material in wastewater purification enables the use of mineral wastes to efficiently alleviate the burden of landfill.

It is hoped that MMWM could be promoted to be a synergic adsorption material with AC. This study aims at obtaining the most effective purification unit by applying the adsorption mechanism to remove heavy metals in water. It also aims to promote the use of MMWM. A purification unit is designed with adsorption materials of AC and MMWM, and its efficiency is expectedly improved to perform optimally. Besides the adsorption materials, optimum conditions of removal efficiency including the most suitable size ration of activated carbon and MMWM, the height of adsorption materials, as well as the inner diameter of purification unit are optimized. This research focuses on removal of three heavy metals in water, namely the Pb, Cd, and Cr.

2. Materials and methods

2.1. Materials

2.1.1. Solutions of contaminated water.
The influents used for purification treatment by different testing columns were designed. Three types of heavy metals were added for stage I and stage II: Cd (0.1ppm), Cr (0.5ppm), Pb (1.0ppm). These solutions were prepared in the laboratory by diluting the standard stocks of 1000ppm of concentrated heavy metals with deionized water. The concentrations of heavy metals are based on the standard of GB 8978-1996

2.1.2. Packing materials
One of the packing materials—Coconut derived granular AC (200, 60-40, and 40-20mesh in size) with an iodine value of around 800mg/g was purchased from YAOU Company.

The other packing material is MMWM (1-0.3mm, 0.3-0.075mm, and 0.074-0.045mm in size). The characteristics, including the SEM images, XRD and the mechanism of binding heavy metals, of MMWM were previously studied and provided in the other published paper [7]. Both AC and MMWM were directly packed into the column without any pre-treatment.

2.1.3. Instruments
Peristaltic pump—BT100-4 (Shanghai Yue Ming scientific instrument co., LTD) was employed to control the flow rate of inlets. Chromatographic columns (Shanghai mansion biochemical science and technology development co., LTD) served as purification columns loading with adsorbents. ICP-OES—Optima_2100DV (PerkinElmer, Inc,.) was required in ICP-OES analysis to obtain results of concentrations of heavy metals.
2.2. Methods

2.2.1. Experimental setup

The experimental setup of purification unit is presented in Figure 1.

![Figure 1. Experimental setup of purification unit.](image)

Generally, based on the purification unit setup, the influents with known concentrations of heavy metals were pumped into the testing column by a constant flow pump. After the solutions going through the column, the effluents were collected with containers and stored in a fridge at 4°C.

2.2.2. Orthogonal experimental design

The orthogonal experiments were designed and demonstrated separately in stages.

Five factors of the experimental design were involved in stage I: the height of packing materials (H), the inner diameter of purification unit (D), the sizes of activated carbon (S\text{AV}) and MMWM (S\text{MMWM}), and the ratio between MMWM and AC on the composition of purification materials (MMWM/AC). In this experiment, orthogonal experimental design method was used to analyze the influence degree of H, D, S\text{AV}, S\text{MMWM}, and MMWM/AC on purification efficiency of purification units, then the best overall performance setup was selected. It is assumed that any two factors are independent of each other. The orthogonal experimental design table L\text{18}(3)^{5} employed in the test program is presented in Table 1.

| No. of test | H(cm) | D(cm) | SAC (meshes) | S\text{MMWM} (mm) | MMWM/AC |
|-------------|-------|-------|--------------|-------------------|---------|
| 1           | 5     | 5     | 200          | 1-0.3             | 0:1     |
| 2           | 5     | 3.5   | 60-40        | 0.3-0.075         | 1:1     |
| 3           | 5     | 2.6   | 40-20        | 0.075-0.045       | 1:0     |
| 4           | 10    | 5     | 200          | 0.3-0.075         | 1:1     |
| 5           | 10    | 3.5   | 60-40        | 0.075-0.045       | 1:0     |
| 6           | 10    | 2.6   | 40-20        | 1-0.3             | 0:1     |
| 7           | 20    | 5     | 60-40        | 1-0.3             | 1:0     |
| 8           | 20    | 3.5   | 40-20        | 0.3-0.075         | 0:1     |
| 9           | 20    | 2.6   | 200          | 0.075-0.045       | 1:1     |
| 10          | 5     | 5     | 40-20        | 0.075-0.045       | 1:1     |
| 11          | 5     | 3.5   | 200          | 1-0.3             | 1:0     |
| 12          | 5     | 2.6   | 60-40        | 0.3-0.075         | 0:1     |
| 13          | 10    | 5     | 60-40        | 0.075-0.045       | 0:1     |
| 14          | 10    | 3.5   | 40-20        | 1-0.3             | 1:1     |
| 15          | 10    | 2.6   | 200          | 0.3-0.075         | 1:0     |
Three factors of the experimental design were involved in stage II: the height of packing materials (H), inner diameter of purification unit (D), and the ratio between AC and MMWM on the composition of purification materials (MMWM/AC). As opposed to stage I, this stage consists of 4 levels of each factor instead of 3 levels. The orthogonal experimental design table L16 (4) 3 employed in the test program is presented in Table 2.

| No. of test | H(cm) | D(cm) | MMWM/AC |
|-------------|-------|-------|---------|
| 1           | 10    | 2.6   | 1:4     |
| 2           | 10    | 3.5   | 2:3     |
| 3           | 10    | 5     | 3:2     |
| 4           | 10    | 7.5   | 4:1     |
| 5           | 20    | 2.6   | 2:3     |
| 6           | 20    | 3.5   | 1:4     |
| 7           | 20    | 5     | 4:1     |
| 8           | 20    | 7.5   | 3:2     |
| 9           | 25    | 2.6   | 3:2     |
| 10          | 25    | 3.5   | 4:1     |
| 11          | 25    | 5     | 1:4     |
| 12          | 25    | 7.5   | 2:3     |
| 13          | 30    | 2.6   | 4:1     |
| 14          | 30    | 3.5   | 3:5     |
| 15          | 30    | 5     | 2:3     |
| 16          | 30    | 7.5   | 1:4     |

2.2.2.1. Analytical method and data handling
The concentrations of heavy metals in both influents and effluents were determined by ICP-OES analysis. The original concentrations of influents and effluent samples can be obtained by timing the dilution factor.

\[ C_x = 2.5 \times C_{rx} \]  \hspace{1cm} (1)

Cx is the actual concentration of metal x
2.5 is the dilution factor
Crx is the raw concentration of metal x given out by ICP analysis

The removal efficiency in percentage for each heavy metal was calculated through equation 2.

\[ E_x = \frac{1 - \frac{C_{xf}}{C_{xi}}}{100\%} \]  \hspace{1cm} (2)

Ex is removal efficiency in percentage of heavy metals x (x can be any one of the 3-type heavy metals)
Cxf is the actual concentration of heavy metal x in effluent from ICP analysis
Cxi is the actual concentration of heavy metal x in influent from ICP analysis

The average Ex(average) of three heavy metals in each test was calculated.

\[ E_{x(average)} = \frac{E_{x1} + E_{x2} + E_{x3}}{3} \]  \hspace{1cm} (3)

Ex1 is the removal efficiency in percentage of Cd
Ex2 is the removal efficiency in percentage of Cr
Ex3 is the removal efficiency in percentage of Pb
The removal efficiencies in percentage for all the tests were handled with SPSS for two statistical analysis methods: range analysis and variance analysis.

3. Results and analysis

3.1. Orthogonal test

Results of heavy metals removal are presented in stages. The analysis methods on the results including range analysis and variance analysis are basing on the book Design and Modeling of Experiments [8].

3.1.1. Stage I

3.1.1.1. Range analysis. The results are shown in Table 3 and Fig 2. The sequence of factors that affected the removal efficiency was: ratio between AC and MMWM > size of AC > size of MMWM > inner diameter > height. The optimal conditions were obtained by using the orthogonal experimental design to be as follows: ratio 1:1 of AC to MMWM, 60-40mesh of AC in size, 0.3-0.075mm of MMWM in size, inner diameter 3.5cm, and height 20cm. The removal efficiency under these conditions was measured individually, and the result was 93.52% regarded as the optimal removal efficiency.

Table 3. Parameters of purification test results and intuitive analysis (Stage I).

| Experimental number | A (H(cm)) | B (D(cm)) | SAC (meshes) | SMMWM (mm) | MMWM/AC | Removal efficiency |
|---------------------|-----------|-----------|--------------|------------|----------|-------------------|
| 1                   | 5         | 5         | 200          | 1-0.3      | 0:1      | 72.34%            |
| 2                   | 5         | 3.5       | 60-40        | 0.3-0.075  | 0.045    | 1:2               | 92.31%            |
| 3                   | 5         | 2.6       | 40-20        | 0.075-0.045| 1:0      | 66.32%            |
| 4                   | 10        | 5         | 200          | 0.3-0.075  | 1:2      | 91.23%            |
| 5                   | 10        | 3.5       | 60-40        | 0.075-0.045| 1:0      | 82.34%            |
| 6                   | 10        | 2.6       | 40-20        | 1-0.3      | 1:0      | 73.26%            |
| 7                   | 20        | 5         | 60-40        | 1-0.3      | 1:0      | 84.20%            |
| 8                   | 20        | 3.5       | 40-20        | 0.3-0.075  | 0:1      | 78.32%            |
| 9                   | 20        | 2.6       | 200          | 0.075-0.045| 1:2      | 82.34%            |
| 10                  | 5         | 5         | 40-20        | 0.075-0.045| 1:2      | 81.54%            |
| 11                  | 5         | 3.5       | 200          | 1-0.3      | 1:0      | 72.30%            |
| 12                  | 5         | 2.6       | 60-40        | 0.3-0.075  | 0:1      | 78.43%            |
| 13                  | 10        | 5         | 60-40        | 0.075-0.045| 0:1      | 74.29%            |
| 14                  | 10        | 3.5       | 40-20        | 1-0.3      | 1:2      | 78.53%            |
| 15                  | 10        | 2.6       | 200          | 0.3-0.075  | 1:0      | 75.02%            |
| 16                  | 20        | 5         | 40-20        | 0.3-0.075  | 1:0      | 74.21%            |
| 17                  | 20        | 3.5       | 200          | 0.075-0.045| 0:1      | 76.13%            |
| 18                  | 20        | 2.6       | 60-40        | 1-0.3      | 1:2      | 83.24%            |
| m1                  | 77.20%    | 79.60%    | 78.20%       | 77.20%     | 75.30%   | 78.63%            |
| m2                  | 79.00%    | 80.00%    | 82.50%       | 81.60%     | 84.90%   | (Average)         |
| m3                  | 79.70%    | 76.30%    | 75.20%       | 77.20%     | 75.70%   |                   |
| Range               | 0.025     | 0.037     | 0.073        | 0.044      | 0.096    |                   |

m: the average removal efficiency in percentage of every factor (5 factors in total) under the same level (3 levels in total). For example, m1 of factor A is the average removal efficiency of factor A when the level is 5cm. m1= ((72.34+92.31+66.32+81.54+72.30+78.43)/6) %≈ 77.20%.
3.1.1.2. Analysis of variance. The orthogonal experimental and analysis of variance results (Table 4) indicated that: there was a significant difference in factor E—the ratio between AC and MMWM with the F value of 7.010 which had the most significant effect on improving the removal efficiency of the purification unit, while there was no significant difference in the sizes of AC and MMWM, height of packing materials and inner diameter of testing column. Overall, the order from high to low significance level of factors was: E>C>D>B>A, which was consistent with the range analysis.

Table 4. Variance analysis table of tests of removal efficiencies (stage I).

| Factors | sum of squares of deviations | Degree of freedom | Mean Square | F   | Fcritical, (95%) |
|---------|------------------------------|-------------------|-------------|-----|-----------------|
| A       | 0.002                        | 2                 | 0.001       | 0.396 | 3.74            |
| B       | 0.0049                       | 2                 | 0.0025      | 0.970 | 3.74            |
| C       | 0.0162                       | 2                 | 0.0081      | 3.208 | 3.74            |
| D       | 0.0077                       | 2                 | 0.0039      | 1.525 | 3.74            |
| E       | 0.0354                       | 2                 | 0.0177      | 7.010 | 3.74            |
| Error (blanks) | 0.0101                | 4                 | 0.0025      |       |                 |
| Total   | 0.0763                      | 14               |             |     |                 |

* A sign indicates that there is a significant difference on the factor with it.

3.1.2. Stage II

3.1.2.1. Range analysis. Similar to analysis in stage I, the results are shown in Table 5 and Figure 3. The order from high to low significance level of the factors that affected the removal efficiency was: ratio between AC and MMWM> height>inner diameter. The optimal conditions were obtained by using the orthogonal experimental design shown as the follows: ratio 3:2 of AC to MMWM, height 25cm, and inner diameter 5cm. The removal efficiency under these conditions was 98.52%.
### Table 5. Purification test results and intuitive analysis table (Stage II).

| Experimental number | A     | B     | MMWM/AC | Removal efficiency |
|----------------------|-------|-------|----------|--------------------|
| 1                    | 10    | 2.6   | 1:4      | 89.02%             |
| 2                    | 10    | 3.5   | 2:3      | 93.08%             |
| 3                    | 10    | 5     | 3:2      | 97.30%             |
| 4                    | 10    | 7.5   | 4:1      | 91.57%             |
| 5                    | 20    | 2.6   | 2:3      | 93.32%             |
| 6                    | 20    | 3.5   | 1:4      | 93.26%             |
| 7                    | 20    | 5     | 4:1      | 94.31%             |
| 8                    | 20    | 7.5   | 3:2      | 98.28%             |
| 9                    | 25    | 2.6   | 3:2      | 98.12%             |
| 10                   | 25    | 3.5   | 4:1      | 93.64%             |
| 11                   | 25    | 5     | 1:4      | 97.30%             |
| 12                   | 25    | 7.5   | 2:3      | 93.49%             |
| 13                   | 30    | 2.6   | 4:1      | 92.90%             |
| 14                   | 30    | 3.5   | 3:5      | 96.79%             |
| 15                   | 30    | 5     | 2:3      | 92.80%             |
| 16                   | 30    | 7.5   | 1:4      | 93.28%             |
| **m1**               | 92.70%| 93.30%| 93.20%   | 94.23%             |
| **m2**               | 94.80%| 94.20%| 93.20%   | (Average)          |
| **m3**               | 95.60%| 95.40%| 97.60%   |                    |
| **m4**               | 93.90%| 94.20%| 93.10%   |                    |
| **Range**            | 0.029 | 0.021 | 0.045    |                    |

m: the average removal efficiency in percentage of every factor (3 factors in total) under the same level (4 levels in total). For example, m1 of factor A is the average removal efficiency of factor A when the level is 10cm. m1 = ((89.02+93.08+97.30+91.57)/4)% = 92.70%

![Relational figure between removal efficiencies and three factors (stage II).](image-url)

**Figure 3.** Relational figure between removal efficiencies and three factors (stage II).
3.1.2.2. Analysis of variance. The orthogonal experimental and analysis of variance results (Table 6) indicated that: there was a significant difference in factor C—the ratio between AC and MMWM with the F value of 5.488 which had the most significant effect on improving the removal efficiency of the purification unit; there were no significant difference in the height of packing materials and inner diameter of testing column, which were consistent with the results of stage I. Overall, the order from high to low significance level was: C>A>B. This consisted with the range analysis but with statistical support.

Table 6. Variance analysis table of tests of removal efficiencies (stage II).

| Factors | sum of squares of deviations | Degree of freedom | Mean Square | F       | FCritical, (95%) |
|---------|-----------------------------|------------------|------------|---------|-----------------|
| A       | 0.001804                    | 3                | 0.000601   | 1.853   | 3.287           |
| B       | 0.000889                    | 3                | 0.000296   | 0.913   | 3.287           |
| C       | 0.005343                    | 3                | 0.001781   | 5.488   | 3.287           |
| Error (blanks) | 0.001947 | 6                | 0.000325   |         |                 |
| Total   | 0.009983                    | 15               |            |         |                 |

* A sign indicates that there is a significant difference on the factor with it.

4. Discussion
The purpose of the study was to find out and optimize the conditions of the purification unit with AC and MMWM as packing materials while increasing the ratio of the use of MMWM, which is the predominant factor to improve the efficiency of purification.

Referring to Figure 2, there were no obvious peaks of the effects of height and the inner diameter of purification unit; in other words, the results of height and inner diameter were not significant. However, Figure 3 shows sharp peaks for the effects of height and inner diameter of purification. Hence, the final optimum conditions of height and inner diameter of the purification unit were 25cm and 5cm, respectively. The significant effects of height and inner diameter on improving the removal efficiency were different between two analyses. This discrepancy further demonstrated that the effects of height and inner diameter were small enough to be neglected.

Among these factors which had sharp peaks, the sizes of AC (60-40mesh) and MMWM (0.075-0.035mm) were determined in stage I, while the ratio between AC and MMWM (3:2) had the best effect on improving the purification efficiency determined by a collaboration testing of both stage I and II. Overall, the best process condition of purification column is ratio 3:2 of AC to MMWM, 60-40mesh of AC in size, 0.3-0.075mm of MMWM in size, inner diameter 5cm, and height 25cm. The removal efficiency was up to 98.5% under these conditions.

Our results are similar to the result of a study on the adsorption of AC for heavy metal ions showed that heavy ion removals were above 98% under optimal conditions of pH, temperature, amount of used AC and the adsorption time [9]. However, according to the study, the adsorption time is 2 hours and other conditions are well designed and strictly controlled while in this research, the adsorption materials including AC and MMWM were not in optimal conditions of pH and temperature and the average adsorption time is around 10 minutes for each purification column. In other words, AC cooperating with MMWM, without strict control of pH and temperature, can achieve a similar effect with pure use of AC under strict conditions. Hence, it can be deduced that with a collaboration of MMWM, AC maximizes its removal efficiency.
5. Conclusion
The process conditions of purification columns removed heavy metals by AC and MMWM were investigated through orthogonal tests in this paper. The best process conditions of the purification column were a ratio of 3:2 of AC to MMWM, 60-40 mesh of AC in size, 0.3-0.075mm of MMWM in size, inner diameter 5cm, and height 25cm. The removal efficiency was up to 98.5% under the best conditions. The sequence of factors that affect the removal efficiency: the ratio between AC and MMWM > the size of AC > the size of MMWM (noted that the effects of height and inner diameter were excluded), was acquired by means of range analysis and variance analysis. There were significantly differences in ratio between AC and MMWM.

Acknowledgements
This research was supported financially by Beijing Normal University-Hong Kong Baptist University United International College (UIC) (Project Code: R201404). I am grateful to Jiasui Li and Redon Xharja who have made valuable comments on this study.

References
[1] Hutton M and Symon C 1986 The quantities of cadmium, lead, mercury and arsenic entering the UK environment from human activities Science of the total environment 57 129-50
[2] Garbarino J R, Hayes H, Roth D, Antweider R, Brinton T I. and Taylor H 1995 Contaminants in the Mississippi river US Geological Survey Circular 1133
[3] Bishop P 2000 Pollution prevention: Fundamentals and practice Boston: McGraw-Hill
[4] Eckenfelder W 1966 Industrial water pollution control New York: McGraw-Hill
[5] Kadirvelu K, Faur-Brasquet C and Cloirec P L 2000 Removal of Cu (II), Pb (II), and Ni (II) by adsorption onto activated carbon cloths Langmuir 16(22) 8404-09
[6] Kobya M, Demirbas E, Senturk E and Ince M 2005 Adsorption of heavy metal ions from aqueous solutions by activated carbon prepared from apricot stone Bioresource Technology 96(13) 1518-21
[7] Jiang Y, Ruan H D, Lai S Y, Lee C H, Yu C F, Wu Z, Chen X, and He S 2013 Recycling of solid waste material in Hong Kong: I. properties of modified clay mineral waste material and its application for removal of cadmium in water Earth Sciences 40-40
[8] Fang K., Liu, Q and Zhou Y 2011 Orthogonal experiments design Design and Modeling of Experiments Higher Education Press.
[9] Hong H, Chen H, Ji H, and Fan X 2013 The adsorption of activated carbon for heavy metal ions Tianjin Chemical Industry 27(2)