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# INTERNATIONAL CONFERENCE ON RESEARCH, IMPLEMENTATION AND EDUCATION OF MATHEMATICS AND SCIENCES 2014

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*Global Trends and Issues on Mathematics and Sciences and the Education*

# PROCEEDING

Conference Proceedings

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- Mathematics & Mathematics Education
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# USING DYNAMIC VISUAL REPRESENTATIONS TO DISCOVER POSSIBLE SOLUTIONS IN SOLVING REAL-LIFE OPEN-ENDED PROBLEMS

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## Abstract

Having launched the National Standard Mathematics Curriculum in Vietnam in 2006, classroom mathematics teachers have learnt more about innovative teaching strategies as a means of implementing more effective lessons by focusing on mathematical thinking. The main question that needed to be explored was how classroom teachers could create mathematical activities that would give students an opportunity to demonstrate their ability to build different forms of representations, observe puzzling fact, predict, rationalise and apply logical reasoning when solving open-ended problems. The aim of the first part of this paper is to report on how students translate among dynamic visual representations as a strategy to tackle an open-ended problem that was used in regular classrooms to discover possible solutions. The results showed that open-ended problem created an abductive learning environment in the classroom and students had opportunities to discover new mathematical ideas. The sencond part, we use the area models as new representations for our secondary students to investigate three problems related to the average speed of a particle. Students show their ideas in the process of investigating arithmetic mean, harmonic mean, and average speed through their created dynamic figures. These figures really utilize dynamic geometry software.

**Keywords:** dynamic multiple representations, abductive learning, possible solutions; open-ended problems, arithmetic mean, harmonic mean, average speed.

## 1. TRANSLATING AMONG DYNAMIC VISUAL REPRESENTATIONS TO DISCOVER POSSIBLE SOLUTIONS

Currently, in Vietnam, there are a few drawbacks and inadequacies in the mathematics curriculum and its accompanying textbooks. School mathematics emphasizes rigours and does not show the relevance of the subject in real-life. Students find it difficult to understand when all mathematics results need to be proved logically. Teachers often present mathematical evidence in the form of formal deduction which applies abstract symbols in mathematical reasoning. Studentsthen use these mathematics results when doing practice exercises and consolidating learned knowledge.

Since the emphasis of the old curriculum was on procedural knowledge and memorization of algorithms, students often worked independently to complete exercises from textbooks and workbooks. When asking students questions, most teachers seek one "*right*" answer to the mathematical problem and will explain why that answer is correct.

The reform curriculum tries to reduce the amount of basic skills and procedures in mathematics, while increasing hands-on activities that help students to grasp new ideas and develop mathematical thinking. School reforms in mathematics education aim to help students achieve the following four broad objectives: development of knowledge, skills, thinking and attitudes (MOET, 2009). The objective that concerns thinking aims to provide opportunities for students to develop:

- the ability to observe, verify, predict, apply rational and logical reasoning;
- the ability to express clearly and precisely their own new ideas and to understand the ideas of others;
- spatial imagination;
- the characteristics of thinking, especially flexible, independent and creative thinking; and
- effective operations: comparison, analogy, generalization, and specialization.

The formative assessment of students' mathematical competencies by using open-ended problems with multiple representations in classrooms provides evidence that they can express mathematical ideas by speaking, writing, demonstrating and depicting them visually. In the regulation of professional standards for school teachers, there is a section on the application of teaching methods which promotes students' positivity, perseverance and creativity, as well as enhancing their self-motivation and thinking (MOET, 2009).

Mathematics educators in Vietnam are seeking innovation in teaching and learning strategies. The teachers should think of teaching in terms of several principal hands-on activities with multiple representations, problematic real life situations, and open-ended problems. The innovation of mathematics teaching is to help students construct their own knowledge in an active way and to enhance their thinking through solving non-routine problems, while working cooperatively with classmates, so that their talents and mathematical competencies are developed (Tran, 2006a, 2006b).

### Open-ended Problems

Traditional problems used in mathematics teaching in both elementary and secondary classrooms have a common feature: that is students are expected to produce a predetermined solution. The problems are so well formulated that answers are either correct or incorrect, and there is one unique solution. These problems are called "*closed*" problems. Shimada (1997) proposed to call problems that are formulated to have multiple correct answers "*incomplete*" or "*open-ended*" problems. Pehkonen (1997) stated that closed problems will not leave much room for creative thinking. The idea of using open-ended problems to improve school mathematics teaching, to develop and foster methods for teaching problem-solving and thinking skills, has received support in the curriculum of increasing number of countries in a form that allows teachers freedom to adopt an "open approach" (Pehkonen, 1997; Foong, 2000). Nohda (2000) held the view that open-ended problems are atypical problems which should have two prerequisites. Firstly, they should suit every single student by using familiar and interesting subjects. This implies that students realize it necessary to solve the problems, feel it possible to solve them with their own knowledge and have a sense of achievement after solving. Therefore, the problems should be sufficiently flexible to take into account the students' different mathematical abilities. Secondly, open-ended problems should be suitable for mathematical thinking and it should be possible to restructure them into new problems.

Foong (2000) summarized three basic criteria for an open-ended problem:

- it should give all students a chance to demonstrate some mathematical knowledge, skill and understanding;
- it should be rich enough to challenge students to reason and think; to go beyond what they expect they can do;
- it should allow the application of a wide range of solution approaches and strategies.

For the purposes of this study, open-ended problem is defined as a problem that has many possible answers, and multiple ways to the possible answers.

**Example of an Open-ended Problem**:

The graphs of two functions $f(x) = x^2$ and $g(x)$ are given in the coordinate system *Oxy* as in Figure 1. Investigate possible equations for the function $g(x)$ in the form of $g(x) = a(x-h)^2 + k$.

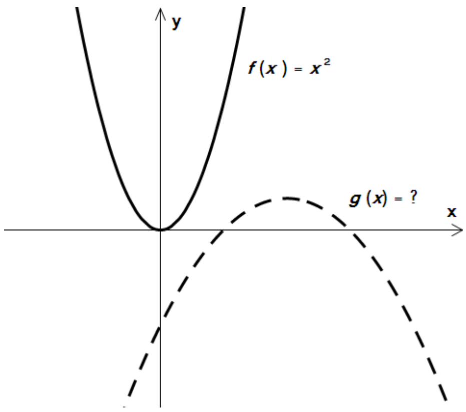


Fig. 1. *The graphs of two functions f and g.*

There are multiple solutions and methods for producing these solutions to the above problem.

In the process of solving an open-ended problem, students may commit mistakes, and give both correct and incorrect answers but, at the end of the problem-solving process, students would have constructed new ideas in mathematics. In this kind of activity, the teacher could help students delve deeply into a textbook problem and build up a habit of questioning achieved results, encourages students to be interested in seeking alternative solutions, and promotes creativity when learning mathematics.

Discovery is an important element in the exploration of open-ended problems. A discovery requires creative thinking and it is executed on the basis of the knowledge of a rule, while the given facts have not been associated conceptually with that rule before. Since the discovery of new knowledge alone does not guarantee certainty, the hypothetical knowledge has to be verified. To express a discovery only means an explanatory hypothesis is becoming plausible. Nevertheless, the correctness of the rule and the case, as well as the coherence between the rule and the observed fact, could remain vague (Meyer, 2007, 2010).

**Using Multiple Representations in Solving Open-ended Problems**

There is strong support in the mathematics education community that students can grasp the meaning of mathematical concepts by constructing multiple mathematical representations in the process of solving challenging problems (Sierpinska, 1992). The term “representations” is interpreted as the tools used for representing mathematical ideas such as tables, graphs, and equations (Confrey & Smith, 1991).

A student can demonstrate deep understanding of a concept by translating a representation of that concept to other modes of representation. For instance, asking a student to restate a problem in his or her words, draw diagrams to illustrate the problem, or act out the problem are some ways of translating among representations. This translational skill among different modes of representation can support students’ relational thinking and algebraic reasoning (Suh & Moyer, 2007).

We try to make the best use of multiple representations for successful thinking and investigating school mathematics. Developing a new representation, that is, finding a new angle into an open-ended problem, basically means a restructuring of the problem representation. For example, in finding the solution of a problem, the problem solver might suddenly become aware of new relations between elements of the given material by mentally changing, amplifying or restructuring the material (Montgomery, 1988). For a long time, mathematics educators have been designing and using multiple representations to make the formal, abstract mathematics accessible for students.

The use of multiple mathematical representations has been shown to increase students’ capability in exploring mathematical ideas. Nonetheless, while research indicates positive gains in student learning of mathematical topics, these gains appear in case when the multiple modes of mathematical representations are used effectively. The importance of such an approach is it facilitates students’ coordination of established mathematical representations such as tables, graphs and symbolic equations.

**Abductive Learning in Constructing Possible Answers to an Open–ended Problem**

Broadly speaking, abduction is a reasoning process invoked to explain a puzzling observation. Abduction is thinking from evidence to explanation, a type of reasoning characteristic of many different situations with incomplete information. Abduction itself does not guarantee certainty but leads the solver to the development of hypotheses that have to be verified. To express an abduction suggests making an explanatory hypothesis become plausible.

Cifarelli and Cai (2005) argued that in open-ended problem solving, new ideas can be developed and explored, free of rigid constraints.

Teachers and students usually use abductive, inductive and deductive methods in their classrooms:

- When we create a scientific hypothesis, we make an abduction.
- When we collect empirical data, we make use of an inductive way of gathering knowledge.
- When we try to prove an equation, we make use of a deduction.

These three ways of working with information are crucial for creative thinking. Abductive learning is a matter of constructing possible answers to a given challenge. We often develop knowledge by guessing or sensing a certain connection. Abductive learning based upon the principle that the learner himself comes up with hypotheses, interpretations or models of problem solving as possible solutions to a certain problem, challenge or proposition (Laursen, 2010).

Abductive teaching and learning implies divergent thinking, which means that the mental activity is directed towards different alternatives and new ideas. The answer is not unequivocal and there are several possible solutions.

Meyer (2007) argued that by using abduction as a tool for a better understanding and for the reconstruction of the generation of ideas in the mathematical classroom, the social processes of knowledge construction became analysable. The students have to be confronted with surprising facts which can be identified as results of new general rules.

**Methodology**

**Design**: In the present study, a case study design was adopted as this design is appropriate for in-depth investigation of student problem solving activity and associated cognition. This design has been argued to be suitable for investigations involving cognitive processes (Kelly & Lesh, 2000).

**Participants**: 125 Grade 10high school students(15-16 year olds) from three classes participated in this study. They had learnt the shape of a parabola and square root function prior to the commencement of the study. The school was located in Hue city, a regional city in Vietnam.

**Task**: The researcher developed the Tsunami Problem (TP) that was used in three classes. This problem was considered to be open-ended because there are multiple ways to construct the relationship between the two key variables: depth and velocity. This relationship can be established in different ways, an important characteristic of open-ended problem. In developing the TP, the researcher was interested in supporting students create multiple representations such as tables, graphs, and equations to discover potential solutions. The solution to the TP involves accessing and use of knowledge about parabola and square root function.

**Tsunami Problem**:

The data that are related to the depth and velocity of a tsunami wave are given in the Fig. 2.

| Depth (m) | Velocity (km/h) |
|---|---|
| 7000 | 940 |
| 4000 | 713 |
| 2000 | 504 |
| 200 | 159 |
| 50 | 79 |
| 10 | 36 |

Fig. 2. *The data that are related to the depth and the velocity*

Try to discover as many possible solutions about the relationship between the depth and the velocity of a tsunami.

**Procedure**: The initial TP was trialled with a class of 40 high school students from a different school. The first version of the TP is provided in the Fig. 2. We will refer to the first version of the tsunami problem as TP1. Thus, the trial involved students attempting to solve TP1. According to students and teacher's feedback, we should change the unit of velocity from km/h to m/s. TP1 was revised to TP2 (Fig. 3).

| Depth (m) | Velocity (m/s) |
|---|---|
| 7000 | 261 |
| 4000 | 198 |
| 2000 | 140 |
| 200 | 44 |
| 50 | 22 |
| 10 | 10 |

Fig. 3. *The TP*2: *revised version of TP*1 *with unit of velocity is m/s.*

In the first trial, students experienced difficulty in using the rectangular coordinate system to plot points with their coordinates are large numbers. In TP2, a sheet of a rectangular grid coordinate system (Fig. 4) with *x*-axis is the depth in meters (m) and the *y*-axis is the velocity in m/s with scale is appropriate for students to plot all points was provided to assist the students.

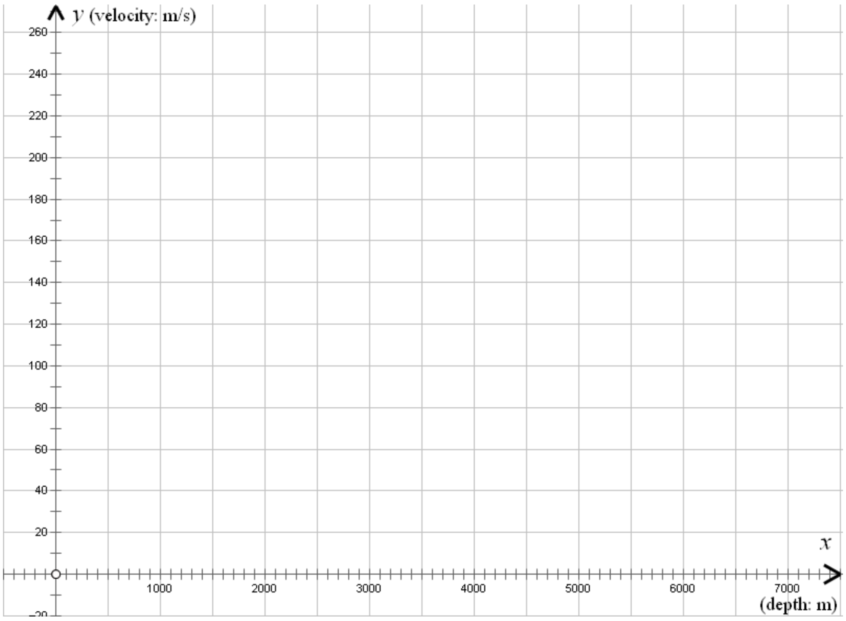


Fig. 4. *A sheet of a rectangular grid coordinate system*

TP2 was then given two classes with similar mathematics background. Students were instructed to find as many solutions as possible to the given problem. They were encouraged to use multiple representations to show their solutions. The students worked in groups of four to solve the TP2 and presented their answers to the whole class for discussion. Students were given a maximum of 45 minutes to complete the problem.

**Data and Analysis**

The main source of data was solutions provided by the students in sheets of papers. In the sessions below, we provide these cases of students' works.

**Case 1.**

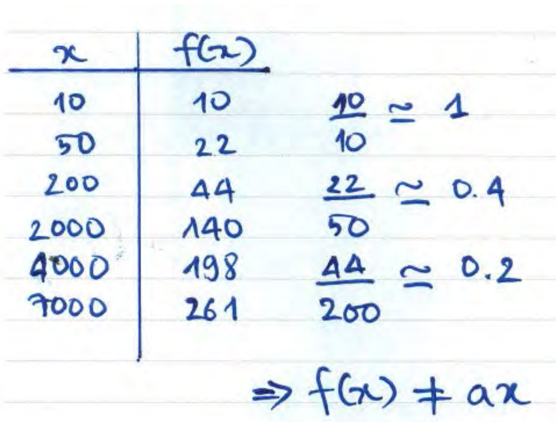


Fig. 5.*Student A used table to find connection between the two variables*

Student A used the table in Fig. 5 to examine connection between the two variables. He defined that from the information given in Fig. 5, the depth will be the variable in the velocity function. He reasoned that the relationship was not a linear equation. This reasoning led the student to the conclusion that a graphic solution is required in order to make further progress. However, this student could not generate the required graph.

**Case 2.**

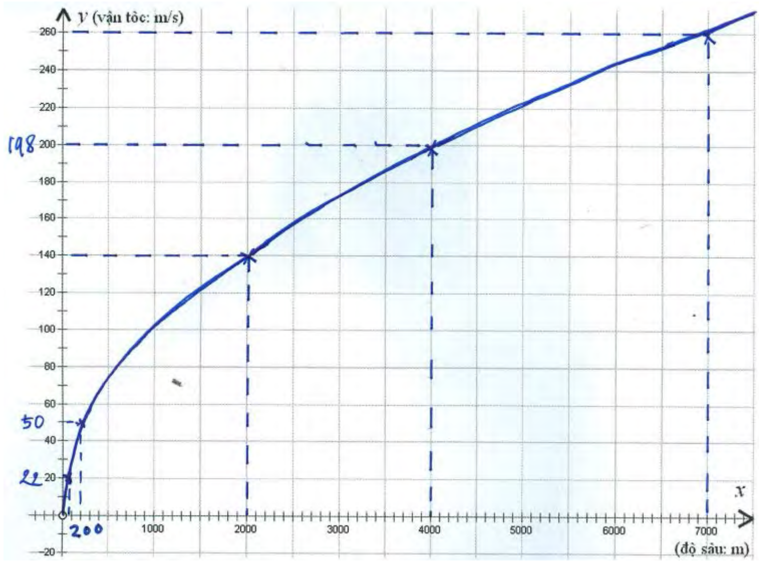


Fig. 6. *Student B constructed the relationship in terms of graphs.*

Student B generated a graphical representation for the solution by plotting various points. This is powerful visual representation of the relationship among the two key variables in the problem. This student used the various coordinates from the table to construct the graph. He joined these plotted points by a smooth curve. He argued that "*the curve looked like a parabola*".

In order to assist students such as student B to make further progress, the teacher provided a hint asking the students to consider the graph of function $f(x) = \sqrt{x}$ which represents a general shape of a parabola. The graph that s/he drew (Fig. 6) is a specific case. The rationale for the above prompting was for students such as student B to reflect on the graph that he has drawn and select a general one that is better aligned with changes the tsunami waves. The student could have modified his graphic solution as in Fig. 6.

**Case 3.**

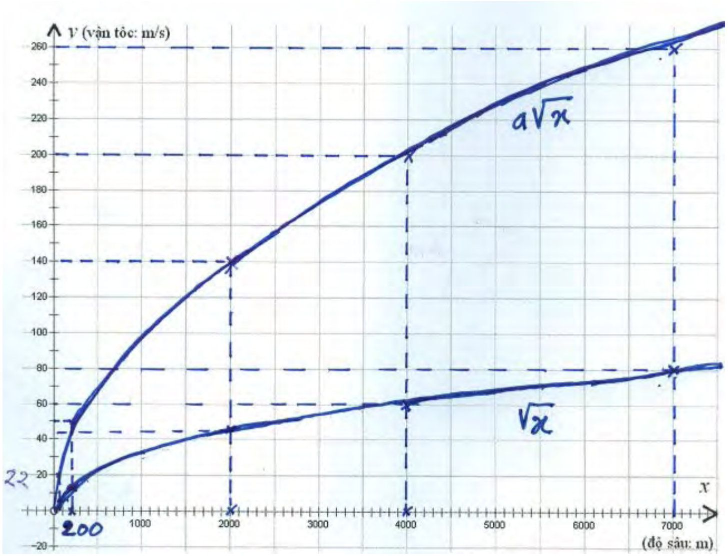


Fig. 7. *Student C guessed the symbolic equation for TP*

Student C observed and recognized the drawn curve has the shape of a parabola. This is really a surprising result. He came up with the idea that the graph of velocity function is similar and above the parabola with the function $f(x)=\sqrt{x}$ as in Fig. 7. He guessed that the velocity function has the form of $g(x)=a\sqrt{x}$ (with *a*> 1). He tried to find a value for *a* but his attempt was not successful.

**Case 4**

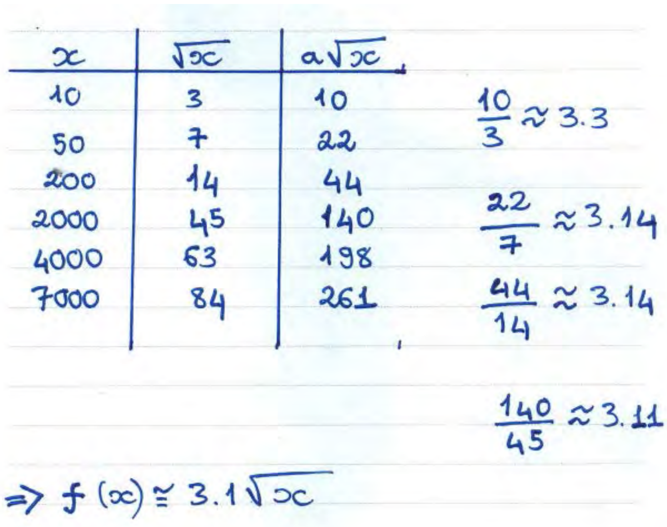


Fig. 8. *Student D estimated the value for the coefficient a*

Student D established a systematic table to find the relationship in terms of a symbolic equation as in Fig. 8. He estimated that the value for coefficient *a* was 3.1. This coefficient can also be verified by other values of *x*.

We notice that the coefficient *a* explored by scientist is $\sqrt{g}$, where *g* is the gravity. The number most often used for the gravity in schools is 9.8 m/s$^2$. So all the values of *a* that ranges from 2.8 to 3.3 are acceptable. The solution of student D is a possible one.

The TP created a learning environment that students can observe surprising facts while translating among multiple representations and then create their own possible solutions as analyzed above.

## 2. INVESTIGATING ARITHMETIC MEAN, HARMONIC MEAN, AND AVERAGE SPEED THROUGH DYNAMIC VISUAL REPRESENTATIONS

While written forms of representation are still important, it is necessary to consider how mathematical ideas can be represented through a visually dynamic medium. This strategy itself may help students to investigate and explore interesting mathematical ideas in a new way of mathematical representations.

The use of multiple dynamic visual representations which promote students' exploration of mathematical ideas is relevant.Multiple modes of representation improve transitions from concrete manipulation to abstract thinking, and provide a foundation for continued learning. This study investigates the effectiveness of experimental environments for students-with-computers to explore mathematical ideas through dynamic multiple representations.We found out that students discover possible solutions in the process of solving problems with dynamic visual representations in mathematics classrooms. Students show their capability to construct their own dynamic models and conduct their experimentation.

### Investigating Average Speed, Arithmetic Mean, and Harmonic Mean

We construct dynamic visual representations for grade 10 students who have learnt the average speed of a particle, ratio and scale. The data emerged from classroom experiments in the 10$^{th}$ grade (15-16 years old, in Hue City, Vietnam). Altogether 3 classes had been visited for 3 lessons in second semester, school year 2012-2013. The study aims at the use of dynamic representations to discover mathematical ideas in the process of investigating arithmetic mean, harmonic mean, average speed, and also the relationship among them. In the three following problems, we use the area models as new representations for our students to investigate the distance of a particle that travels in specific times and with given speeds.

For giving them the opportunities to come up with new mathematical ideas as possible solutions for a non-routine problem rooted from real life, the students were exposed to a problematic situation they could not solve with their former knowledge. They had to construct new ideas as plausible solutions. The general situation is: "*there are two arbitrary rectangles, construct a rectangle such that its area is the total of the two given rectangles*". To investigate this situation we use three following problems.

***Problem 1*** *(Arithmetic mean): A fellow travels from city* ***A*** *to city* ***B****. For the first half of the traveled time, he drove at the constant speed of a km per hour. Then he (instantaneously) increased his speed and, for the next half of the time, kept it at b km per hour. Find the average speed of the motion.*

***Dynamic Visual Representation1*** *(Designed by the Geometer's Sketchpad, Tran et al. 2007).*

There are two rectangles *AEGD* and *EBCH* with the bases *AE* = *EB*.

Assume that

*AD* = *a*, *AE* =*t* = *EB*, *BC* = *b*; 0 <*a*<*b*.

Students work in group of four students to construct two rectangles with the same base as in the Fig. 9.

Construct a rectangle such that the base is 2*t* and its area is the total of the two given rectangles.

Students can drag points *D*, *C*, and *E* to change *a*, *b*, and *t* respectively.

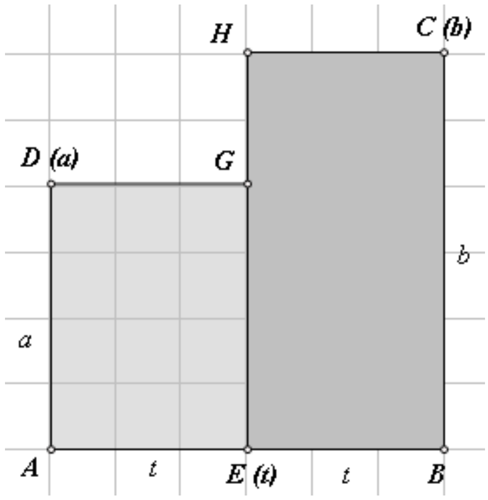


*Fig.* 9. *Two rectangles with the same base*

Students observe the area of rectangle *AEGD* representing the distance that the fellow travels in the first half of traveled time. They discover some interesting mathematical ideas.

**Idea 1.**

The distance $d_1 = a \times t$, $d_2 = b \times t$.

The total distance $d = (a + b)\, t$.

Average speed $v = \dfrac{d}{2t} = \dfrac{a+b}{2}$.

In the trapezoid *ABCD*, let *E*, *F*be the two midpoints of *AB* and *CD* respectively.

$EF - a = b - EF$ ; so $EF = \dfrac{a+b}{2}$.

The area of the rectangle *ABLM* is $\dfrac{a+b}{2} \times 2t = (a+b)t$.

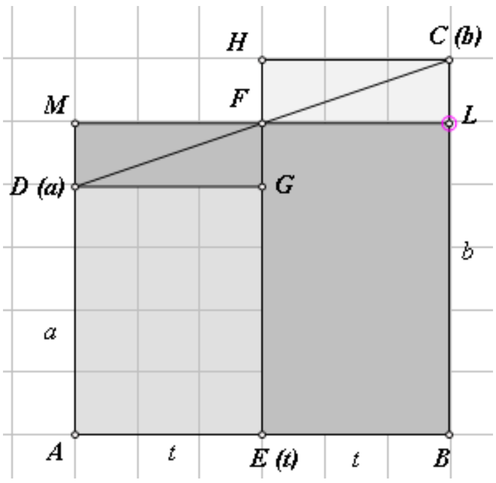


*Fig.* 10. *"Arithmetic mean" in a trapezoid*

**Idea 2.**

For the given two quantities, *a* and*b*, by dragging *E* to change *t*, the number ($a + b$)/2 is known as their *arithmetic mean* and represented by*EF*.Area of the rectangle *ABLM* represents the distance that a particle moves in the time of 2*t* with the average speed is ($a$+$b$)/2. The area of the trapezoid *ABCD* is equal to the area of the rectangle *ABLM*.

**Idea 3.**

Construct a similar area model such that $a + b$ is constant. Dragging *D* to change *a*.

If$a + b$ is constant, so $EF = \frac{a+b}{2}$ is also a constant. *CD* always passes through fixed point *F*.

**Problem 2** (Harmonic mean): A fellow travels from city **A** to city **B**. The first half of the way, he drove at the constant speed of a km per hour. Then he (instantaneously) increased his speed and traveled the remaining distance at b km per hour (0 <a<b). Find the average speed of the motion.

**Dynamic Representation 2** *(Designed by the Geometer's Sketchpad).*

There are two rectangles *AMLD* and *MBCN* with the same area, assume that $AD = a$, $AM = t_1$, $MB = t_2$, $BC = b$; $0 < a < b$.

Students work in group of four students to construct two rectangles with the same area as in the Fig. 11.

Construct a rectangle such that the base is $t_1 + t_2$ and its area is the total of the two given rectangles.

Students can drag points *D*, *(b)*, and *M* to change *a*, *b*, and $t_1$ respectively.

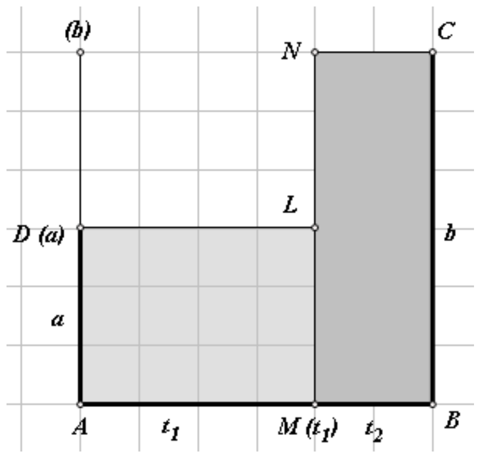


*Fig.* 11. *Two rectangles with the same area*

**Idea 4.**

*a*, *b*: speed, *t*: time, distance $d = a \times t_1 = b \times t_2$ is also the area of the two given rectangles.

The total distance is 2*d*. The average speed is:

$$S = \frac{2d}{t_1 + t_2} = \frac{2d}{\frac{d}{a} + \frac{d}{b}} = \frac{2ab}{a+b}$$

Construct a rectangle with the base is

$t_1 + t_2$ and the height is $\frac{2ab}{a+b}$.

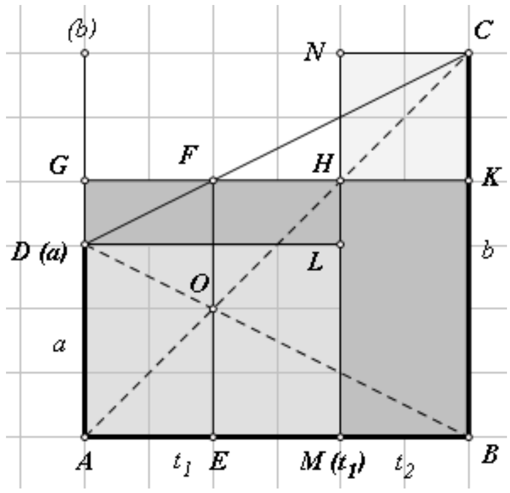


*Fig.* 4. "Harmonic mean" in a trapezoid

**Idea 5.**

In the trapezoid *ABCD*, let *EF* be the line parallel to the sides *AD* and *BC* through the intersection point *O* of the diagonals *AC* and *BD*.

Since $\frac{OE}{a} = \frac{BE}{BA}$ and $\frac{OF}{a} = \frac{CF}{CD} = \frac{BE}{BA}$, we have *OE* = *OF*.

From $\frac{OE}{a} = \frac{BE}{BA}$; $\frac{OF}{b} = \frac{AE}{AB}$, we derive $(\frac{1}{a} + \frac{1}{b})OE = 1 \Rightarrow OE = \frac{ab}{a+b}$;

so $EF = \frac{2ab}{a+b}$.

Area of the rectangle *ABHK* is $AB \times EF = (t_1 + t_2) \times \frac{2ab}{a+b} = 2d$.

**Idea 6.**

Area of the rectangle *DLHG* = $DL \times LH = \frac{d}{a} \times (\frac{2ab}{a+b} - a) = \frac{d(b-a)}{a+b}$

Area of the rectangle *HKCL* = $HK \times KC = \frac{d}{b} \times (b - \frac{2ab}{a+b}) = \frac{d(b-a)}{a+b}$

Area (*DLHG*) = Area (*HKCL*)

**Idea 7.**

If a vehicle travels a certain distance at a speed *a* (e.g. 40 kilometers per hour) and then the same distance again at a speed *b*(e.g. 60 kilometers per hour), then its average speed is the harmonic mean of *a* and *b* (48 kilometers per hour), and its total travel time is the same as if it had traveled the whole distance at that average speed.

**Problem 3** *(Average speed)***:** *A fellow travels from city A to city B. For the first period of time, he drove at the constant speed of a km per hour. Then he (instantaneously) increased his speed and, for the next period of time, kept it at b km per hour. Find the average speed of the motion.*

**Dynamic Representation 3** *(Designed by the Geometer's Sketchpad)*

There are two rectangles *AEGD* and *EBCH* with the arbitrary areas, assume that $AD = a$, $AE = t_1$, $EB = t_2$, $BC = b$; $0 < a < b$.

Students work in group of four students to construct two arbitrary rectangles whose bases are *AE* and *EB* as in the Fig. 13.

Construct a rectangle such that the base is $t_1 + t_2$ and its area is the total of the two given rectangles.

Students can drag points *D*, *C*, *E*, and *B* to change $a$, $b$, $t_1$and $t_2$ respectively.

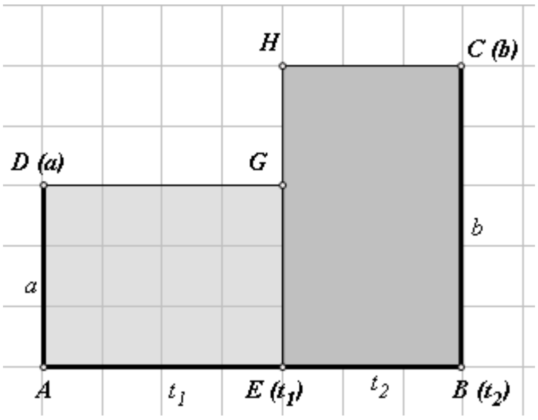


*Fig.* 13. *Two arbitrary rectangles*

**Idea 8.**

We try to define the point *F* by geometric approach by calculating some ratios.

$$EF = \frac{at_1 + bt_2}{t_1 + t_2} \qquad (1)$$

$$\frac{RB}{RE} = \frac{b}{a} = \frac{RE + t_2}{RE} = 1 + \frac{t_2}{RE}$$

$$RE = \frac{at_2}{b - a}; \qquad (2)$$

$$RB = \frac{bt_2}{b - a} \qquad (3)$$

$$\frac{QB}{QE} = \frac{b}{EF} = \frac{b(t_1 + t_2)}{at_1 + bt_2}$$

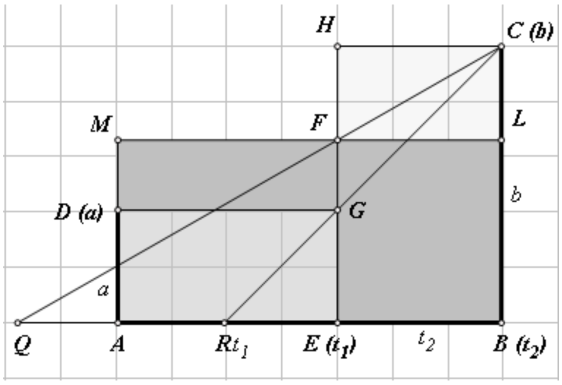


Fig. 14. *"Average speed" in area models*

$$\frac{QB}{QE} = \frac{QE + EB}{QE} = 1 + \frac{t_2}{QE} = \frac{b(t_1 + t_2)}{at_1 + bt_2}$$

$$QE = \frac{t_2(at_1 + bt_2)}{(b - a)t_1} \qquad (4)$$

$$QB = \frac{b(t_1 + t_2)}{at_1 + bt_2} \times QE = \frac{b(t_1 + t_2)t_2}{(b - a)t_1} \qquad (5)$$

$$\frac{BQ}{BR} = \frac{t_1 + t_2}{t_1} = \frac{AB}{AE} \qquad (6)$$

From the ratio calculated by (6), we can define the point *F* as follows. We create point *Q* by dilating *R* by ratio (6) with center *B*. The segment *CQ* intersects *EH* at *F*. Then the length of *EF* will represent the average speed.

**Idea 9.**

If $t_1 = t_2$, then the average speed is the arithmetic mean $EF = \frac{a+b}{2}$.

If $at_1 = bt_2$, the average speed is the harmonic mean $ST = \frac{2ab}{a+b}$.

The arithmetic and harmonic means are special cases of "*average speed*".

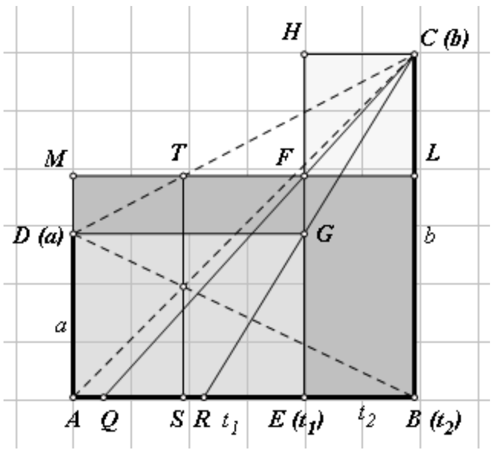


*Fig.* 15. Harmonic mean as a special case

**Dynamic Visual Representations**

This section emphasizes some of the positive effects of visualizing in mathematical concept formation and to show how dynamic visual representations can be used to achieve more than just a basic, procedural and mechanical understanding of mathematical concepts.

Arcavi (2003) proposed that:

> Visualization is the ability, the process and the product of creation, interpretation, use of and reflection upon pictures, images, diagrams, in our minds, on paper or with technological tools, with the purpose of depicting and communicating information, thinking about and developing previously unknown ideas and advancing understandings.

The computer is a rich source of visual and computational images that makes the exploration of mathematical conjectures possible. In this sense, the function of the software is important, providing the students with the opportunity to explore mathematical ideas, analyze examples and counter-examples, and then gain the necessary visual intuitions to attain powerful formal insights.

A *visual approach* in the mathematical thinking process would be characterized by:

- Use of graphical information to solve mathematical problems that could also be approached algebraically.
- Difficulty in establishing algebraic interpretations of graphical solutions.
- No need to first run through the algebra, when graphical solutions are requested.
- Facility in formulating conjectures and refutations or giving explanations using graphical information.

In this case, the computer is used to verify conjectures, to calculate, and to decide questions that have visual information as a starting point.

## 3. DISCUSSION AND CONCLUSION

**Lesson on Tsunami Problem**

The main aim of the study was to capture and analyse different solutions that students could generate for a real-life problem (TP). On the basis of four students' solutions, it would seem that TP provided sufficient room for exploring different solutions. The focus was on the construction of relationship between velocity and depth of waves in a tsunami. All students, except Student A, showed flexibility in modifying his/her graph. The result here supported the contention that open-ended problems are effective in promoting the search for different solutions (Cifarelli & Cai, 2005).

Responses of student C and student D showed that, there are students in our classrooms who can benefit with appropriate scaffolding if we are to assist them to discover alternative solutions. The symbolic representation of the graph in the form of $f(x) = a\sqrt{x}$ is challenging for most students. However, we contend that there is value in extending such students in discovering this symbolic relationship (Laursen, 2010).

The study was conducted in three normal classroom settings. Students and teachers found the problem to be most effective to extend their students' thinking via the process of exploration. Thus, it would seem that open-ended tasks such as the one used here could be deployed in regular classroom practice.

In this study, asking students to identify information, making tables, drawing graphs, writing an equation to illustrate the problem are some ways of building and translating among representations. This translational skill in shifting among different modes of representations can support students to unearth new mathematical general ideas. To support the process of discovery, our students have to be confronted with emerging and surprising facts which can be used to extend students' thinking in productive directions in the problem space (Meyer, 2007).

While the study has provided useful information about the benefits of open-ended problems, we are guarded in making strong claims on the basis of data from four students. The potential benefits of students engaging with the TP should be further investigated with a larger sample of students.

**Lesson on Investigating Average Speed**

At the beginning of the lessons, we realize that students got some difficulties in constructing two rectangles with the same area in the problem 2 with the Geometer's Sketchpad. Students were not familiar with the fact that every rectangle represents the distance of a particle traveling in a specific time with a given speed. When students really understand the situation, in the process of investigating three mentioned problems, students can demonstrate deep understanding of a concept by translating a representation of that concept to other modes of representation. In this study, asking students to construct the area models for arithmetic mean, harmonic mean and average speed, they constructed dynamic representations, dragged some sliding points to observe the invariant mathematical properties. Dynamic visual representations encourage students to incorporate many different types of representations into their sense-making; the students will become more capable of solving mathematical problems and exploring underlying mathematical ideas. Dynamic mathematical software generates environments that can be considered as laboratories where mathematical experiments are performed. Good dynamic geometric software gives students more opportunities to construct their own models and observe many mathematical facts. Students can use "*Measure Menu*" to measure length, perimeter, angle, area, ratio... to get more numerical data. From these data students make more conjectures based on their incomplete knowledge.

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**C-1**

# THE EFFECTS OF MICRO- AND NANOHYDROXYAPATITE APPLICATION IN METAL CONTAMINATED SOIL ON METAL ACCCUMULATION IN IPOMOEA AQUATICA AND SOIL METAL BIOAVAILABILITY

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**Abstract**

The potential of microhydroxyapatite (MHA) and nanohydroxyapatite (NHA) to immobilise heavy metals in a 25-year old active firing range soil was investigated. The effects of immobilisation were evaluated in terms of metal accumulation in water spinach (*Ipomoea aquatica*) and soil metal bioavailability. A pot trial was conducted by amending firing range soil with MHA and NHA at application rates of 0%, 1% and 3% (w/w). Both amendments increased biomass yield and reduced plant metal uptake. The bioconcentration factor (BCF) values of the metals were in the order of Zn > Cu > Pb. The bioavailable fraction of Cu, Pb and Zn in firing range soil decreased significantly ($p < 0.05$) following MHA and NHA treatments. No toxicity symptoms were observed in water spinach over the pot trial. Therefore, MHA and NHA are two promising immobilising agents for the remediation of metal contaminated land.

**Key words**: Contaminated soil, heavy metal, soil stabilisation, water spinach, microhydroxyapatite, nanohydroxyapatite

## INTRODUCTION

Soil contamination by heavy metals is a serious environmental problem all over the world [1]. For example, about 3.5 million sites of industrial and mine sites, landfills, energy production plants and agricultural land in Europe were reported to be contaminated by heavy metals [2]. In fact, soil contamination and strategy for soil protection were classified as two important issues for action in the European Community [2]. Meanwhile, 20 million hectares of arable land, accounting 20% of the total agricultural land area in China have been identified for heavy metal contamination [3]. In recent years, the concentration of heavy metals in soil has increased tremendously due to rapid global industrialisation. Waste emissions from industrial production, mining activities, biosolids and manure application, wastewater irrigation, and inadequate management of pesticides and chemicals in agricultural production have significantly contaminated soil and groundwater [4]. The level of heavy metals in soil has also influenced by firing range activities. Firing bullets are mainly composed of Pb-alloy slugs enclosed with Cu-alloy jackets [5,6]. Metal particulates originating from multiple impacts of bullet fragments during range operations can be oxidised and transformed into compounds that can be mobilised in soil environment [7-9]. An analysis on metal concentration in military firing range soil collected from Busan Metropolitan City, Korea by Moon et al. [6] found 11,885 mg/kg Pb. Parra et al. [10] measured 9,600 mg/kg Pb in topsoil samples collected from a firing range in New Mexico, USA. Meanwhile, firing range soil of the Small Arms Training Area, Aiken, USA was reported to contain 3,282 mg/kg Pb and 1,762 mg/kg Cu [11].

Toxic metals are not biodegradable and persist for a long period of time in soils. They are not only harmful to ecosystems and agricultural production, but also a serious threat to human wellbeing. Their presence in soil may pose a great risk to food chain and water supplies. Considerable efforts have been made to remediate metal contaminated soils. There are many techniques available for the remediation of metal contaminated soils, such as mechanical separation, solidification, soil washing, heap leaching, soil flushing and electrokinetic [12,13]. However, many of these techniques are costly and not practical to implement. Soil stabilisation is a cost-effective and promising soil remediation technique, and has been extensively used in immobilisation of heavy metals in contaminated soils [14]. This technique relies on application of the soil amendments to help retain metals in the stable solid phase by sorption, precipitation, complexation, ion exchange or redox process, thereby decreasing mobility and bioavailability of metals [14,15].

Liang et al. [14] studied the effects of biochar and phosphate application on Cd leachibility from a contaminated soil. The Cd concentration in TCLP (toxicity characteristics leaching procedure) extract was reported to reduced by 19.6% and 13.7%, respectively. They also reported that the concentration of Cd in the groundwater was reduced by up to 62.7%. The immobilisation of Pb and Zn in a contaminated soil using water treatment sludge, blast furnace slag and red mud was assessed by Zhou et al. [16]. Amending contaminated soil using the three amendments was reported to reduce $CaCl_2$, $CH_3COOH$, HCl and EDTA-extractable Pb and Zn significantly. The Pb and Zn uptake by Rhodes grass was found to decrease with amendments application. A significant immobilising effect was reported for 10% (w/w) treatment. Fang et al. [17] has shown that phosphate rock tailing and triple superphosphate fertilizer were able to reduce $CaCl_2$-extractable Pb and Zn by 55.2-73.1% and 14.3-33.6%, respectively.

The overall aim of this work was to evaluate the potential of microhydroxyapatite (MHA) and nanohydroxyapatite (NHA) as immobilising agents for the remediation of metal contaminated soil.

## RESEARCH METHOD

In this study, the soil sample was collected from a 25-year old active firing range in Selangor, Malaysia. The soil samples were taken at the surface layer of up to 25 cm depth using a stainless steel trowel. The samples were air-dried for 1 week, thoroughly mixed and passed through a 2 mm mesh sieve. The soil consists of sand (45%), clay (36%) and silt (19%). The soil pH measured in deionised water with a soil:solution ratio of 1:2.5 using a pH meter, was 4.82. The total Cu, Pb and Zn concentrations in the soil determined by aqua regia extraction were 725, 2337 and 364 mg/kg, respectively. In addition to the total fraction, the bioavailable fraction of metals in soil was also determined using ammonium acetate (1.0 mol/L, pH 7) at a soil:extractant ratio of 1:10. The ammonium acetate extractable Cu, Pb and Zn were 318, 1066 and 135 mg/kg, respectively.

MHA and NHA (purity > 97%) were purchased from Sigma-Aldrich. Pots with a diameter of 15.0 cm and a height of 18.0 cm were filled with 400 g of soil. MHA and NHA were added to the soil at 0%, 1% and 3% (w/w), in six replicates. The soils were left to equilibrate for two weeks. As the soil has a poor plant nutrient content, ¼ strength Hoagland's nutrient was added to each pot thrice a week at application rate of 20 mL. The Hoagland's nutrient solution was applied to the soils for two weeks only (equilibration period). The addition of nutrient solution was discontinued when the pot experiment began.

After two weeks, each pot was tipped out and remixed to ensure homogeneity and to prevent the soil samples from becoming anaerobic. A pot experiment was carried out for 8 weeks. Water spinach (*Ipomoea aquatica*) seed was sown two weeks after addition of amendments. The pots were arranged in a randomised block design. The water content of the soils was adjusted to obtain 70% of the water holding capacity by adding deionised water daily, avoiding prolonged water logging. Plants were allowed to grow under natural lighting and temperature. Mean daily temperature and humidity were monitored with a digital thermometer. At the end of the pot experiment, the soil pH and ammonium acetate extractable metal content in the soil were determined, as previously described.

The plants were harvested at 8 weeks of growth. The aerial parts were cut at 1.0 cm above the soil surface to avoid contamination by soil using a pair of scissors, which was wiped after each use. Roots were carefully extracted from the soil and washed thoroughly with deionized water to remove soil particles. Plant tissues were washed thoroughly with deionised water and dried in an oven at 70 ºC for 48 h. After two days, the dry weight of plant tissue was measured. Dried shoots and roots were milled using a grinder. Milled samples were ashed at 450 ºC for 3 h in a furnace and digested in hot concentrated $HNO_3$. Metal concentrations in the plant digests and soil extracts were measured by flame atomic absorption spectrometry (AAS).

Standard reference plant materials (SRM 1573a Tomato Leaves – National Institute of Standards & Technology, USA, and SRM 1575 Pine Needles – National Bureau of Standards, USA) and certified reference soil material (LGC 6135 Hackney Brick Works Soil – Laboratory of the Government Chemist, UK) were used to verify the accuracy of metal determination. Reference materials were treated and analysed using the same procedures applied for plant tissue and soil samples. The recovery rates were within 90-106% for soil and 86-95% for plant tissue, respectively.

All statistical analyses were performed using Minitab 15 Statistical Software (Minitab Inc., PA, USA). The data were analysed using the general linear model of one-way analysis of variance (ANOVA), followed by Tukey's test at a significance level of $p = 0.05$ to determine least significant difference (LSD) for the comparison of means. Correlation was by Pearson's coefficients at $p < 0.05$.

## RESULTS AND DISCUSSION

**Plant Growth.** The water spinach seeds germinated four days after sowing and no obvious difference in plant growth was observed up to two weeks of the pot experiment. Water spinach grown on compost (uncontaminated soil) were observed to be healthier than plants cultivated on untreated contaminated soil. MHA and NHA treatments resulted in healthy appearance on the plant leaves, whereby the leaves were greener as compared to plants grown on zero treatment (untreated) contaminated soil. Table 1 presents the dry biomass yield of water spinach after 8 weeks of growth. From Table 1, it is clear that the shoot and root yields increased with the rates of amendment application. A pronounced effect was obtained for NHA treatment at 3% (w/w), of which the shoot yield for this treatment was found to be higher than zero treatment by a factor of 3.0. MHA 3% and NHA 1% (w/w) treatments gave almost similar shoot yield, with 178-186% increment in biomass production. The highest percentage of increment in root yield was achieved with NHA 3% (w/w) treatment, followed by application of NHA at 1% (w/w). Although there was an increase in the root yield following application of the MHA, statistical analysis revealed no significant difference was obtained between the MHA 1% and MHA 3% (w/w) treatments.

Table 1. Biomass yield of water spinach.

| Treatment | Dry weight (g/pot) | |
|---|---|---|
| | Shoot | Root |
| Compost* | 13.26 | 4.51 |
| Zero | 3.38 a | 1.49 a |
| MHA 1% | 4.68 b | 2.14 b |
| MHA 3% | 6.02 c | 2.77 b |
| NHA 1% | 6.27 c | 2.95 c |
| NHA 3% | 10.16 d | 3.53 d |
| LSD | 1.01 | 0.59 |

* Plants grown on compost only (uncontaminated soil). Values represent mean of 6 replicates. Letters a, b, c and d show the significant differences between the soil treatments, where letter a represents the lowest mean. Different letters indicate significant statistical differences (Tukey's test at $p < 0.05$).

MHA and NHA were beneficial as growing media through improvement of soil fertility and provision of plant nutrient. Hydroxyapatite (HA) is a naturally occuring mineral form of calcium apatite with the formula $Ca_{10}(PO_4)_6(OH)_2$. It is an important material in the manufacture of fertiliser, as a source of phosphorus [18]. Due to its role as a plant nutrient provider, HA has been regarded as one of the key materials in agrochemicals formulations. In general, NHA amendment has resulted in higher biomass yield than MHA. This scenario can be related to the particle size of the HA used. The particles sizes of MHA and NHA are 3 μm and 40 nm, respectively. The smaller size of NHA accelerates the rate of degradation process. And therefore, release the phosphorus to soil-plant environment much faster than MHA. Lower yield of biomass obtained for zero treatment plants can be attributed to metal toxicity. No toxicity symptoms were observed on the plant leaves over the pot experiment. This suggests that water spinach is a robust plant species and has great tolerance to high metal concentrations.

**Metal Concentration in Plant Tissue**. The concentrations of Cu, Pb and Zn in plant shoots after 8 weeks of growth are given in Table 2. It is apparent that MHA and NHA treatments reduced metal concentrations in the shoot tissue of water spinach. From Table 2, metal concentrations in shoots decreased with the rates of amendments application. Marked reductions in metal concentrations were obtained for NHA treatment at 3% (w/w).

Amending contaminated soil with MHA and NHA increased soil pH from 4.82 to 7.72, therefore reducing metal availability for plant uptake. The pH values of MHA and NHA were determined as 7.53 and 7.24, respectively. The reduction in metal concentrations can also be related to the presence of functional groups ($PO_4^{3-}$ and $OH^-$) on its surface. These functional groups are able to bind or complex heavy metals [15]. Fourier Transform Infrared (FTIR) analysis has confirmed the presence of functional groups on the surface of amendments, as well as the interaction between functional groups and metals (data not shown). It is clear that the accumulation of heavy metals in plant tissues is greatly affected by several factors such as the nature of the amendment, application rate of amendment, the nature of the metal contaminant, plant species and soil pH.

Table 2. Metal concentration in plant shoots.

| Treatment | Concentration (mg/kg) | | |
|---|---|---|---|
| | Cu | Pb | Zn |
| Zero | 954 d | 125 d | 1623 c |
| MHA 1% | 827 c | 109 c | 1485 c |
| MHA 3% | 575 bc | 90 b | 1296 bc |
| NHA 1% | 513 b | 98 b | 1144 b |
| NHA 3% | 418 a | 75 a | 605 a |
| LSD | 84 | 15 | 429 |

Values represent mean of 6 replicates. Letters a, b, c and d show the significant differences between the soil treatments, where letter a represents the lowest mean. Different letters indicate significant statistical differences (Tukey's test at $p < 0.05$).

Correlations between metal concentrations in soil and metal concentrations in plant shoot were assessed using two extractants, namely EDTA and ammonium acetate (Table 3). It was found that ammonium acetate gave significant correlation between metal concentrations in soil and metal concentration in plant shoot. In contrast, EDTA exhibited poor correlations. The poor correlation between EDTA extractable metal concentrations and plant tissue metal concentrations may be because EDTA is a good extractant for metal associated with organic matter, which may not be available for uptake by plants [4,6].

Table 3. Correlations between metal concentrations in soil and metal concentrations in plant shoot.

| Extractant | Metal | Shoot tissue | |
|---|---|---|---|
| | | Correlation coefficient | *p*-value |
| EDTA | Cu | 0.029 | NS |
| | Pb | 0.013 | NS |
| | Zn | 0.042 | NS |
| Ammonium acetate | Cu | 0.633 | 0.000* |
| | Pb | 0.145 | 0.001* |
| | Zn | 0.826 | 0.003* |

$n = 65$, NS: Not significance, Pearson's correlation coefficient and significance at $p < 0.05$.

**Bioconcentration Factor.** The bioconcentration factor (BCF) is defined as the ratio of metal concentration in plant shoots to metal concentration in soil [19]. As discussed by Yoon et al. [20], BCF is a measure of the ability of a plant to accumulate metals from soils. In this study, the influence of MHA and NHA treatments on BCF values of the metals was determined, and the values are given in Table 4. The BCF value of Zn for plants grown on zero treatment soil was calculated as 1.24, suggesting that water spinach has great potential for phytoextraction of Zn from contaminated soil. The BCF values suggest that the ability of water spinach to take up Cu, Pb and Zn from soil decreased significantly with the addition of amendments. This can be attributed to metal binding to functional groups of amendments and reduction in metal availability for plant uptake, as discussed in the preceding section.

Table 4. BCF values for Cu, Pb and Zn.

| Treatment | BCF | | |
|---|---|---|---|
| | Cu | Pb | Zn |
| Zero | 0.33 d | 0.22 d | 1.24 c |
| MHA 1% | 0.25 c | 0.17 d | 0.62 b |
| MHA 3% | 0.24 c | 0.14 c | 0.53 ab |
| NHA 1% | 0.20 b | 0.09 ab | 0.42 b |
| NHA 3% | 0.14 a | 0.06 a | 0.26 a |
| LSD | 0.04 | 0.03 | 0.13 |

Values represent mean of 6 replicates. Letters a, b, c and d show the significant differences between the soil treatments, where letter a represents the lowest mean. Different letters indicate significant statistical differences (Tukey's test at $p < 0.05$).

Metal concentration in plant shoots and soil greatly affects the BCF values. When comparing to Cu and Pb, more Zn was measured in the plant shoots (Table 2). In addition, the total concentration of Zn in the soil (364 mg/kg) was lower than the 725 mg/kg measured for Cu. Therefore, Zn had a greater BCF value than Cu.

**Off-take Values.** The effect of MHA and NHA application on metal accumulation in plant tissues was further evaluated in terms of off-take value. The off-take value considers both metal concentration in plant tissues and biomass yield [19,20]. The amount of Cu, Pb and Zn removed by water spinach from soil is given in Table 5. It is also important to estimate the off-take value in kg/ha unit as this will provide an insight into the real effect of soil amendments if applied on a contaminated site [2]. The off-take value (kg/ha) was based on conversion factor of pot area to hectare.

From Table 5, it is observed that the removal of Cu, Pb and Zn by water spinach decreased following MHA and NHA treatments. Overall, Zn was the metal most extracted by plants, whereas Pb was the least. At the end of the pot experiment, it is estimated that 0.39 mg/pot of Cu, 0.07 mg/pot of Pb and 3.78 mg/pot of Zn were removed from the untreated contaminated soil. It is also estimated that the off-take value of Zn could be reduced from 9.45 kg/ha (zero treatment) to 5.30 kg/ha (NHA 1% w/w) and 3.00 kg/ha (NHA 3% w/w).

Table 5. Removal of Cu, Pb and Zn from soil.

| Treatment | Off-take (mg/pot) | | | Off-take (kg/ha)* | | |
|---|---|---|---|---|---|---|
| | Cu | Pb | Zn | Cu | Pb | Zn |
| Zero | 0.39 | 0.07 | 3.78 | 0.98 | 0.18 | 9.45 |
| MHA 1% | 0.28 | 0.06 | 3.22 | 0.70 | 0.16 | 8.05 |
| MHA 3% | 0.21 | 0.06 | 2.49 | 0.53 | 0.16 | 6.23 |
| NHA 1% | 0.22 | 0.05 | 2.15 | 0.56 | 0.13 | 5.30 |
| NHA 3% | 0.17 | 0.05 | 1.20 | 0.43 | 0.10 | 3.00 |

* Estimation was based on conversion factor of pot area to hectare.

**Bioavailable Fraction of Metals.** The uptake of heavy metals by plants is mainly influenced by the bioavailable fraction of metals, not the total fraction of metals in soil [14,15]. Therefore, the effect of application of MHA and NHA on bioavailable fraction of Cu, Pb and Zn in soil was studied using ammonium acetate extraction. The ammonium acetate extractable metals in soil after 8 weeks of the pot experiment are presented in Table 6.

Table 6. Ammonium acetate extractable metal in soil.

| Treatment | Concentration (mg/kg) | | |
|---|---|---|---|
| | Cu | Pb | Zn |
| Zero | 280 d | 1018 d | 118 d |
| MHA 1% | 223 c | 902 cd | 103 c |
| MHA 3% | 208 bc | 745 b | 75 b |
| NHA 1% | 166 b | 857 c | 52 ab |
| NHA 3% | 110 a | 633 a | 44 a |
| LSD | 53 | 102 | 25 |

Values represent mean of 6 replicates. Letters a, b, c and d show the significant differences between the soil treatments, where letter a represents the lowest mean. Different letters indicate significant statistical differences (Tukey's test at $p < 0.05$).

Amending soil with MHA and NHA decreased the bioavailability of Cu, Pb and Zn significantly, particularly at application rate of 3% (w/w). A lower reducing effect was obtained when amendments were applied at 1% (w/w). For example, the ammonium acetate extractable Pb in soil (1066 mg/kg) decreased to 1018 mg/kg (zero treatment), 857 mg/kg (NHA 1% w/w) and 633 mg/kg (NHA 3% w/w) after 8 weeks of pot experiment. The reduction in the amount of metal extracted after the pot experiment can be related to immobilisation effect of the amendments and uptake by plants.

## CONCLUSION AND SUGGESTION

Results from this study highlight the potential of MHA and NHA as immobilising agents for the remediation of metal contaminated land. Due to its smaller size, larger surface area and more active sites, NHA was more effective than MHA in immobilising Cu, Pb and Zn in contaminated soil, and reducing plant metal uptake. Pot experiment however is only one aspect of such utilisation. The effectiveness of both amendments as soil amendments rely on their stability in the soil-water environment. It is necessary to study the biodegradation of MHA and NHA and their effect on metal bioavailability.

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# ELECTROCOAGULATION OF DETERGENT *WASTEWATER USING ALUMINIUM WIRE NETTING ELECTRODE (AWNE)*

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**Abstract**

Electrocoagulation of detergent wastewater using aluminium wire netting electrode has been carried out. The electrocoagulation method was performed in a two electrodes system using aluminium wire netting as an anode and cathode electrode. Detergent wastewater is characterized by chemical oxygen demand (COD) concentrations and absorption spectra using spectrophotorometer UV-Visible. Electrocoagulation is carried out in electrochemical cell containing 100 mL detergent wastewater, without supporting electrolyte. In this study electrocoagulation of detergent using applied voltage 5, 10, 15 and 20 Volt with various electrolysis time. The result, of the study showed aluminium wire netting electrode has higher degradation of detergent wastewater.

**Keywords:** electrocoagulation, detergent, waste water, aluminium wire netting

## INTRODUCTION

Water pollution with detergents, is of great importance to satisfy the increasing demands for water for various uses. These detergents compounds do not decompose or degrade in aquatic systems. These detergents are very harmfully and toxic. The accumulation of some detergents in waste water represents a serious environmental problem. The removal of detergents from aqueous solutions is very important from the environmental point of view (El-Said 2004).

Detergents are substances or preparations containing soaps or other surfactants intended for water based laundry or dishwashing processes. Detergents may be used in any form (liquid, powder, paste, bar, cake, molded piece, shape, etc.), widely for household laundry products, domestic and industrial cleaners, cosmetic products, and industrial purposes. Surfactants are organic substances, used in detergents, intentionally added to achieve cleaning, rinsing and/or fabric softening due to its surface-active properties (Bruns and Jelen 2009). They consist of one or more hydrophilic and hydrophobic groups of such nature and size that they are capable of forming micelles Surfactants belong to a group of chemicals of high environmental relevance due to their large production volumes. They are mainly discharged into the environment by the wastewater pathway, either after treatment in a wastewater treatment plant or directly where no treatment system is available. Environmental compartments which may be influenced by surfactants are the freshwater environment (water body and sediment), the soil if surfactant-loaded sewage sludge is added, and the marine environment (Bruns and Jelen 2009). Surfactants are widely used for domestic and industrial purposes, primarily as detergents in cleaning applications.

Surfactants removal operations involve processes such as chemical and electrochemical oxidation (Lissens, *et al.*, 2003; Mozia, *et al.,* 2005), membrane technology (Sirieix-Plénet, *et al.,* 2003; Kowalska, *et al.,* 2004; Fernández , *et al.,* 2005), chemical precipitation (Talens-Alesson, *et al.,* 2002), photocatalytic degradation (Ohtaki, *et al.,* 2000; Zhang, *et al.,* 2003), adsorption (Ogita, *et al.,* 2000; Lin, *et al.,* 2002; Adak, *et al.,* 2005) and various biological methods (Dhouib, *et al.,* 2003; Chen, *et al.,*2005). Among the currently employed chemical unit processes in wastewater treatment, coagulation-flocculation has received considerable attention for yielding high pollutant removal efficiency. This process can be directly applied to wastewaters without being affected by the toxicity in the wastewater and can constitute a simple, selective and economically acceptable alternative.

Electrochemical technologies such as electrolysis have been successfully employed for the treatment of many wastewaters on an industrial scale, for example, oil and grease (O&G) containing wastewaters. The electrochemical technologies have reached such a state that they are not only comparable with other technologies in terms of cost but also are more efficient and more compact (Dae et al. 2013). The electrochemical oxidation of detergent to $CO_2$ occurs without chemical agent and with a significant rate the potential region of oxygen evolution. It is commonly assumed that electrogenerated hydroxyl radicals are very active in the degradation of organic molecules. This species is the most powerful oxidant in water.

This paper reports a study of the electrocoagulation of detergent wastewater. Electrochemical degradation of organic pollutants, presence in the wastewater needs specific electrodes (Aboulhasan et al. 2006). Electro coagulation experiments on detergent were carried out with aluminium wire netting electrode. Electrocoagulation involves the in situ generation of coagulants by dissolving electrically either aluminum or iron ions from aluminum or iron electrodes, respectively. The metal ions generation takes place at the anode, hydrogen gas is released from the cathode. The hydrogen gas would also help to float the flocculated particles out of the water. This process sometimes is called electroflocculation (Songsak, 2006).

## EXPERIMENTAL

### Materials

All solutions were prepared by dissolving their analytical grade reagent (Merck) in deionised distilled water. AWN electrodes (Aldrich Chemical Company) and $H_2SO_4$ from Merck was used for preparation of an AWN electrode. All solutions for COD analysis were prepared from Merck using deionised distilled water.

### Sampling procedures

Samples of effluent are collected from domestic laundry wastewater in Sleman, Yogyakarta, Indonesia. The generated effluent is discharged into the sea without any treatment. Sampling of the detergent wastewater is carried out according to standard methods for the examination of wastewater.

### Electrode preparation

A metal electrode made of aluminium was used, and the length of each electrode with a width of 10mm was 10mm. Electrodes are made as tube (Figure 1B for anode and 1C for cathode), so as to have more surface area.

### Electrochemical measurements

Electrochemical measurements were carried out in a two electrode using DC Power Supply. Aluminium wire netting electrodes were used as anode and cathode electrodes with difference size electrode (Figure 1B and 1C). The electrochemical process of detergent wastewater was performed at room temperature (without electrolyte). The electrochemical coagulation studies by potential constant were performed in 100 mL capacity glass electrochemical cell. The experiments were performed in a two electrodes system using *AWNE* as a anode and cathode electrode.

**Analytical procedures**

The detergent wastewater degradation results were analyzed using Spectrophotometer UV-Visible Hitachi U-2010 at wavelength 200-400 nm. The chemical oxygen demand (COD) was determined by common photometric tests using Spectrophotometer UV-Visible Hitachi U-2010 according to Standard Methods (SNI 6989.2-2009).

**RESULT AND DISCUSSION**

(A) (B) (C)

Figure 1. Physical structure of Aluminium Wire Netting Electrode (AWNE) of electrode surface (A); anode (B) and cathode (C)

Figure 1 showed type of aluminium used in studies is woven mesh or aluminium wire netting (AWN). Woven mesh was more effective in increasing current than expanded mesh and solid electrode (Yimin et al. 2010). The larger current per applied voltage produced by AWNE result from larger active surface areas than those calculated or different effects of structures on electro coagulation of detergent. Based on superior performance of the aluminium woven mesh, solid electrode was not examined in further studies. According to (Yimin et al. 2010), the impact of mesh configuration on current was further examined through correlations between mesh number, wire diameter, pore size and surface area and current densities. In this analysis, larger correlation coefficients indicate the factor to be more relevant to variations in current generation. Electrodes are made as tube (Figure 1B and 1C), so as to have more surface area.

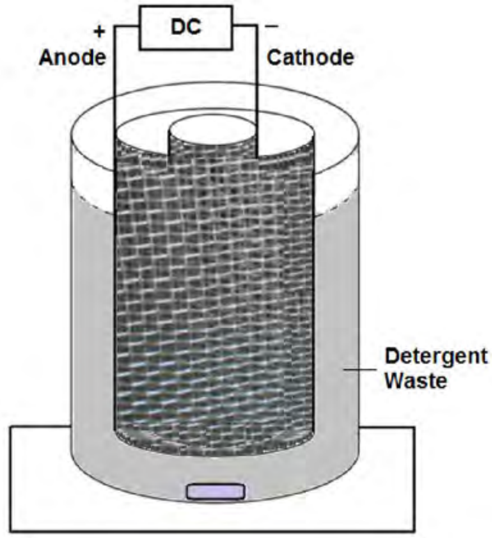


Figure 2. Schematic diagram of electrocoagulation system

The electrocoagulation system in this study is comprised of three parts: reactor for electrolysis, power supply, and AWN electrode in Figure 2. The electrolysis reactor consists of a total liquid volume of 200 mL. Reactor for electrolysis was composed of a cathode and anode. The electrode gap between the cathode and anode was 1.0 cm. A metal electrode made of aluminium was used, and the length of each electrode with a width of 10 mm was 10 mm. The continuous electrolysis system was designed to adjust the potential constant. The electrolysis experiment was performed under constant voltage of 5-20V. DC power supply was used in the system.

Figure 3. showed of scheme of electrocoagulation organic compounds using Al anode. The $Al^{3+}$ or $Fe^{2+}$ ions are very efficient coagulants for particulates flocculating. The hydrolyzed aluminum ions can form large networks of Al–O–Al–OH that can chemically adsorb pollutants. Aluminum is usually used for water treatment and iron for wastewater treatment (Comninellis 1994). The advantages of electrocoagulation include high particulate removal efficiency, compact treatment facility, relatively low cost and possibility of complete automation. The chemical reactions taking place at the anode are given as follows (Songsak, 2006).

For aluminum anode:

$$Al \rightarrow Al^{3+} + 3e^{-} \quad (1)$$

At alkaline conditions

$$Al^{3+} + 3OH^{-} \rightarrow Al(OH)_3 \quad (2)$$

At acidic conditions

$$Al^{3+} + 3H_2O \rightarrow Al(OH)_3 + 3H^{+} \quad (3)$$

In addition, there is oxygen evolution reaction

$$2H_2O \rightarrow O_2 + 4H^{+} + 4e^{-} \quad (4)$$

The reaction at the cathode is

$$2H_2O + 2e^{-} \rightarrow H_2 + 2OH^{-} \quad (5)$$

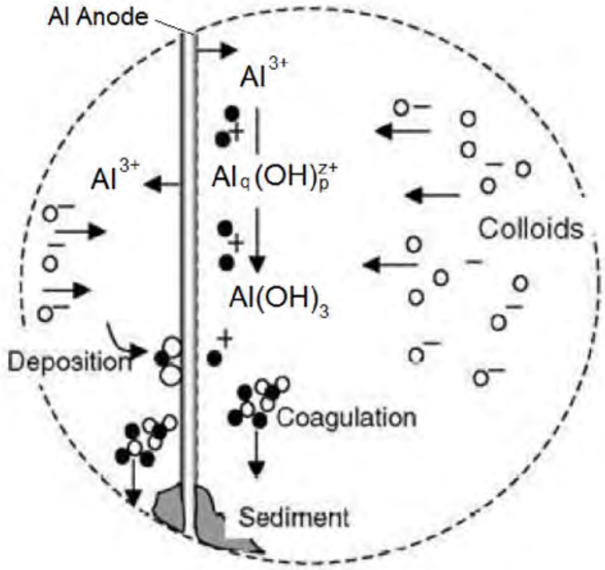


Figure 3. Scheme of electrocoagulation, modified from Den and Huang (2005)

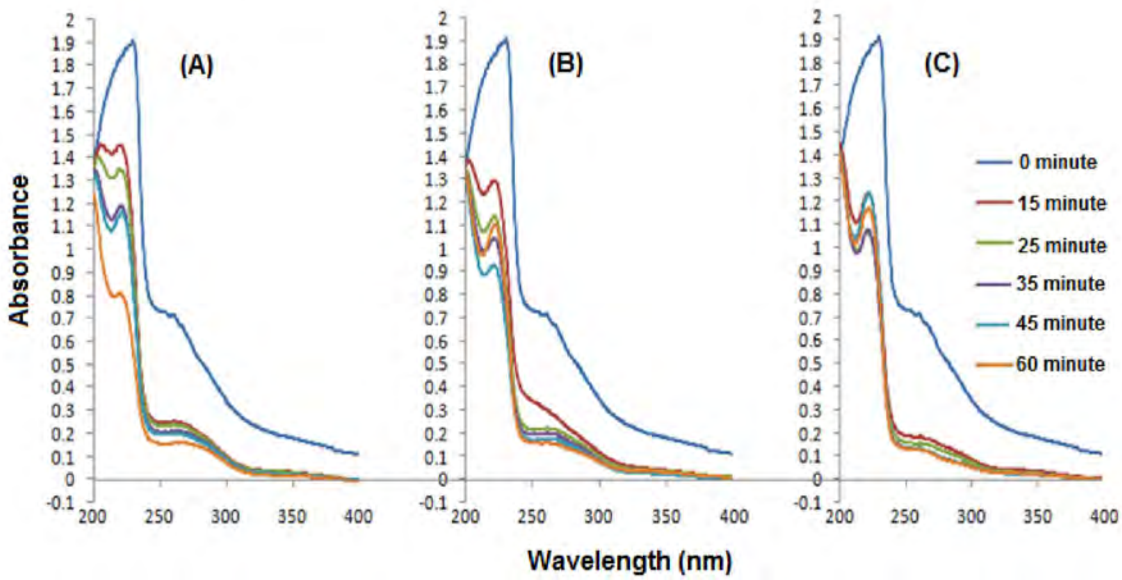


Figure 4. UV scan results at 200–400nm of the electro coagulation at different electrolysis time, with aluminium wire netting electrode of: (A) 10 Volt (B) 15 volt and (C) 20 volt.

Figure 4. showed UV scan results of selected electrolysis runs at a potential of 10, 15 and 20 Volt. It can be concluded that electrocoagulation of the detergent took place from the disappeared peak of 240 nm in the electrolysis process. Electrolysis then stopped at different stages with various carboxylic acids. These results showed that high efficiency both for phenol oxidation to benzoquinone, and benzoquinone oxidation, which is related to the aromatic rings opening can be obtained on anodes (Dae et al. 2013).

Figure 4A, showed a maximum decrease of absorbance with electrolysis time 60 minutes. While, Figure 4B, showed a significant decrease at electrolysis time 15 minutes. The decline occurred only up to 45 minutes. Based on Figure 4, the optimum conditions of wastewater electrolysis at potential and electrolysis time are 15 Volt and 45 minutes, respectively. The longer of the contact time of the wastewater with electrodes will be the efficiency removal. The ability of the aluminium electrode in detergent wastewater is limited so despite prolonged contact time. The effect of the formation of $Al(OH)_3$ at the anode surface will be cause covered electrode surface. In addition, the reaction at the anode is also inhibited so that the oxygen binding of surfactant alkyl benzene is also reduced. Decreased surfactant as an organic compound can be determined by analysis of wastewater COD. Although not very accurate to say so, but examination of COD had to know include organic ingredients. The chemical oxygen demand (COD) was determined by Spectrophotometer UV-Visible Hitachi U-2010 according to SNI 6989.2-2009.

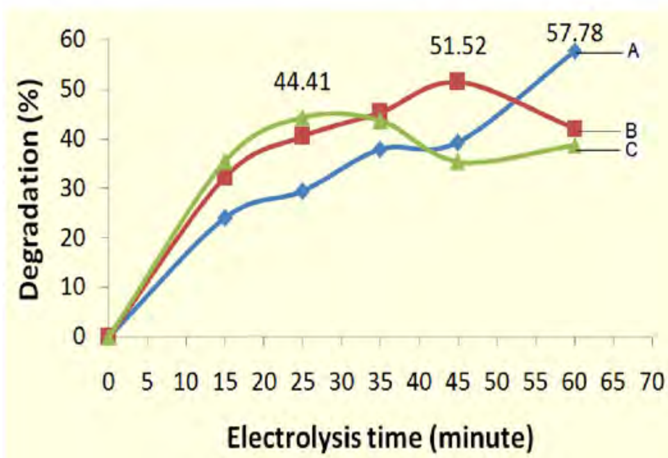


Figure 5. Percent degradation after electrocoagulation of detergent wastewater with various electrolysis time and potential at 10 Volt (A), 15 Volt (B) and 20 Volt (C)

Table 1. Results of the COD determination experiments performed before and after electrocoagulasi with electrolysis time 60 minutes

| Detergent Wastewater | Potential (Volt) | COD (mg/L)* |
|---|---|---|
| Initial Detergent Wastewater | 0 | 2270 |
| After electrolysis | 10 | 407 |
| After electrolysis | 15 | 523 |
| After electrolysis | 20 | 587 |

*Average of three determinations

The chemical oxygen demand (COD) is used as a measure of the oxygen equivalent of the organic matter content of a sample that is susceptible to oxidation by a strong chemical oxidant. For samples from a specific source, COD can be related empirically to BOD, organic carbon, or organic matter (Songsak, 2006). Table 1 showed the electrocoagulation studies performed to good chemical oxygen demand (COD) removals. The specific removals in COD are very dependent on the time necessary to perform the electrocoagulation and, in general, the electrocoagulation times increased with stirring. For the applied current densities, and since the initial COD contents of the samples were high, the degradation process, apart from the final stage of the assays with UP samples, must be controlled by current. The values of COD showing that, in fact, they performed anodic oxidations must have been controlled during most of the assay by current. The electrocoagulation of laundry wastewater using aluminum electrodes, maximum percent degradation and COD are 57.78% and 82.07%, respectively (Figure 5).

**CONCLUSIONS**

According to the obtained results, the application of combined electrochemical techniques, namely electrocoagulation is very good for degradation of laundry wastewater. The combined treatment, COD removals for laundry wastewater samples were always higher than 82%. In general, the use of stirring increases the time needed to start, with a visible rate, the precipitation of the flocs formed in the electrocoagulation. On the other hand, the electrocoagulation time is reduced by an increase in the applied potential, due to a higher rate of aluminium oxidation. The result of the study showed aluminium wire netting electrode has higher degradation of detergent wastewater. The electrocoagulation of laundry wastewater using aluminum electrodes, maximum percent degradation and COD are 57.78% and 82.07%, respectively.

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