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A Study of the Effects of Waste Egg and Shrimp Shells on the Toxicity Immobilisation of Chemicals

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ABSTRACT

Natural resources are declining rapidly. Water scarcity is one of the biggest crises that the world faces. Even though there are many treatment methods, it still leaves a large carbon foot print. Hence, biological treatment is desired. However, there are many toxic compounds that contaminate wastewater, which inhibit biological treatment. Therefore, waste egg and shrimp shells were introduced as adsorbents to immobilize toxicity as a pre-treatment method. Egg and shrimp shells were tested for their surface charge with zeta potential. Then, *E.coli coli* cells were exposed to the toxic compounds, copper sulfate and carbonyl phenol, for 15 minutes. Subsequently, *E.coli* cells were regrown on the agar plates to determine the recuperation rate of the colonies. It was found that egg shells decreased the toxicity of the tried concoction to *E.coli*, and enabled the colonies to recover by up to 62%. Moreover, it has proved that there is potential that the surface charge has an effect on the adsorption process. Egg shells, which have -21.85 zeta potential, adsorb copper sulfate, which is positively charged, better than carbonyl phenol, which is negatively charged and *vice versa* for shrimp shells.

Keywords: Adsorption, Toxicity immobilisation, Waste materials, Zeta potential.

INTRODUCTION

Global environmental concerns are growing intensely with such a sharp decline in natural resources, pollution, and climate change. Moreover, with the continuous increase in world population[1] has caused serious resource scarcity such as water. Water is an important resource for life and now, our waterways are polluted with chemicals from industry, agriculture, and household activities.

There are several wastewater treatment methods such as reverse osmosis[2], vacuum evaporation[3], ultrafiltration (UF)[4], and chemical oxidation[5]. These strategies are costly and resource intensive. Natural treatment is an exceptionally appealing treatment technique as it requires less energy and is sustainable. It avoids utilizing excess additional chemical compound[6], which means financially feasible and environmentally friendly. However, wastewater is often contaminated with harmful chemicals, for example, biocide from agricultural activities, and toxic chemical additives from the manufacturing; which biological treatment is impractical. Hence, toxicity immobilisation is necessary as a pre-treatment to remove toxins[7, 8]. and achieve successful biological treatment.

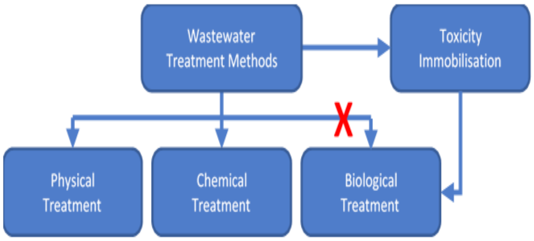

Fig. 1. The chart shows that hybrid technology of toxicity immobilisation can aid biological treatment.

To immobilise toxicity, one of the popular methods is adsorption. Adsorption is the mechanism where particles or atoms of either gas, fluid, or solid attached to a surface of adsorbent. There are many materials that could be employed as an adsorbent such as clay[9], zeolite[10], and nano-iron[11]. Natural adsorbents that are also well-acknowledged are, for instance, kaffir lime leaves[12], and rice husk[13]. According to the green technology principle, the objective of this research was to employ natural waste materials, egg and shrimp shells as adsorbents and evaluated the ability to immobilise toxicity. This would not only act as hybrid technology and facilitate biological treatment of the wastewater, but also make the most of natural materials. In addition, in this work was aim to observe the relationship of surface charge to the adsorption ability as an another dimension of understanding.

MATERIALS AND METHODS

Sample preparation

Copper sulfate and carbonyl phenol were selected as candidates for toxic compounds, where copper sulfate represents negatively charged toxic compounds and carbonyl phenol represents positively charged toxic compounds. A dilution series of both samples were prepared. Samples were diluted in distilled water to 7 concentrations; 0.005% v/v, 0.01% v/v, 0.05% v/v, 0.1% v/v, 0.5% v/v, 1.0% v/v, and 5.0% v/v, respectively. The test was done in triplicates. The ideal fixation is chosen and applied in a toxicity test.

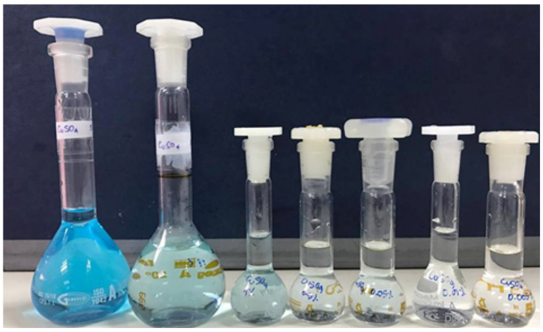

Fig. 2. Preparation of dilution series of copper sulfate at 7 concentrations; 5.0% v/v, 1.0% v/v, 0.5% v/v, 0.1% v/v, 0.05% v/v, 0.01% v/v, and 0.005% v/v

Preparation of Adsorbents and its Zeta Potential

Two waste materials, egg and shrimp shells were prepared. The egg shells represented calcium carbonate and the shrimp shells represented Chitosan, which is the main component of each material. Both materials were tested for their surface charge. They were ground into a fine powder, diluted in distilled water, mixed with a vortex mixer, and the zeta potential was measured by Photon Correlation Spectroscopy (Delsa Nano C., Beckman Coulter). The experiment was done in triplicates.

Toxicity Test

Carbonyl phenol and copper sulfate at 1% v/v were prepared in flasks. Adsorbents (60g/L) were added to each flask equally. Samples were then taken out from the flask at 10 time points (30 min. 1, 2, 3, 4, 5, 6, 12, 24, 48 h) and the toxicity test was conducted by bioassay. *E.coli* were utilized as a bio-assay in the toxicity test. *E.coli* was developed to mid-exponential expression in LB broth. For each tube (2 samples at 10 time points), cultures were suspended in 1% v/v for 15 min. and quantify the toxicity impacts by Miles and Misra technique[14]. For Miles and Misra technique, sample that contained *E.coli* after 15 min. were resusitate on LB agar plate and incubated at $35^{\circ}C$ for 18 hours. The colonies were tallied and colony forming units (CFU) were recorded. Tests were done for 10 time points amd all tests were done in triplicates.

RESULTS AND DISCUSSION

Optimum sample concentration

From the screening test, it was found that at 0.5% v/v there was some growth of bacterial cells, but there was 0% growth or a lethal effect at

1% v/v of both samples, copper sulfate and carbonyl phenol (Fig. 3). Therefore, the suitable optimum concentration to conduct toxicity immobilization or an adsorption test was at 1% v/v as shown in Figure 4.

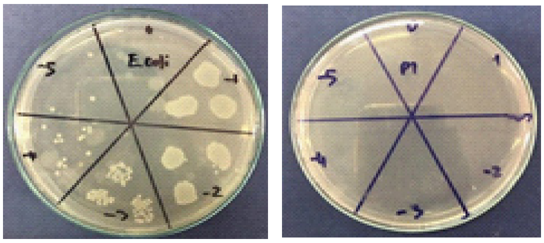

Fig. 3. Bacterial (*E.coli*) growth after exposure to water control (Left) 1% v/v Carbonyl Phenol (Right) for 15 minutes

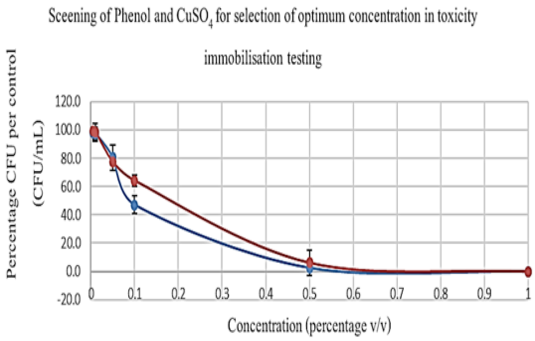

Fig. 4. Bacterial (*E.coli*) growth after exposure to Carbonyl Phenol and Copper Sulfate for 15 min. in 7 dilution series. The test was done in triplicates

Zeta Potential

The two types of adsorbents were tested for their surface charge and it was found that egg shells have a negative charge on the surface and shrimp shells have a positive charge on the surface as shown in Table 1.

Table 1: Experimental set up for adsorption and toxicity testing

Flask	Test Sample	Adsorbent
1	Carbonyl Phenol	Egg Shell
2	Carbonyl Phenol	Shrimp Shell
3	Copper Sulfate	Egg Shell
4	Copper Sulfate	Shrimp Shell

Toxicity Test

From the experiment, it was found that both adsorbents allowed bacteria *E.coli* to recover on the agar when plated out on LB following 15 min. of exposure introduction, which showed the

Table 2: Zeta potential of tested adsorbents (egg and shrimp shell)

Adsorbent Type	Zeta Potential (mV)
Egg shell	-21.85
Shrimp shell	+29.05

capacity to immobilized toxicity. The best duration for adsorption was found to be 12 hours. The eggshells as an adsorbent proved to be more effective in immobilizing toxicity compared to the shrimp shells in general. Bacteria culture recovered more than 60% and 50% on copper sulfate and carbonyl phenol, respectively. For the shrimp shells, the recovery rate was slightly lower at 34% and 9% for carbonyl phenol and copper sulfate, respectively (Figure 5).

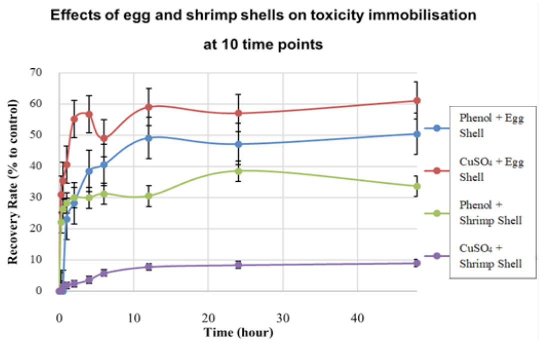

Fig. 5. Toxicity immobilisation ability of egg and shrimp shells at 10 time observed by recording recovery rate (%) of bio-assay after post exposure to the phenol and copper sulfate samples. The experiment was done in triplicates

CONCLUSION

Adsorption pre-treatment process employing waste materials such as egg and shrimp shells research was carried out. The optimum condition was when adsorbents were exposed to the toxic chemicals, copper sulfate and carbonyl phenol for 12 hours. Subsequently, an acute toxicity test was carried out by exposing *E.coli* to the treated toxic chemicals for 15 min. and recovered on the agar. From the results, it was found that both chemicals were lethally toxic to *E.coli.* However, egg and shrimp shells proved the ability to immobilize toxicity and allow biological treatment. In general, eggshells were more effective in immobilizing toxicity. To be precise, eggshells, which are negatively charged on the surface from zeta potential experiment, enabled it to immobilize 62% toxicity of carbonyl phenol, which is positively charged, better than copper sulfate at 50%, which is negatively charged. Similarly, shrimp shells, which are positively charged on the surface, immobilize copper sulfate by 34%, which is negatively charged, better than carbonyl phenol by 9% (Fig. 5). This shows some connection between surface charges to the ionic charge of the sample. This information could be useful in selecting a suitable adsorbent for the different types of wastewater and the buffering of toxicity could be a very effective way of aiding biological treatment. Future work will focus on more details of adsorbent characteristic identification and its mechanism. Then, these waste natural materials could potentially be used to manage the toxicity of real world waste that is toxic to microbial cells.

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