Stability and durability studies of zwitterionic adsorbent coating for the removal of organic pollutants: Chemical and thermal tolerance

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Abstract. The zwitterionic adsorbent coating (ZACC) was used to eliminate both cationic and anionic dyes. The ZACC was developed in a way to improve the current ordinary form of adsorbents (beads, powder) for flexible working application especially in treating the industrial textile effluents. Since it is in a coating form, a number of factors have to be considered especially in terms of its stability and durability in wastewater. This is to prevent any detected adsorbent leaching and fast loss in treated water. This study was investigated for harsh conditions (chemical and thermal) to prove its strength. The chemical tolerance has established the stability of ZACC strip by showing a highly robust and potent structure even after 100 days in acidic, neutral and mix dyes solution. Result also showed the percentage removal of BG dye could attained within 87.4 - 97.1 % as increased the pH from 3 to 11. While higher removal of AR 1 obtained in acidic medium (99.4 %). The percentage weight loss obtained were 0.25 % and 0.11 % respectively for thermal stability test in drying oven and outside building.

1. Introduction
The zwitterionic adsorbent coating (ZACC) is a novel adsorbent used to adsorb both cationic and anionic dyes from aqueous solution. Our previous studies have confirmed the formulation of this adsorbent coating using acrylic polymer emulsion (APE) as binder, epichlorohydrin dimethyl amine (EPIDMA) as surfactant and bentonite as an additive for their functionalized materials involved [1–3]. The performance of ZACC was proven through a series of promising result in adsorbing ionic charges such as Acid Red 1 and Brilliant Green dyes. The adsorbent coating is a new approach of adsorbent where their ordinary form (powder, beads and flakes) has been reformulating and transform into a liquid/slurry form which then coated onto inert surfaces or substrate. After undergoing a drying procedure, a hardened layer of adsorbent was developed. The adsorbent coating modifies the classical adsorption concept, with simpler synthesis procedure and flexible working application afterward. This new innovative solutions aimed at simultaneous increase of performances in terms of dyes removal and decrease the energetic footprint by bringing to cost minimization in operation and time saving [4,5]. Besides, this adsorbent with substrate/support also possesses good mechanical stability that is highly required for different typologies of mechanical stresses including vibrations or collision during adsorption processes [6–8]. The flexibility of the adsorbent coating to be applied at any condition is an

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advantage since it can be layered or slotted in a narrow, small or bigger spaces within a treatment plant. As long as the support used also flexible.

The sorbent with surface coating requires an optimized chemical and physical stability to strongly adhere to the targeted support materials. This is to prevent peel off of the adsorbent from the substrate during the adsorption process. Otherwise, the consequences will be not favorable if the adsorbent itself creating secondary pollution for the treated water. Harsh condition in effluent and treatment plant especially in terms of thermal situations (high temperature) and pH level were also being investigated. The chemical tolerance towards strong acid/alkali is desired to be deliberated throughout the synthesis and evaluation of the formulation of the adsorbent coating so that it can stay attached at any condition or up to a certain extent. Besides, the durability of adsorbent at various ranges of temperature, pH, in broad types of pollutants and reusability should also be encountered. Therefore, this study evaluated the stability and durability of ZACC in terms of its chemical and thermal tolerance. The experimental test was conducted in order to identify the strength of ZACC so that it can be applied without generating secondary pollution to the environment.

2. Experimental

2.1. Chemical and reagents

The cationic dye, Brilliant Green (BG) and anionic dye, Acid Red 1 (AR1) are analytical grade dyes supplied by Modern Lab Sdn. Bhd. The cationic polyelectrolyte, poly-epichlorohydrin-dimethyl-amine (EPIDMA) (50 wt. % in H2O) and acrylic polymer emulsion (APE) were obtained from NHA Scientific Resource, Malaysia. The laboratory grade bentonite was purchased from Modern Lab Sdn. Bhd. The preparation method of ZACC has been synthesized as in our previous study [3].

2.2. Adsorbent coating stability studies

2.2.1. Determination of adsorbent coating durability in chemical solutions

The durability of ZACC in chemical solutions was tested under four main conditions; acidic, alkaline, neutral and mixed dyes. The samples (with the dimensions of 10 cm x 10 cm) were immersed in 50 mL solution of hydrochloric acid and sodium hydroxide for 10 days and prolong to 100 days. One mol per liter solution of each solvent was simulated as a harsh environment test under the acidic and alkaline conditions (acidic at pH 1 and alkaline at pH 14). Distilled water and mix dyes solution of BG and AR1 were also simulated for comparison study. The final result was examined qualitatively based on the physical appearance of the samples in terms of coating condition using photographic images and snap using SAMSUNG Tab 7, model SM-T211. The quantitative values obtained from the percentage weight loss of adsorbent before and after experiments were carried out.

2.2.2. Determination of adsorbent coating durability in various pH of effluent solution

The initial pH of Acid Red 1 and Brilliant Green dyes solution was ranging at pH 3, 5, 7, 9 and 11 and adjusted either by adding NaOH (0.1 M) or HCl (0.1 M) solutions. The initial pH was measured using pH meter (model Martini Instrument, Mi 151). The pH of 200 mL dye solution at 50 mg/L concentration was adjusted and pours into a 250 mL beaker containing adsorbent coating clipped in it. The setup was placed on a stirrer at 330 rpm and the temperature was maintained at room temperature. The agitation was carried out for 8 hours to ensure that the equilibrium was reached and dye concentrations were drawn out at 30 minutes time intervals. The concentration of dyes in solution was measured using a spectrophotometer. The experiments were carried out triplicate to assure accuracy and reproducibility and the error bar was shown in the graph.

2.2.3. Determination of adsorbent coating durability under thermal condition

The durability test for ZACC was carried out based on 3 situations and methods; tested on high temperature in the oven, water bath and real weather conditions outside the building. The adsorbent coating with the dimensions of 10 cm x 10 cm in sizes were placed as in condition, duration and temperature stated in Table 1. The final results were employed based on physical appearance and
percentage weight loss. The images of adsorbent coating before and after testing was visualized in photographic images and snap using SAMSUNG Tab 7, model SM-T211).

Table 1. Durability test of the adsorbent coating under thermal condition

| Thermal condition                              | Duration | Temperature       |
|-----------------------------------------------|----------|-------------------|
| 1 Temperature in oven                         | 7 days   | 100 °C            |
| 2 Temperature in water bath                   | 4 hours  | 30 °C, 50 °C, 70 °C |
| 3 Temperature surrounding (outside the building) | 5 days   | Ambient temperature (25 °C – 32 °C ) |

3. Results and discussion

3.1. Chemical stability test

The test for chemical stability of ZACC was evaluated by soaking a piece of the samples in different tests solution. They were acidic (1 M), alkaline (1 M), neutral (pH 7) and colored medium. The physical appearance of strips after 10 days (Figure 1) revealed a highly robust and the texture of ZACC remained intact as the original sample even after undergone different exposure conditions of strong acidic, alkaline, neutral, as well as colored solution. The supernatant liquid was crystal clear and no solid object could be seen in solution by naked eyes. This has established the stability of ZACC in chemical solutions. The stability testing of ZACC was prolonged to 100 days in each of the solutions. For this duration, all of the strips maintained their appearance in square shape except for ZACC in alkaline solution. The coating was about to desquamate from cotton cloth. Therefore, the stability of any adsorbents in a high concentration of hazardous chemicals is essential in a real environment, especially in terms of economic issues.

Figure 1. Photographic images of ZACC after 10 days (a) and 100 days (b) of soaking in acidic, alkaline, mixed dyes and distilled water solution

The chemical stability of ZACC was further investigated by pH study. The pH of dye solution can alter the surface charge of the adsorbent, which then can affect the dye sorption efficiency. Besides, another important factor such as the degree of ionization would also impact the solubility of dyes and the dissociation of surface functional groups on the active sites of the adsorbent. AR1 gives anions when dissolved in an aqueous medium while BG gives cations. The dye uptake capacity at different pH (pH 3.14 to pH 11.02) with constant initial concentration (50 mg/L) and 320 min contact time were
depicted in Figure 2. Initially, the color of AR 1 and BG solution was changed with the variation of pH values. This was attributed to the change of dye molecular structural stability at the pH range and also due to the resonance among charged canonical structures of dyes [9,10].

![Figure 2. Effect of initial solution pH on adsorption of BG and AR 1 dyes using ZACC. [Constant condition: 50 mg/L of initial dye concentration, atmospheric temperature, adsorbent dosage 0.3 g]](image)

In acidic medium, the adsorbent surface gets protonated due to availability of a large number of H\(^+\) ions and attracted available anions from the medium. AR 1 exists as an anionic dye, where it contains charged sulfonated group \(–\text{SO}_3\text{Na}^+\) in an aqueous medium. Therefore, the electrostatic attraction occurs between protonated ZACC surface and anionic dye, hence higher removal of AR 1 dye could be observed in acidic medium (99.4\(±\)0.1 %). Meanwhile, the percentage removal of AR 1 dye was decreased when the pH of AR 1 solution goes in alkaline range (97.4\(±\)0.1 %). This is due to the electrostatic repulsion occurred between the anionic dye and deprotonated of adsorbent surface. In addition, the availability of OH\(^-\) ions in the alkaline medium will also compete with anionic dye resulting in decreasing in AR 1 percentage removal. Nevertheless, still the adsorption rate of anionic dye shown excellent performance with a very slight variation within 97 % to 99 % in adsorption over a long pH range (3-11). Other possible reasons might be due to the presence of weak van der Waals forces between dyes and ZACC surfaces [11].

In the case of BG dye, dye removal increased once the solution pH increases. BG dye exists in the cationic form in aqueous solution. In acidic medium, electrostatic repulsion occurs between protonated surfaces and BG cations, which decreased adsorption of BG in acidic condition. Besides, there will be a strong competition between BG cations and H\(^+\) ions for the adsorbent surface in acidic medium. While in alkaline medium, deprotonated surface favors cationic dye due to the electrostatic attraction between deprotonated surface of ZACC and BG cations. By increasing pH from 3.14 to 11.02, the percentage removal of BG dye was attained within 87.4 % and 97.1 %. The isoelectric point of ZACC was recorded at pH 8.2. The ZACC surface gets positively charged when the pH of the solution is \(<\text{8.2}\) which will favor anionic species while at higher pH \(>\text{8.2}\), negatively charged adsorbent surface will favor cationic species. Thus, BG removal was higher in alkaline medium and AR 1 removal was higher in acidic medium.

Theoretically, at low pH, adsorption coating showed lower adsorption for cationic dyes while higher adsorption efficiency was found for anionic dyes. It was due to the presence of a large number of H\(^+\) and H\(_3\)O\(^+\) in the aqueous solution which competes with the dye ions for available adsorption sites on the adsorbent surface. Thus, most of the functional groups present in the adsorbent are protonated (present in the form of positive charge). Therefore, electrostatic repulsion between dye
molecules and positively charged adsorbent surface resulted in lower adsorption [12]. At higher pH, a number of positively charged decreases and the adsorbent surface appears negatively charged which resulted in higher cationic dye adsorption compared to anionic dye.

Furthermore in Table 2, even initially the pH were set accordingly for both dyes before the adsorption, the pH reading after adsorption were demonstrated a neutral pH (7 < pH < 8) for each of the solution, except for pH 11 where it was shown the alkalinity of solution (8.29 and 8.57 for AR 1 and BG dyes, respectively). The result provides information that ZACC surfaces have stabilized the AR 1 and BG dyes solution into a normal pH along with the adsorption treatment. Therefore, looking into the situation, by applying ZACC, the water can be neutralized from any acidic and alkaline condition.

As a conclusion, these findings suggested that the adsorption of cationic and anionic dyes on ZACC was not strongly and significantly pH-dependent. The variation in percentage efficiencies was very small and claimed as excellent performance for both types of dyes even in acidic or alkaline solution. Therefore, the amphoteric functionality of ZACC was proved by its accessibility to remove anionic (AR1) and cationic (BG) dyes using a single strip even in various pH. The result is consistent and in lined with earlier literature by [13] that found their cationic and anionic dyes were fairly stable in relatively wide pH range from 4 to 8 [13]. Similar findings were observed in other studies [10,11].

| Table 2. Value of pH before and after adsorption of AR 1 and BG dyes. |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
|                 | pH variation    |                 |                 |                 |                 |
| AR 1            | Before adsorption | 3.14 | 5.275 | 7.045 | 9.175 | 11.017 |
|                 | After adsorption | 7.48 | 7.38 | 7.42 | 7.57 | 8.29 |
| BG              | Before adsorption | 3.008 | 5.087 | 7.065 | 9.045 | 11.087 |
|                 | After adsorption | 7.38 | 7.49 | 7.34 | 7.7 | 8.56 |

3.2 Thermal stability test

The test for the harsh environment under thermal stability study was classified into three conditions. There was thermal stability in extreme dry temperature (1), in water (2) and outside building (3). The tests were carried out in such conditions in order to examine the durability and stability of ZACC in various situation.

The thermal stability study was conducted on ZACC strips (5 cm x 5 cm) in order to investigate the stability of an adsorbent coating at high temperature. Figure 3 exhibited the photographic images of four pieces of ZACC strips after 5 days in 100 °C drying oven. All four pieces of ZACC had similar sizes and were used for repetition studied. The physical appearance of ZACC samples (A), (B), (C) and (D) after 5 days in the oven with a high degree of temperature shown no changes in sizes and color. The sizes remained as original, stayed in white color and not get burnt. Table 3 provides a percentage weight loss of ZACC after thermal stability test in a drying oven. The percentage average was about 0.25 % and the value can be claimed as very low. This also indicated that an adsorbent coating was strongly attached/coated on cotton cloth. Higher the temperature will bring to the weight loss of adsorbent coating. As a conclusion, the ZACC has strong thermal stability, especially under dried temperature condition. This characteristic is required for the adsorbent to stand longer under various environmental circumstances in the industry, specifically.

The thermal stability of ZACC was further investigated by immersing the coating strips in water with different temperature condition, at 30 °C, 50 °C and 70 °C. The studied was aimed to examine the strength of adsorbent coating anchored on cotton cloth especially in water circumstances. The thermal stability of ZACC was determined based on changes of spectrum through wavelength measurement using UV-VIS spectrophotometer in 4 hours duration from 800 nm to 300 nm wavelength reading. The result was plotted in the graph as shown in Figure 4. At 30 °C, there were no changes of spectrums from 0 hours of ZACC once exposed to water up to 4 hours of the process. This result showed the stability of ZACC at atmospheric temperature. However, as time increased and
temperature increase, the measurement through absorbance value started to increase in a very medium gap.

![Photographic images of ZACC after 5 days in 100 °C drying oven.](image)

Table 3. Percentage weight loss of ZACC after thermal stability test in drying oven.

| Samples | Weight before (g) | Weight after (g) | Percentage weight loss (%) |
|---------|-------------------|------------------|---------------------------|
| A       | 0.3518            | 0.3512           | 0.17                      |
| B       | 0.3333            | 0.3323           | 0.30                      |
| C       | 0.3226            | 0.3222           | 0.12                      |
| D       | 0.3428            | 0.3414           | 0.40                      |
| Average |                  |                  | 0.25                      |

The water solution at 50 °C showed no changes in absorbance value up to 3 hours of experiment, however, increased in absorbance gap after 4 hours. The graph shows upwards trend especially at wavelength approaching 300 nm. The changes in absorbance value were due to the disturbance of water content. The water might be disturbed/affected by the presence of adsorbent coating in a solution. In a nutshell, the presence of ZACC in the water at higher temperature showed very minimum changes in absorbance value after 4 hours of experiment especially at temperature 50 °C and 70 °C.

![Wavelength changes detected in water at temperature (a) 30 °C, (b) 50 °C, (c) 70 °C](image)
In addition, the other study related to the thermal stability of ZACC samples were tested at the outside of the building. The temperature outside the building was based on the environment condition of the located samples. Four ZACC strips were exposed to the various temperature conditions outside building aimed to get information regarding the stability of samples. Along seven days of testing starting from 3rd March 2019 to 9th March 2019, the environment temperatures were approximately at 30 °C at noon and around 25 °C at night. The samples have also been exposed to the raining day, once. Similar ZACC samples marked as (A), (B), (C) and (D) were cut into 5 cm x 5 cm sizes and used for repetitive studied (Figure 5). The observation based on the physical appearance of all samples after 7 days been exposed to environment temperature outside the building seems no changes in sizes and colors. However, quantitatively, the percentage weight loss of ZACC was calculated and result shown in Table 4. The average weight loss obtained was about 0.109 % and considered very less. The ZACC proved a good strength of adsorbent coated on cotton cloth even been exposed to various weather condition and open to the outside building environment.

![Figure 5. Thermal stability testing outside building](image)

| Samples | Weight before (g) | Weight after (g) | Percentage weight loss (%) |
|---------|-------------------|-----------------|----------------------------|
| A       | 0.4107            | 0.4097          | 0.243                      |
| B       | 0.4014            | 0.4013          | 0.025                      |
| C       | 0.4156            | 0.4150          | 0.144                      |
| D       | 0.4000            | 0.3999          | 0.025                      |
| Average |                  |                 | 0.109                      |

4. Conclusions
The stability and durability of adsorbent materials were considered as an important factor in order to deals with the harsh environment such as at high chemical and thermal condition. The additional procedure after the adsorption process such as centrifugation and filtration should be prevented. This extra process will indirectly increase the operation cost, energy consumption and maintenance and time-consuming. The zwitterionic adsorbent coating revealed their tolerance in both chemical and thermal stability and durability studied. The ZACC was stable in various pH condition (acidic to alkaline) and could maintained the strength of coating without peel off at extreme pH studied. The ZACC was also can stand especially under extreme temperature (100 °C for 5 days), exposed to various weather condition and at outside building environment as proved from a very minimum percentage weight loss tested (within 0.11 % to 0.25 % loss).

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