Experimental Study for Efficiency of Natural and Modified Seagrass as Low-Cost Adsorbent for Removal Malachite Green Dye

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ABSTRACT

The removal of dyes from wastewater is a matter of great interest in the field of waste water treatment. The effluents from many industries often contain one or more toxic dyes. Therefore, an increased interest has been focused on removing such dyes from wastewaters. Malachite green (MG) is one of the most common water-soluble dyes. In general, several methods are used for the removal of dyes from wastewater. Among the treatment methods, adsorption is comparatively superior. Sea wastes are renewable and available abundantly at no or low costs. In the present study, the use of low-cost, abundantly available, highly efficient and eco-friendly adsorbent biodegrade seagrass materials, as a sea by-product has been reported as an alternative to uptake of malachite green (MG) dye from its aqueous solution. Batch experiments were used to carried out for the removal of Malachite Green dye from its aqueous solution using seagrass material as adsorbent. A batch mode was used to study several factors, dye concentration solution (10-90) ppm, adsorbent dosage (15-35) mg, contact time (0-120) min, size (355-710), pH (3-11) and agitation speed (150-250). The results indicated that the removal efficiency increases with the increase of adsorbent dosage, contact time and pH, while inversely proportional to the increase in size, dye concentration solution and agitation speed. The adsorption's resulting data were in agreement with both Langmuir and Freundlich isotherm models according to the regression analysis, and the kinetics data followed pseudo-second-order kinetic.

KEYWORDS: Adsorption, Malachite Green, adsorbent, Seagrass, kinetics, isotherm models

1. INTRODUCTION

The textile industry is spread globally, generating around 1 trillion dollars, contributes with 7% of the total world exports and employs around 35 million workers around the world [1], Despite its undeniable importance, this industrial sector is one of the biggest global polluters and it consumes high amounts of fuels and chemicals. The special emphasis is placed on the enormous use of drinking water in various operations of its production chain, such as washing, bleaching, dyeing, among others. The textile industry is responsible for an extensive list of environmental impacts [2].

The dyes are soluble organic compounds, especially those classified as reactive, direct basic and acids. They exhibit high solubility in water making it difficult to remove them by conventional methods [3],

One of its properties is the ability to impart color to a given substrate because of the presence of chromophoric groups in its molecular structure. However, the property of fixing the color to the material is related to the auxotrophic groups, which are polar and can bind to polar groups of textile fibers [4], The special mention should be made to azo-type textile dyes which, around 15–50%, do not bind to the fabric, during the dyeing process, and are released into wastewater which is commonly used, in developing countries, for the purpose of irrigation in agriculture [5]. The use of these azo compounds is very negative to soil microbial communities and to germination and growth of plants [6].

Malachite green (MG) is a cationic triphenylmethane dye used in the industries of silk, wool, leather, and

distilleries. Medical applications of MG include the treatment against the infections of parasites, bacteria, fungi and as antiseptic in the industrial sector of aquaculture to control fish parasite and associated diseases [7]. The detrimental effects associated with MG are cytotoxic, carcinogenic, damage liver, intestine, gill, kidney, gonads and pituitary gonadotrophic cells, causes irritation to respiratory and gastrointestinal tract, skin redness and permanent eye injury. The discharge of even low dye concentrations from the industrial effluents to the environment posed a significant threat due to their toxicological and aesthetic properties. To minimize the harmful effects associated with the dye contaminated wastewater to ecological environment and human health, proper treatment methods are obligatory before discharge into the water bodies [8].

A number of efficient methods have been reviewed for the removal of dye such as chemical precipitation, ion exchange, reverse osmosis, electrodialysis, ultrafiltration, nanofiltration, coagulation, adsorption, floatation, etc. However, these methods have several disadvantages such as high reagent requirement, unpredictable metal ion removal, generation of toxic sludge, etc. Adsorption process being very simple, economical, effective and versatile has become the most preferred methods for removal of toxic contaminants from wastewater. Comparatively, the adsorption process seems to be a significant technique due to its wide applications, such as ease of operation, economic feasibility, wide availability and simplicity of design [9].

The overall objective of this research work is to synthesize a cost-effective, environmentally friendly and sustainable sea solid waste based bio-char adsorbent and evaluate its effectiveness in the removal of organic MG dye from their aqueous solution by adsorption.

2. Materials and Methods
2.1. Preparation of the Adsorbent
2.1.1. Preparation of raw seagrass
Seagrass were collected locally from located at Sabratha city. It was collected between April and May, 2021. Then, part of the dried sample was soaked in distilled water in an amount sufficient to cover the raw materials completely, mixed vigorously for 30 min. After mixing, the washed seagrass pieces were oven dried at 100°C for 48 h. The prepared bio sorbent seagrass was stored in an airtight plastic container in order to avoid moisture, then the seagrass are crushed in a home blender and crushed with different sieves and then saved for use.

2.1.2. Preparation of the Adsorbent modification
Base and acid modified seagrass powder materials used as adsorbent was prepared by mixing 10 g of raw seagrass materials powder with 100 ml of 0.1M Hcl solution (SE1) and with 100 ml of 0.1 M NaoH solution (SE2). The whole reaction mixture was stirred in a magnetic stirrer for a period of 24 hr and then the powders were filtered and repeatedly washed with distilled water. The washed powders were then oven dried overnight at 50 °C and ware used as adsorbent.

2.2. Preparation of Adsorbate
The basic cationic dye, malachite green (MG), was tested as the model dye adsorbate in this study. The formula of MG has $C_{25}H_{25}C_lN_2$ (Figure 1) and the molar mass is 364.91 g/mol [9]. The stock dye solution was prepared by dissolving 1g of malachite green in 1000 ml distilled water to obtain the concentration of 1000 ppm. The experimental solutions were obtained by diluting the stock dye solution with deionised water to give the appropriate concentration of the experimental solutions. The pH of the experimental solutions was adjusted by addition of either dilute 0.1 M Hcl or 0.1 M NaoH solutions.
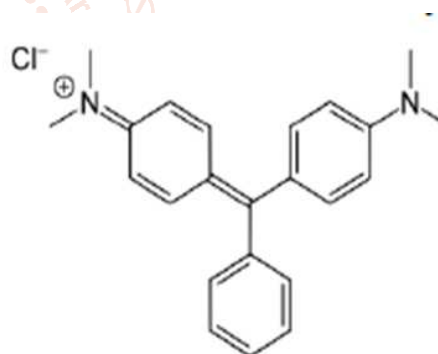

Figure 1 Chemical structure of malachite green

2.3. Batch adsorption studies
Adsorption measurement was determined by batch experiments of known amount of the adsorbent with 50 ml of aqueous malachite green solutions of known concentration in a series of 250 ml conical flasks. The mixture was shaken at 150 rpm at a constant temperature for 120 min. At predestined time, the bottles were withdrawn from the shaker, and the residual dye concentration in the reaction mixture was measuring the absorbance of the supernatant at the wavelength that correspond to the maximum absorbance of the sample. Dye concentration in the reaction mixture was calculated from the calibration curve. Adsorption experiments were conducted by varying initial solution pH, contact time, adsorbent dose, initial malachite green dye concentration and size of adsorbate, under the aspect of adsorption kinetics and adsorption isotherm, the dye

concentrations were measured by UV/vis spectrophotometer(DR-2800) at 617 nm. The amount of equilibrium

Adsorption, qt (mg/g), was calculated by:

$$q_t = \frac{(c_0 - c_t)}{m} * V \qquad (1)$$

Where Co is the initial dye concentration (mg L^{-1}), Ct is the concentration of dye at any time t, V is the volume of solution (L) and m is the mass of seagrass in (g)

The removal percentage at equilibrium condition was calculated by using the following equation:

$$\%Removal = \frac{(C_0 - C_t)}{C_0} * 100 \qquad (2)$$

The same experiments were repeated by using seagrass to compare the amount of adsorption qt (mg/g) and extent of adsorption% between raw and treated seagrass.

Adsorption isotherms models used to illustrate the adsorbent interaction with the adsorbate and provide the relationship between the adsorption capacity and the liquid phase concentration of adsorbate under equilibrium condition at constant temperature.

The linearized form of Langmuir can be written as two different forms [10];

$$\frac{c_e}{q_e} = \frac{c_e}{q_m} + \frac{1}{K_a q_m} \qquad (3)$$

The slope and intercept of plot between Ce/qe vs. Ce will give K$_a$ the isotherm constants for Langmuir, (L mg $^{-1}$) and q$_m$ The maximum adsorption capacity, (mg/g).

The Freundlich adsorption isotherm model considers a heterogeneous adsorption surface that has unequal available sites with different energies of adsorption. The Freundlich adsorption isotherm model is represented as follows [11].

$$\ln q_e = \ln K_f + \frac{1}{n}(\ln C_e) \qquad (4)$$

Where q$_e$ is the amount of metal ion adsorbed at equilibrium time (mg/g), Ce is equilibrium concentration of dye in solution (mg L^{-1}). K$_f$ is the capacity of the adsorbent and n is the intensity of adsorption constant for Freundlich. The plot of lnqe versus lnC$_e$ is employed to determine the K$_f$ and n from intercept and slope respectively.

Meanwhile adsorption kinetic models used in this study were pseudo–first–order and pseudo–second–order. The linear form of pseudo–first–order rate equation is expressed as Equation 5 [12]:

$$\log(q_e - q_t) - \log q_e - \frac{K_1}{2.303} t \qquad (5)$$

Where qe and qt (mg/g) are the amount of MG absorbed onto adsorbent at equilibrium and at time t (min), respectively and k$_1$ (min–1) is the rate constant of pseudo–first–order adsorption. The straight-line plots of log (qe–qt) against t will yield the values of rate constant, k$_1$ and qe from the slope and intercept, respectively.

The pseudo–second–order equation is based on the assumption that chemisorption is the rate determining step and is expressed as given by Equation 6 [13]:

$$\frac{t}{qt} = \frac{1}{K_2 qe^z} + \frac{1}{qe} t \qquad (6)$$

Where; K_2 (g (mg min)$^{-1}$) is the second-order rate constant of adsorption.

3. Result and Discussion
3.1. Calibration curve

The calibration curve was plotted between the absorbance and concentration of MG dye solution to obtain the linear calibration equation as shown in Figure 2. The concentration of the MG dye was measured from the calibration plot. Chemical risk assessment was carried out through the use of material safety data to detect and regulate any hazards associated with the use of MG dye.
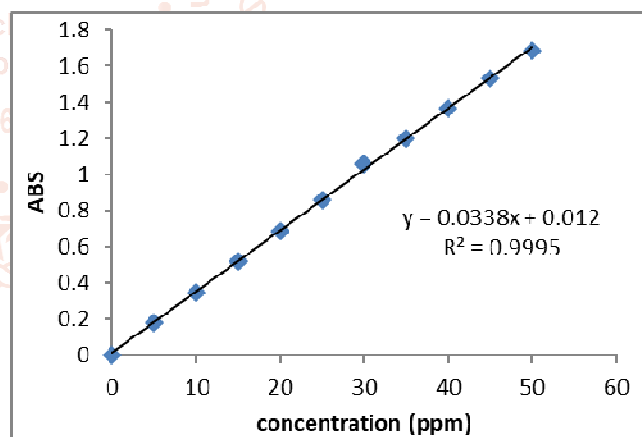

**Figure 2 The calibration curve of MG**

3.2. Effect of pH

The pH of the solution affects the surface charge of the adsorbent and degree of ionization of the dye [14]. In the present study, the pH values were varied from 3 - 10 (Figure 3) while the other parameters were kept constant. 0.1 M Hcl and 0.1 M NaoH solutions were used to correct the pH to the desired value. The percentage (%) adsorption of the dye increased with increase in pH up to an optimal value of pH 10.
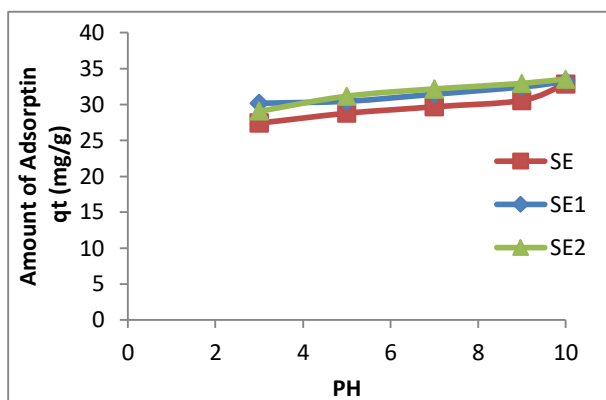
Figure 3 Effect of initial solution pH on the amount of adsorption of MG onto raw and treated sea grass

3.3. Effect of Initial Dye Concentration

The influence of initial concentration of malachite green (MG) onto seagrass was investigated with dye concentrations ranging from 10 to 90 ppm and adsorbent dosage of 0.15 g. The percentage (%) removal decreased with increase of initial dye concentration of MG (Figure 4). The % decrease in adsorption is ascribed to saturation of the active binding sites of the seagrass at higher concentrations of malachite green.
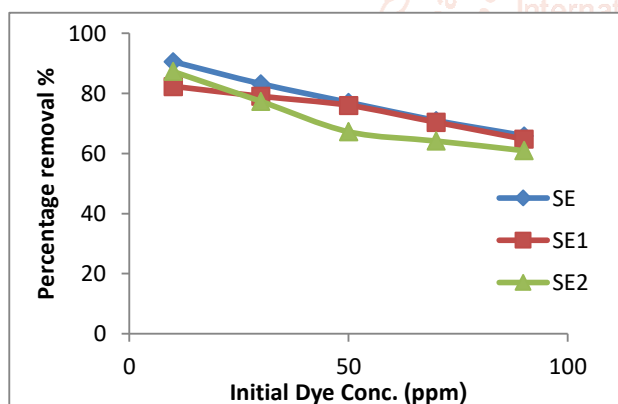
Figure 4 Effect of initial MG dye concentration on the percentage removal of MG onto raw and treated sea grass

3.4. Effect of Contact Time

The effect of contact time was evaluated with dye concentration of 10 ppm, adsorbent dosage of 0.15 g, a solution volume of 50 mL and agitation speed of 150 rpm. The results revealed that the uptake of the dye was rapid at the initial stages of adsorption reaction (30 minutes) and thereafter the adsorption was slow as it approached equilibrium (Figure 5). The above trend of adsorption is ascribed to substantial amount of vacant surface sites accessible for adsorption at the initial stage. However, as the reaction approached equilibrium all the sites were already occupied by the dye hence the adsorption was slow.
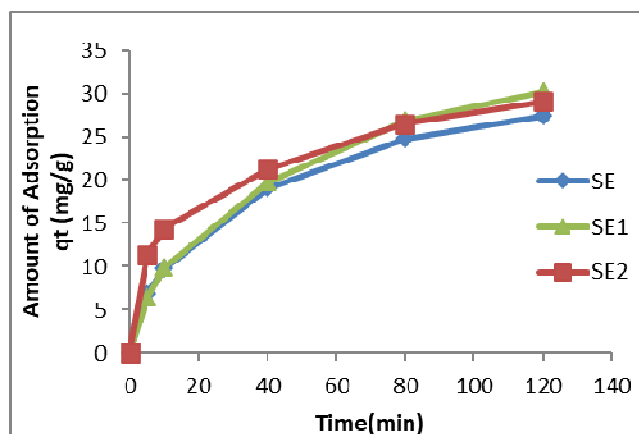
Figure 5 Effect of contact time on the adsorption of MG onto raw and treated sea grass

3.5. Effect of Agitation Speed

The study was conducted by varying the speed from 150 to 250 rpm. Adsorbent dosage was kept constant at 0.15 g. The maximum removal of malachite green onto seagrass was achieved at 250 rpm (Figure 6). Increasing the agitation speed decreases the boundary of the transfer of dye molecules from the bulk solution to adsorbent surface.
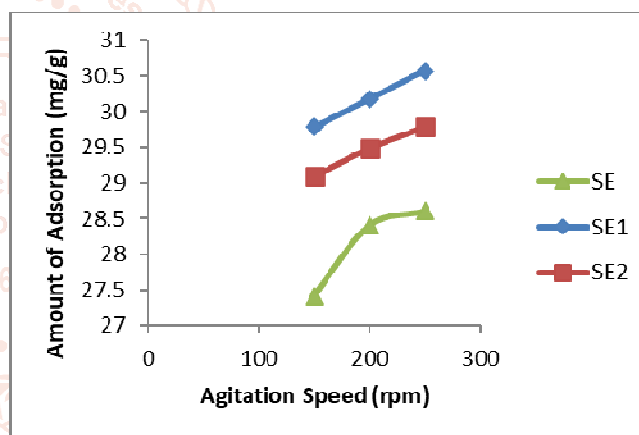

Figure 6 Effect of agitation speed on the adsorption of MG onto seagrass materials

3.6. Effect of Adsorbent Particle Size on Dye Removal

The influence of adsorbent particle size on adsorption of malachite green (MG)

Was tested using three different meshes (355, 500, and 710 μm). The adsorbent dosage was 0.15 g; volume of the dye solution was 50 mL, pH of 3 and shaking speed of 150 rpm. The highest adsorption efficiency obtained was 90.83% at particle sizes of 355μm (Figure 7). The higher adsorption of MG onto smaller particle size of the adsorbent was attributed to increased accessibility of binding sites due to increased surface area for bulk adsorption of the dye.
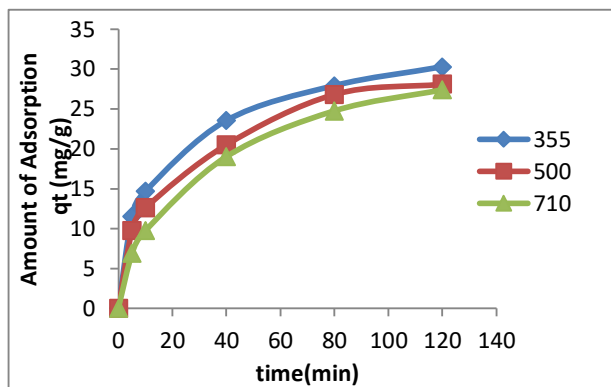
Figure 7 adsorbent particle different plot for the adsorption of MG onto raw seagrass (SE).

3.7. Effect of adsorbent dosage

The effect of adsorbent dosage is illustrated in Figure 8. The percentage removal increases with the increasing adsorbent dosage an adsorbent dosage of 15mg to 35 mg. However, the adsorption capacity, which is the amount of MG adsorbed per unit weight decreased with increasing adsorbent dosage. Percentage removal is increased because the availability of adsorption surface is increased yet the decrease in adsorption capacity with increase adsorbent dosage is due to saturation of adsorption sites.
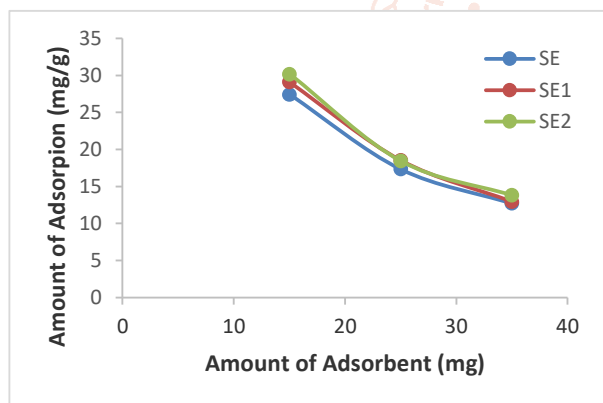
**Figure 8 Effect of adsorbent seagrass materials dosage on the percentage removal of MG**

Adsorption equilibrium isotherms

An adsorption isotherm is an expression that shows the relationship between the amounts of adsorbate adsorbed per unit weight of adsorbent (qe, mg/g) and the concentration of adsorbate in the bulk solution (Ce, mg/L) at 298 K under equilibrium conditions. The Langmuir and Freundlich models are often used to describe equilibrium adsorption isotherms. The Langmuir isotherm usually indicates individual chemical adsorption (chemisorption) and reflects a relatively high affinity between adsorbate and the adsorbent within a low concentration range [15].

The results showed that the Langmuir model was fitting for both raw and treated system, it give good

linear correlation coefficient R^2 as shown in figures 9,10 and 11. The maximum monolayer adsorption capacity was 29.87 mg/g occurred at pH of 7 for an initial dye concentration of 10 ppm by raw seagrass. While maximum adsorption capacity was 30.14 mg/g occurred by SE1and 27.63 for SE2.

Figure 12,13, 14, show the freundlich isotherm fitting for raw and modified seagrass, adsorption capacity K_f and rate of adsorption, n, are calculated from these plots for raw and modify (SE1,SE2) seagrass. The adsorption capacity K_f, and rate of adsorption n, are 1.449 mg/g 1.839 mg/g 1.763 mg/g respectively, whereas the adsorption capacity K_f were 20.232, 32.456 and 4.0959 respectively.
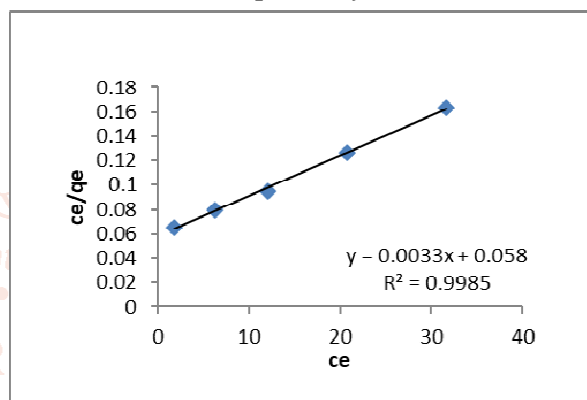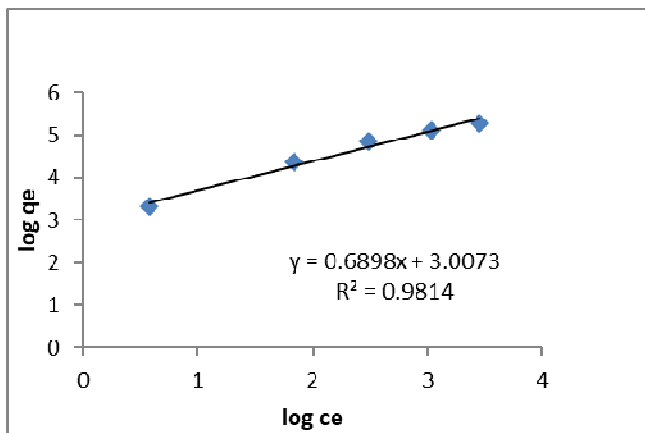

Figure 9 Langmuir plot amount of adsorbent raw SE
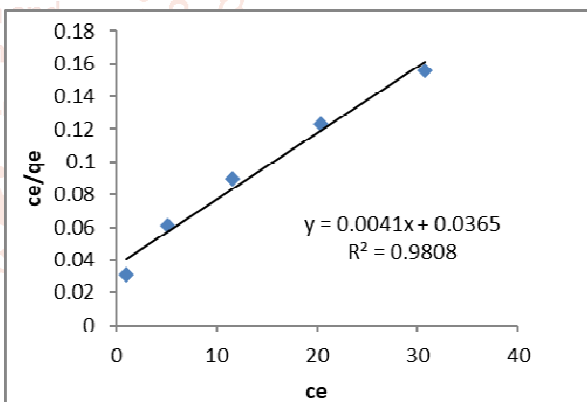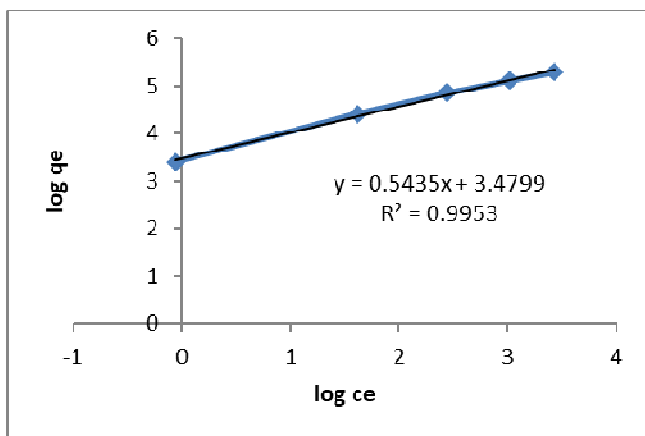

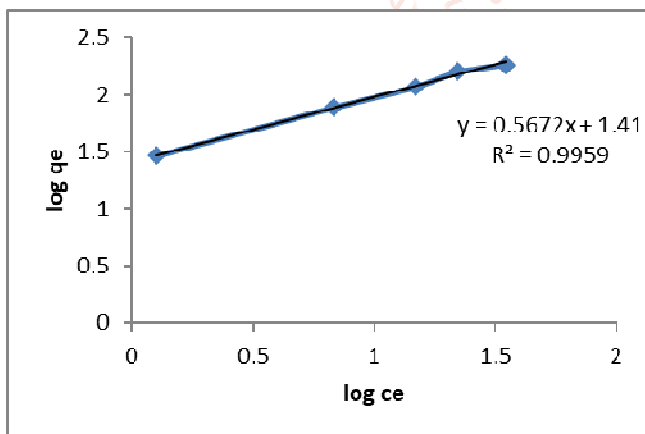**Figure 10 Langmuir plot amount of adsorbent SE1**
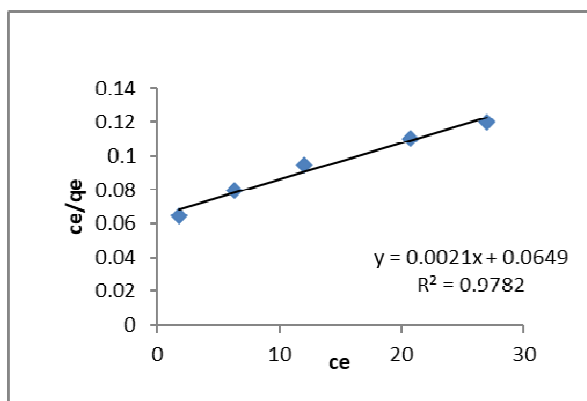
Figure 11 Langmuir plot amount of adsorbent SE2

Figure 12 Freundlich plot: amount of adsorbent raw SE

**Figure 13 Freundlich plot : amount of adsorbent SE1**

**Figure 14 Freundlich plot: amount of adsorbent SE2**

Adsorption kinetics

The kinetics of adsorption is applied to determine the adsorption rate of MG uptake on the beads. The linear fitting plots of pseudo-first-order kinetic model are presented in figures (15, 16, and 17). Similarly the linear fitting plots of pseudo-second-order kinetics model are shown in figures (18, 19, and 20) at

deferent solution pH. So, the obtained results were described using two kinetic models; pseudo-first-order and pseudo-second-order. It was found from that the adsorption data is more suitable with the pseudo-second-order model.
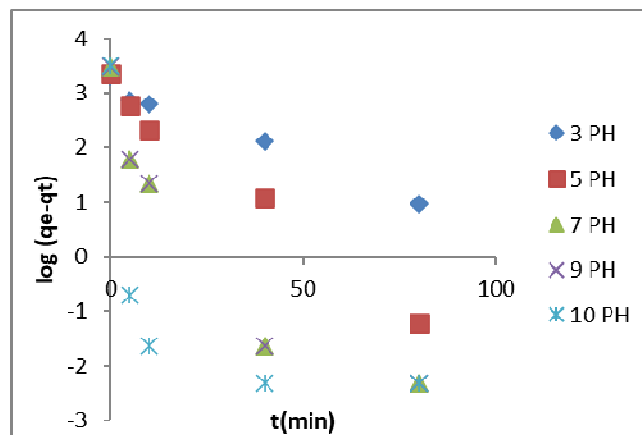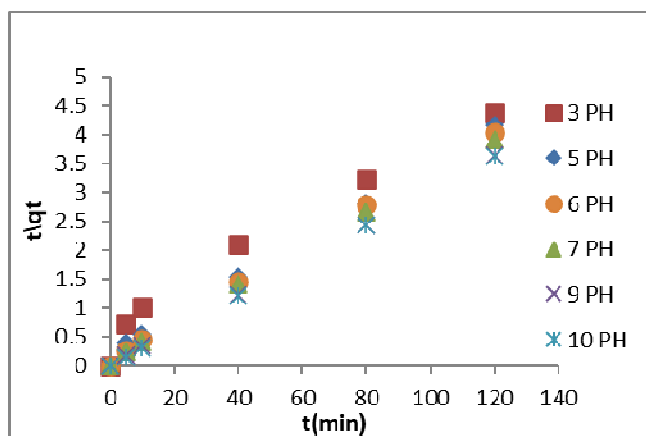

Figure 15 Pseudo-first-order plot for the adsorption of MG onto raw seagrass (SE) materials at different solution pH
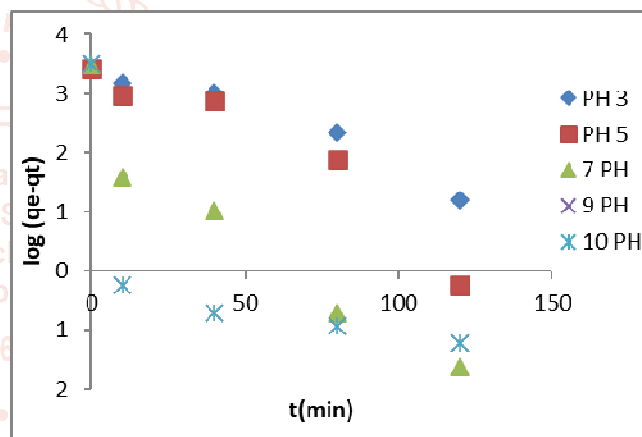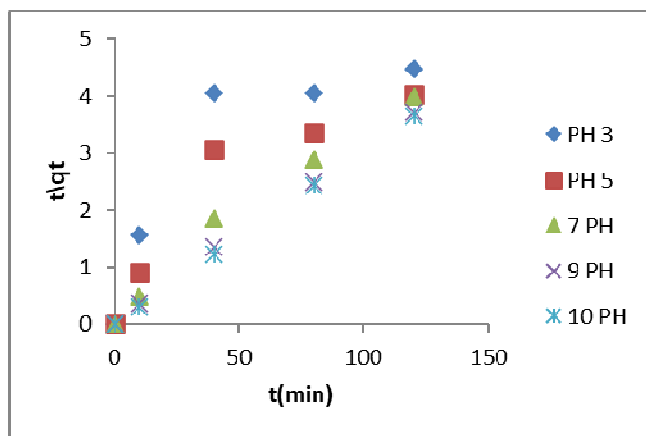

Figure 16 Pseudo-first-order plot for the adsorption of MG onto treated seagrass (SE1) materials at different solution pH
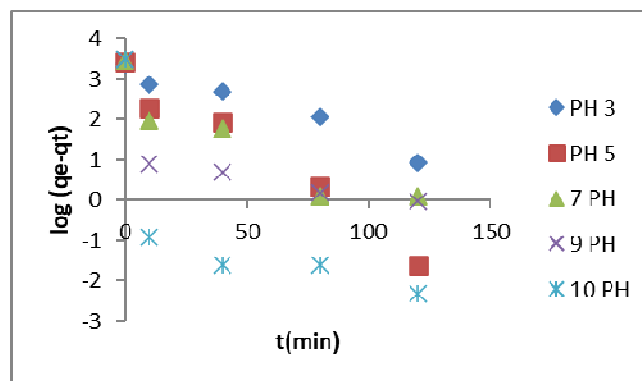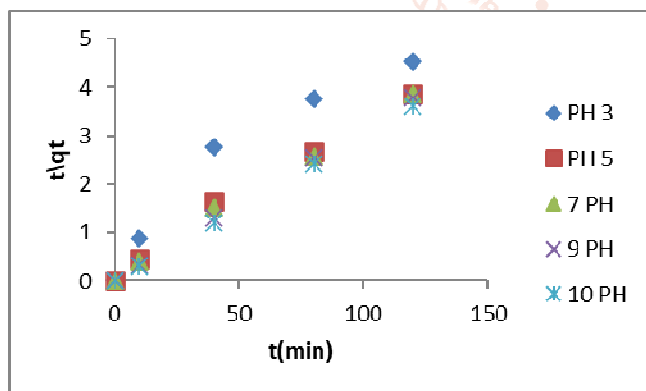

Figure 17 Pseudo-first-order plot for the adsorption of MG onto treated seagrass (SE2) materials at different solution pH

Figure 18 Pseudo-second-order plot for the adsorption of MG onto raw seagrass (SE) materials at different initial MG concentration

Figure 19 Pseudo-second-order plot for the adsorption of MG onto treated seagrass (SE1) materials at different solution pH

Figure 20 Pseudo-second-order plot for the adsorption of MG onto treated seagrass (SE2) materials at different solution pH

4. Conclusions

In this study, the effectiveness of raw SE and modified biomass seagrass, SE1, SE2 were tested for removal of Malachite green MG from aqueous the amount of Malachite green dye uptake on raw, acid and basic modified seagrass biomass were found to increase with increase in initial dye concentration, contact time, adsorbent particle size, agitation speed, adsorbent dosage and solution pH. In batch study, the

kinetic experiments revealed that adsorption of dyes were rapid at initial stage followed by a slower phase where equilibrium uptake was achieved. The kinetic studies showed that the Malachite green adsorption process followed pseudo-second-order kinetics models. Langmuir and Freundlich equations both are applicable to describe the adsorption of malachite green on raw and treated modified seagrass biomass within this initial dye concentration range. The maximum monolayer adsorption capacity was 29.87 mg/g occurred at pH of 7 for an initial dye concentration of 10 ppm by raw seagrass. While maximum adsorption capacity was 30.14 mg/g occurred by SE1and 27.63 for SE2.

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