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The Influence of Eggshell Particle Sizes on the Adsorption of Organic Dye

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Abstract

This work aimed to use effective, low-cost, available, and natural adsorbents like eggshells for removal of hazardous organic dye result from widely number of industries and study the influence of different eggshell particle size (75, 150) Mm. The adsorbent was characterized by SEM, EDX, BET and FTIR . The initial pH of dye solutions varying from 4 to 10 , the initial concentrations of methyl violet (MV) 2B range (20-80) mg/L, dosage range (0.5-10) g, contact time (30-180) min, and particles size of the adsorbent (75, 150) Mm were selected to be studied. Two adsorption isotherms models have been used to fit the experimental data. Langmuir and Freunlich models were found to more represent the experiments with high correlation coefficient. The results showed that the variation in particle size of eggshells powder statistically has slight effect on the removal of (MV). The highly percentage of dye removal (97.27%) by using eggshells was observed with particle size of 75Mm, pH 4, at room temperatures for 30 min, 10 g adsorbent dose and 20 mg/L initial dye concentration.

Key words: Eggshell, Methyl violet, Isotherm Model, Particle Size, Adsorption.

Introduction

Water contamination around the world has become serious environmental problem and it is either naturally or of man mad source, is produced by the addition of chemical, physical, biological materials in certain concentrations [1]. The contamination of wastewater in some industries such as dyestuff, textiles which can be difficult to treat leather, plastics, printing, etc. contain various kinds of synthetic dyestuffs [2]. And the main sources of wastewater are the dyeing and finishing processes [3]. As a result of extensive application , production of large-scale and synthetic dyes can be source undesirable pollution and many health-risk. Due to the cancer-causing and mutagenic effects of synthetic dyes the presence even minor quantity colored wastewater is not only destructive the aesthetic nature of streams, also it can affect aquatic life and food webs [4, 5]. Dyes chemicals, which on binding with a material will give color to them [6], are primarily have complex aromatic structures, which makes them biochemically stable [7]. Its removal from wastewater carried out by either (biological or physicochemical) techniques. (e.g., adsorption, oxidation - reduction, chemical coagulation, ozone treatment, and membrane filtration) [8, 9, 10]. Adsorption technique is one of the most effective, low cost methods which is used for dye removal from wastewaters to produce high quality water [11]. Nevertheless the usage of high cost adsorbents can be take in account as a restrictive factor [12, 13]. A variety of inexpensive and effective adsorbents of raw materials from unused to remove dyes have been used [14, 15]. Eggshell, (agricultural waste) material from domestic sources such as hatcheries, poultry farms, egg product factories, homes and restaurant, it is a novel substrate, robust, cost effective and easily available [16]. As a by-product characterizes nearly 11% of the complete egg weight is can be get rid of it as waste [17]. For the reason the vesicular structures and low cost can be used as a suitable adsorbent for contaminant removal [18, 19]. In addition to that porous nature makes it an attractive material to work as an adsorbent agent [20]. Each one eggshell has been assessed to include between 7000-17000 pores [21]. With chemical composition of (94% calcium carbonate, 1% magnesium carbonate, 1% calcium phosphate and 4% organic material), [22]. Therefore the main aim of this study was to investigate the effectiveness of eggshells powder for use as adsorbent material for removal of Methyl violet (MV) 2B from aqueous solution which is widely used in industry and to determine the influence of the adsorbents of varying particle sizes on the adsorption of organic dye at most important factors which contain pH of the solution, initial dye concentration, the adsorbent dose, and contact time.

Materials and Methods

1. Chemicals

In this study Organic Dye was used (MV) 2B with (MW= 393.96g/mol), melting point (MP) 137 °C, chemical formula $C_{24}H_{28}N_3C$ it was purchased from Sigma Aldrich Company. Hydrochloric acid (HCl, 37%). Sodium hydroxide (NaOH, 99%) was purchased from chemical bureaus in Iraq.

2. Eggshells

Eggshells were chosen to be an adsorbent which were collected from house & fast food restaurant. Eggshells were washed thoroughly with distilled water to remove undesirable matters exist on eggshells surface. They were dried in an oven for 120 min at 105 °C and then that may crushed by suitable mill to prepare eggshells powder with different particle size (p.z) ranges (75-150) Mm were obtained after using standard sieves.

3. Stock Solution Preparation

Stock solution of MV dye was prepared by dissolving 1 g of MV in 1 liter of distilled water in conical flask. Varying experimental concentrations of MV (20- 80 mg/L) were prepared via diluting with distilled water.

4. Properties of Adsorbents

Surface morphology of eggshells was obtained by scanning electron microscopy (SEM, VEGA3 LMU TESCAN), EDS is an analytical technique used to detect the chemical composition which forms an elemental analysis of the adsorbents and it is used in combination with SEM. The adsorbents specific surface areas were intended using the Brunauer – Emmett -Teller (BET) method, Quantachrome.com, USA. Information about the chemical bonds between molecules and the functional groups grafted onto the eggshells powder samples that provide using Fourier transform-infrared spectra (FTIR) spectroscopy is a technique which were recorded by using instrument (FT-IR-600 FTIR ,CO.LTD.(UK)) spectrometer, model=(WQF) with (AC:220/50Hz), at room temperature in transmission mode in the range of 4,000 to 600 cm^{-1} at 4 cm^{-1} resolution regions.

5. Batch Adsorption

The experiments were done in 300 mL Erlenmeyer flasks where 10 g of the adsorbent and 50 mL of the MB solutions (20–80 mg/L) be annexed. The pH of each solutions in interaction with adsorbents was found to be in the range of 4–10, and then the prepared solution agitated by using ultrasonic wave device for a predetermined time intervals and at room temperature. After agitating the samples were withdrawn from the device, to get rid from the present suspended adsorbent, the mixtures were filtered through filters papers. By using UV- Visible spectrophotometer (UV-160 A Shimadzu). Final concentrations of (MV) were obtained. The percentages of dye removal or the amount of dye adsorbed were calculated from the following equation:

$$R\% = \frac{C_e - C_o}{C_o} * 100 \qquad \ldots(1)$$

$$q_e = \frac{V}{M}\left(C_o - C_e\right) \qquad \ldots(2)$$

Where R is the efficiency of dye removal, C_o, C_e represent the initial and final dye concentrations, V is the volume of the solution and M is the mass of adsorbent.

6. Effect of pH on Dye Adsorption

To determine the effect of initial pH on adsorption of MV was tested over a range of pH values of (4-10) modified by, using 0.5 N HCl or 0.5 N NaOH through keep other conditions fixed, the best pH attained use in next experiments.

7. Effect of Dye Concentration

This effect was determined by adjusted MV solution with varying concentrations range of (20-80 mg/L), use the best pH 4 that obtained from prior experiment and keep other conditions fixed.

8. Effect of Adsorbent Dose

Two particle sizes (p.z) adsorbent dose of (75, 150) Mm were selected to determine dose effect adding different weights of eggshell (0.5, 1, 3, 5, 7, 10) g to the best concentration 20 mg/L, pH 4 obtained from prior experiments for 3 hr.

9. Effect of Contact Time on Dye Adsorption

To detect this effect varying contact time range was adjusted (30, 60, 90, 120, 180) min, use the best conditions obtained from prior experiments.

10. Adsorption Isotherm

Adsorption is usually described through an isotherm showing in what way the adsorbed particles hand out between the liquid phase and the solid phase at what time the process of adsorption reaches balance state [23]. Several models describe the process of adsorption from which Langmuir and Freundlich isotherm models can be exemplified respectively as follows [24].

K_L (Langmuir constant) were found by linearizing equation:

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \qquad \ldots(3)$$

The Langmuir adsorption isotherm model is valid for monolayer adsorption onto a surface with a limited number of identical sites. The Langmuir isotherm equation is the first theoretically developed adsorption isotherm and it's stay keeps an important location in physisorption in

addition to chemisorption theories. The equation has also been derived using thermodynamic and statistical approaches.
The equation of Freundlich isotherm in linear form is as follows :

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

Where: K_f and n: Freundlich constants, if n between 2 and 10 it shows good adsorption. If numerical value of 1/n is fewer than 1 it refers that adsorption capacity is only slightly suppressed at lower equilibrium concentrations.
The Freundlich isotherm is more broadly used on the other hand provides no data on the monolayer adsorption capacity, in compare to the Langmuir model. This model is depend on adsorption on inhomogeneous surface.
It can be prophesied if an adsorption system is favourable or unfavourable by the necessary characteristic of the Langmuir isotherm represented by means of R_L, a dimensionless fixed referred to like separation factor or equilibrium parameter defined by 5:

$$R_L = \frac{1}{1+K_L C_o} \qquad \ldots(5)$$

where Co is the highest initial concentration. This parameter proposes the kind of isotherm to be irreversible ($R_L = 0$), favourable ($0 < R_L < 1$) or unfavourable ($R_L > 1$).

Results and Discussion

1. Characterization of Adsorbents

Scanning electron microscope observations of eggshell powder can be seen in Figure 1. SEM micrograph magnification factor is 1.00 kx which was taken to locate the micron eggshells powder. It can be seen that eggshells particles were agglomerated and have irregular round shape. However, the shape of particles was uniformly distributed. EDS used together with SEM which forms an elemental analysis of adsorbents powder include (Ca,O, Al) elements of different weight% (66.4, 33.2, 0.4) respectively as shown in Figure 2.
The adsorbents surface area was obtained by the (BET), Test Method (ISO-9277-2010). The result show that the surface area decreased with increased partical size for (75, 150) Mm patical sizes the surface area are (5.485±0.2, 4.656±0.37) m^2/g respectively.

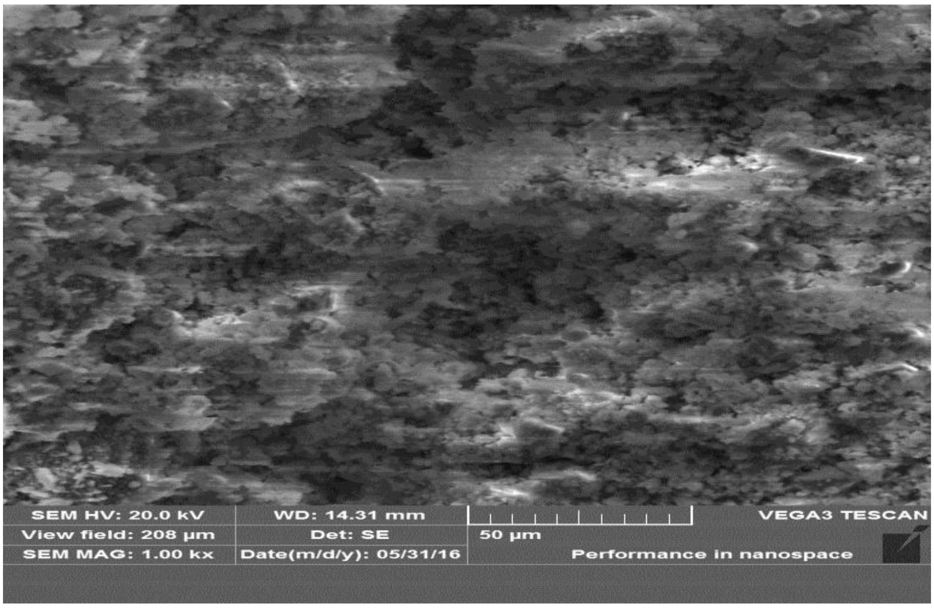

Fig. 1: SEM image of Eggshells powder at a magnification Magnification=1.0000e3

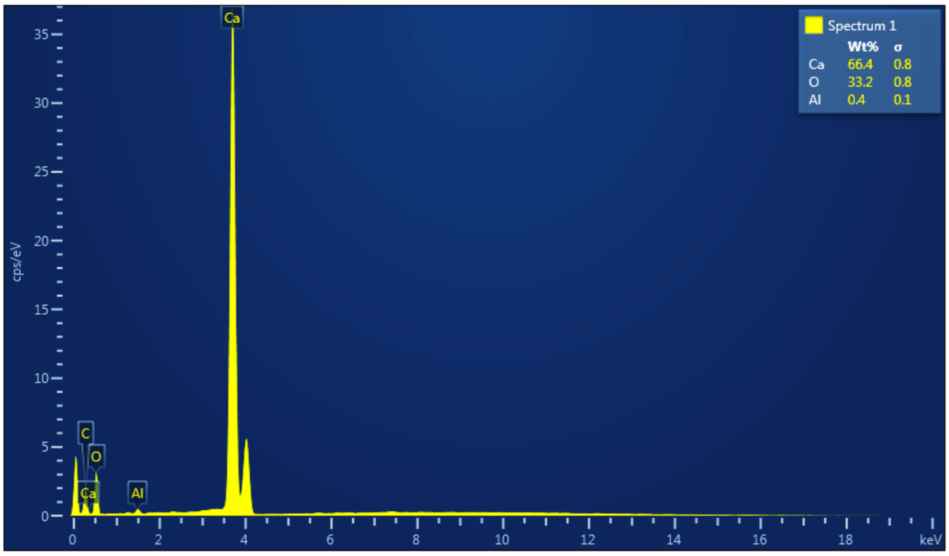

Fig. 2: EDS spectrum of eggshells powder

Figure 3 shown FT-IR analysis to eggshells powder. The peaks at 877, 2871, 2979 and 3070 cm^{-1} are referred to aromatic groups C-H bands. As well, it appears that a prominent absorption peak of carbonate C-C bands was observed at 1429 cm^{-1}, attributed to aromatic group. The peaks at 1078 cm^{-1} is assigned to alcohols,carboxylic acids,esters,ethers groups C-O bands and finely the bandat 3286 cm^{-1} is because of the existence of strong hydrogen-bonding alcohols,phenols groups with surface OH groups interactions between them.

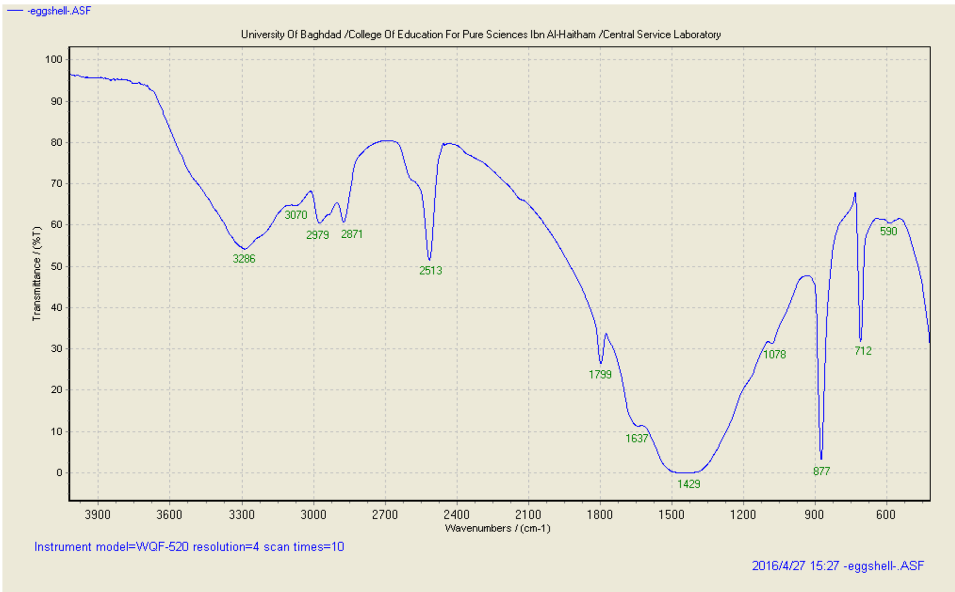

Fig. 3: FTIR analysis for Eggshells powder

2. Adsorption Results

2.1. Effect of pH

As shown in Figure 4. the pH solution effects on the process of adsorption of (MV) dye was obtained, by using eggshell as adsorbent with two particle sizes (75, 150) Mm. These results revealed as pH value increases the percentages of dye removal decreased slightly. Greater percentages of MV removal were noticed (97.7%, 97.3%, 97.1%, 96.7%) for eggshell of 75 Mm particle size and (97.8%, 97.8%, 97.1%, 97.1%, 96.7) for eggshell of

150 Mm particle size respectively, at pH range of (4, 6, 8, 10). These attained results may be ascribed to the surface of adsorbent becomes negatively charged and does not prefer dye adsorption as a result of the electrostatic repulsion [25]. From these results found that maximum removal efficiency occurs at pH = 4 for both particle size.

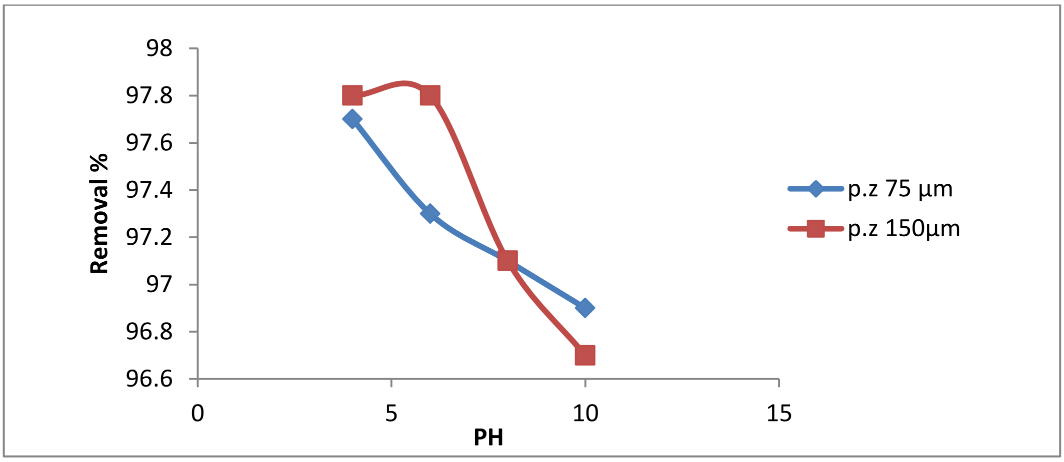

Fig. 4: Effect of PH solution on (MV) removal

2.2. Effect of Initial Dye Concentration

The effects of dye concentration on removal efficiency of (MV) dye by eggshell powder is shown in Figure 5. with pH fixed at 4. The results show that with increasing the initial dye concentration from 20 to 40 mg/L for 75 Mm particle size, the removal efficiency was decreased slightly from 98.4% to 98.3% and then reached equilibrium, further increase in dye concentration have no effect. This slight effect associated with increase dye concentration is attributed to the vacant sites on the eggshell surface in higher dye concentrations become saturation [26], for 150 Mm particle size the removal efficiency was increased from 91.9% to 98.3% as the dye concentration increased 20 to 60 mg/L and then reached equilibrium.

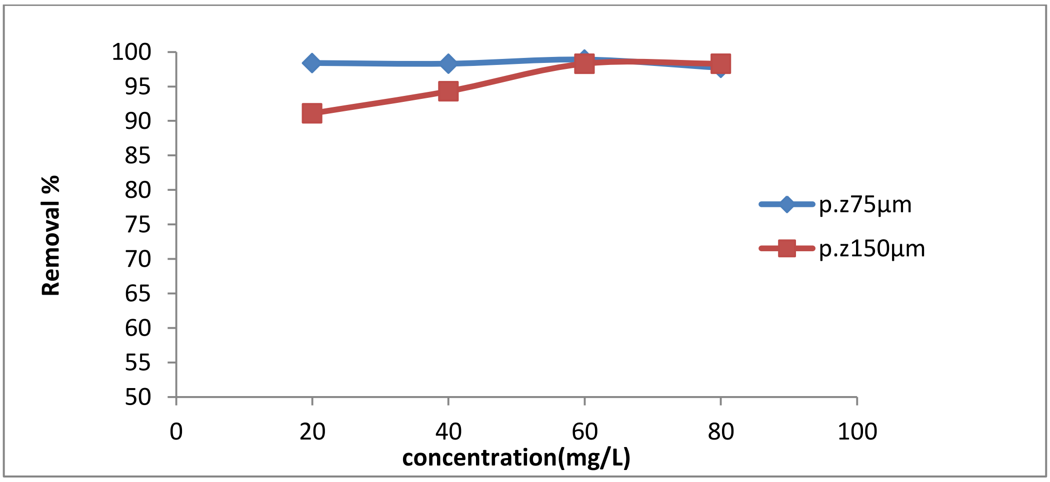

Fig. 5: Effect of concentration on (MV) removal

2.3. Effect Adsorbents Dose

As shown in Figure 6 (MV) dye removal via eggshell powder at different adsorbent weight (0.5-10 g), dye concentrations of 20 mg/L and pH 4. The results show for adsorbent of 75

Mm particle size the increase in dose up to weight of 5 g lead to increase the percentages of dye removal efficiency in the range of (86%, 93.5%, 95.3%, 96.5%, 96.5%, 98.9%) and then reached equilibrium as a result of saturation available active site. For adsorbent of 150 Mm particle size the removal efficiency increase gradually in the range of (78.9%, 85.6%, 92.1%, 93.9%, 95.6, 98.3%) as adsorbent dose increase at 0.5, 1, 3, 5, 7, 10 g respectively, this higher removal of (MV) is due to the increase in adsorbent surface and availability of more adsorption site area of the adsorbent. Therefore the quantity of dye adsorbs increases and therefore leads to a well adsorption [25]. The results show that the best removal occur at 10 g is 98.9% for 75 Mm particle size which will used in the following the experiments.

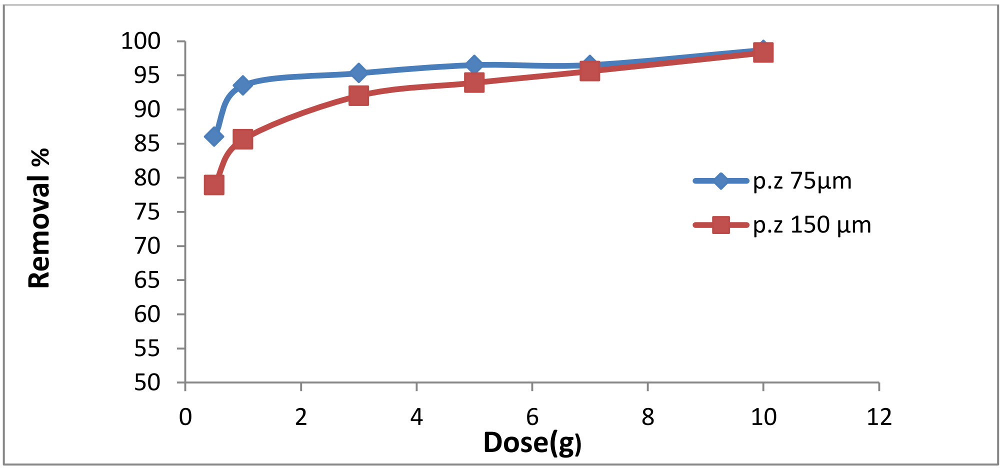

Fig. 6: Effect of dose on (MV) removal

2.4. Effect of Contact Time

As shown in Figure 7 contact time effects onto the removal efficiency of (MV) dye, which is taken in the range of 30-180 min. The results show that the removal percentage was rapid at initial time and reached the best efficiency (97.2%, 96.1%) with first 30 min and then increased slightly for particle size of 75 and 150 Mm respectively. The equilibrium was attained at 120 min for both adsorbent particle size. From thesse results found different eggshells partical size has slit effect on dye removal [25].

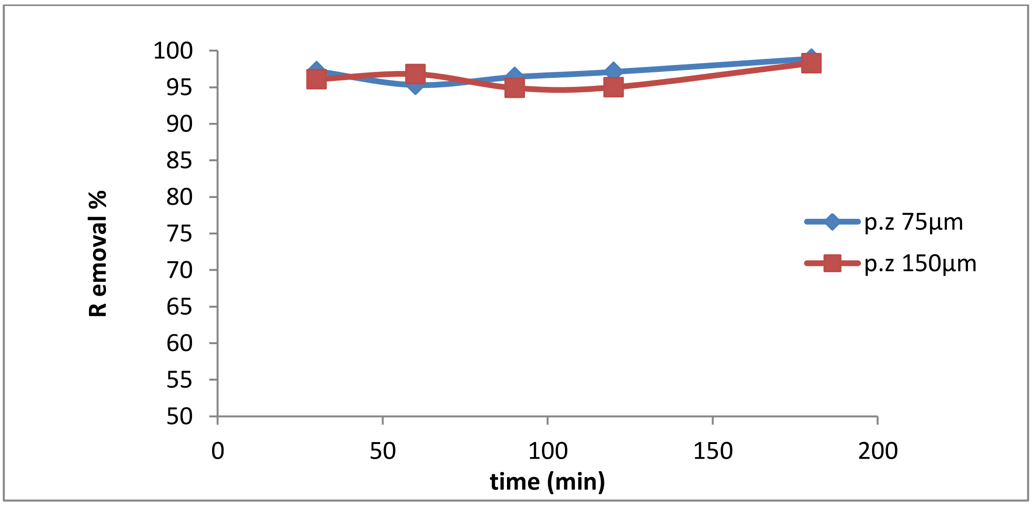

Fig. 7: Effect of contact time on (MV) removal

2.5. Adsorption Isotherm

As shown in Figures 8 and 9 the exemplary schematic representations of the linearized plots for adsorption of methyl violet on eggshell. The results show that the adsorption isotherms experimental equilibrium data (Table 1) were fitted to both the Freundlich and Langmuir isotherm equations and it show good fitting with the highest correlation coefficient values R^2 (0.93, 0.99) respectively for adsorbent with particle size of 75 Mm. For adsorbent with particle size of 150 Mm Langmuir isotherm with R^2 0.86 a better representation of the experimental results than Freundlich isotherm with lower R^2 0.45. As well Langmuir model was found to provide a well fit in the adsorption of MV for both adsorbent particle sizes. This well fit of equilibrium information to the Langmuir isotherm propose monolayer coverage of MV on the eggshell with 75, 150 Mm particle size and the surface of egg shell is known to be homogenous [27]. It can be seen from Table 1, the value of R_L is less 1 in both in both particle sizes which suggests that the adsorption is favourable.

Table 1: Isotherm constants for MV removal by eggshell

	Freundlich isotherm				Langmuir isotherm		
p.z (μm)	K_f	n	R^2	R_L	R^2	K_L	a_L
75	0.69	0.54	0.93	0.032	0.992	0.373	0.405
150	0.95	1.46	0.405	0.0099	0.869	1.24	0.15

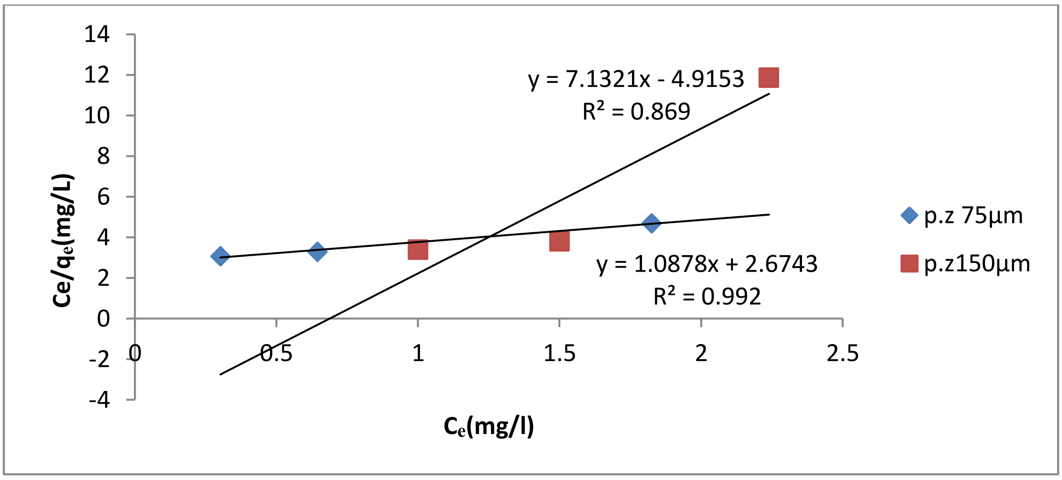

Fig. 8: Langmuir adsorption isotherm model

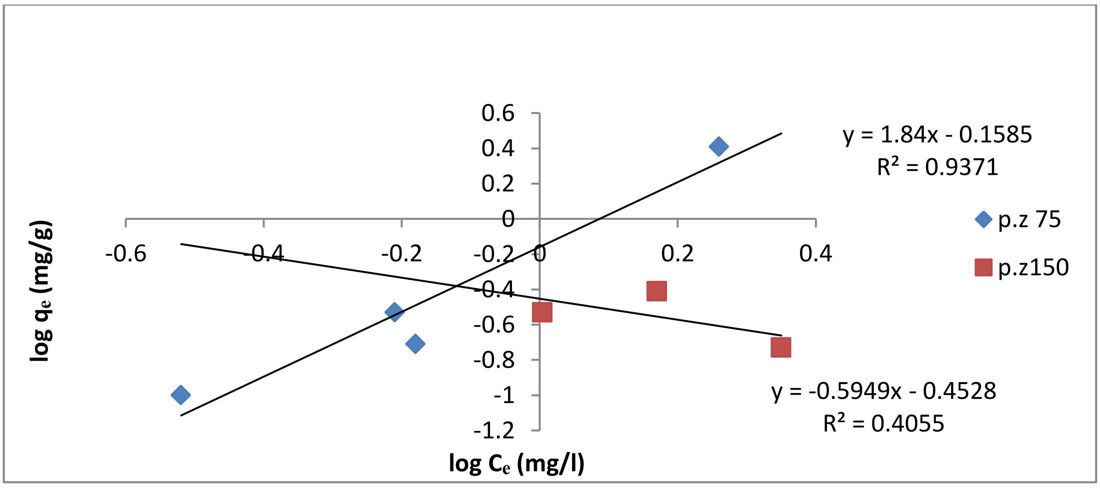

Fig. 9: Freundlich adsorption isotherm model

Conclusions

This study is concentrated on the using eggshells for removal of MV from aqueous solution as a cheap, alternative adsorbent, provide high removal efficiency with short time 30 min and environmental concerns. Furthermore eggshells has superior efficiency to remove the organic dye by adsorption process as a function of many conditions such as (pH, initial dye concentration, adsorbent dosage, contact time and particle size). Process of adsorption basically based on the adsorbent particle size of the, the small particle size the greater surface area, the capacity of adsorption rises. The high percentage of removal for 75 Mm particle size is better than 150 Mm particle size at pH 4, 10 g adsorbent dose, 30 min and 20 mg/L initial dye concentration.

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