

Article

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Design of A New Bead Injection System for Removal Methylene Blue using Nanoparticale Derivative from Selenium(IV) Compound

Alaa Aboudi Obaid and Khdeeja Jabbar Ali

Department of Chemistry, Education for Girls Faculty, Kufa University, Najaf , Iraq

((e mail: alaaa.alzamily@student.uokufa.edu.iq)

Abstract

This research included a study of a new bead injection system design for removing methylene blue dye using selenium nanoparticles at a wavelength of 664 nm. The optimum conditions pH, flow rate, dye volume, and selenium nanoparticle mass were studied and determined. Were 7 ,10 ml/min , 0.157 ml and 0.004 g respectively . The calibration curve was prepared and the linearity range was from (0.5-25) mg/L and the Sandell's sensitivity was = 8.695×10^{-2} . The dispersion coefficient and repeatability were also studied, which were 2.383 , 10 reading respectively , and it was found that the proposed method gave good results with a recovery rate of (99.879 % -100.064%).

Keywords : Bead Injection system , Selenium oxide , Methylene blue , Adsorption , Removal

Introduction

Bead injection technology is a combination of using beads that act as a surface for adsorption of methylene blue dye with a flowing stream of solution in a flow injection system(1,4). Bead injection technology has several advantages, including the accurate measurement of the amount of material on the surface of the beads and the automatic renewal of the beads, thus eliminating the need to replace the device(2,6,7). Bead injection is a method that relies on the size of suspended beads in experiments, which act as a solid phase carrier for reactive groups and chemicals. The beads are characterized by being a carrier of materials that work on adsorption, i.e. removing the dye passing through these beads, the surface of which is covered with a layer of nanoparticles, so that the valve channels are not damaged or blocked by the beads(3). The bead injection system has multiple uses as it can be used to find the concentration of analyte in different sample volumes(5). In this research, the bead injection method was applied using selenium nanoparticles. selenium nanoparticles, they are considered a promising material in many applications because they are characterized by unique properties, including high biological activity, large surface area and low toxicity. Therefore, these particles have received great attention in recent years due to these distinctive properties(8,9,10,13) Selenium nanoparticles are used in many sectors as environmental adsorbents and antitumor agents and thus, they are effective in adsorbing toxins and dyes from aqueous solutions(12). Selenium nanoparticles have the ability to absorb, so on the other hand they work to correct the global degradation of water(11). In this research, selenium nanoparticles were used to remove methylene blue dye. It is a cationic dye, this dye is used in wide applications in paper, textile and leather industries(14). The presence of methylene blue dye in the water stream leads to unusual effects on life(15). Methylene blue dye has a strong affinity for water at normal temperatures (16). It is difficult to remove this dye by simple treatment methods due to the difficulty of its decomposition (17,18). Therefore, removing methylene blue dye from wastewater is important in order to prevent its toxic effects on the environment and

human health (19). Therefore, applying the adsorption process using the bead injection technique is an effective solution to get rid of this dye. Therefore, silicon balls were used with a surface covered with a layer of selenium nanoparticles that were formed within a specific template. The proposed method had good results and gave a high removal rate of methylene blue dye from aqueous solutions.

EXPERIMENTAL

APPARATUS

Absorbance values were measured using the UV-Visible (OPTIMA SP300) spectrophotometer, pH measured using the Oakton 2100 Series pH/mV/Ion/OC/OF Meter. All samples were weighed using an Ohaus PA214 Pioneer Analytical Balance. The maximum wavelength was selected by using Shimadzu UV-1700 spectrophotometer Centrifuged, Magnetic stirrer hot plate. Oven, Peristaltic pump Germany, Flow-through cell 10 mm. Field emission scanning electron microscope (FE-SEM), Energy dispersion X-ray (EDX) and Infrared spectroscopy IR.

Materials

Ascorbic acid (99.99%) purity (chemical formula $C_6H_8O_6$ and molecular weight =176.12 g/mol), sodium selenite pentahydrate ($\geq 98\%$)purity (chemical formula $Na_2SeO_3 \cdot 5H_2O$ and molecular weight =263.014) Selenium dioxide(chemical formula SeO_2 and molecular weight =110.96 g/mol). Methylene blue MB dye (Chemical formula $C_{16}H_{18}N_3S$ and molecular weight =(319.85) g/mol), Tx-100(poly(ethylene glycol)) , deionized water.

Stock Solutions

Ascorbic acid(A.A) solution 0.1 mol/L

Prepared from dissolving 8.8100 g of A.A in 500mL in deionized water in suitable volumetric bottle.

Selenium dioxide solution 5×10^{-3} mol/L

The Selenium dioxide SeO_2 stock solution was prepared by dissolving 0.5548 g of SeO_2 in 1000 ml of deionized water in suitable volumetric flask.

Sodium Selenite Pentahydrate solution 5×10^{-3} mol/L

Prepared from dissolving 1.3151g of $\text{Na}_2\text{SeO}_3 \cdot 5\text{H}_2\text{O}$ in 1000mL in deionized water in suitable volumetric flask.

Methylene Blue Dye solution 1000 mg/L

A stock solution was prepared by dissolving 1.0000 g of M.B dye 1000mL of distilled water, and working solutions were obtained by further dilution.

Triton X-100 Solution

The Triton X-100 solution prepared by dissolved 5 ml of Triton X-100in 100 ml distilled water.

Preparation Selenium nanoparticale

Selenium nanoparticles were prepared by adding (300 ml) of 0.1 mol/L ascorbic acid (vitamin C) drop wise to (600 ml) of sodium selenite solution $\text{Na}_2\text{SeO}_3 \cdot 5\text{H}_2\text{O}$ (5 mmol/L), at room temperature and stirred for 24 h to form SeNPs. In this experiment, ascorbic acid was used (as a reducing agent). After adding the acid, the color of the mixture changed directly from colorless to yellowish orange, and within 24 h the color changed from reddish orange to brick red. Then, a centrifuge was used for 15 min at 8000 rpm, and deionized water was used to remove the residues, and then the particles were then dried overnight in a vacuum as show the figure(1) (20).

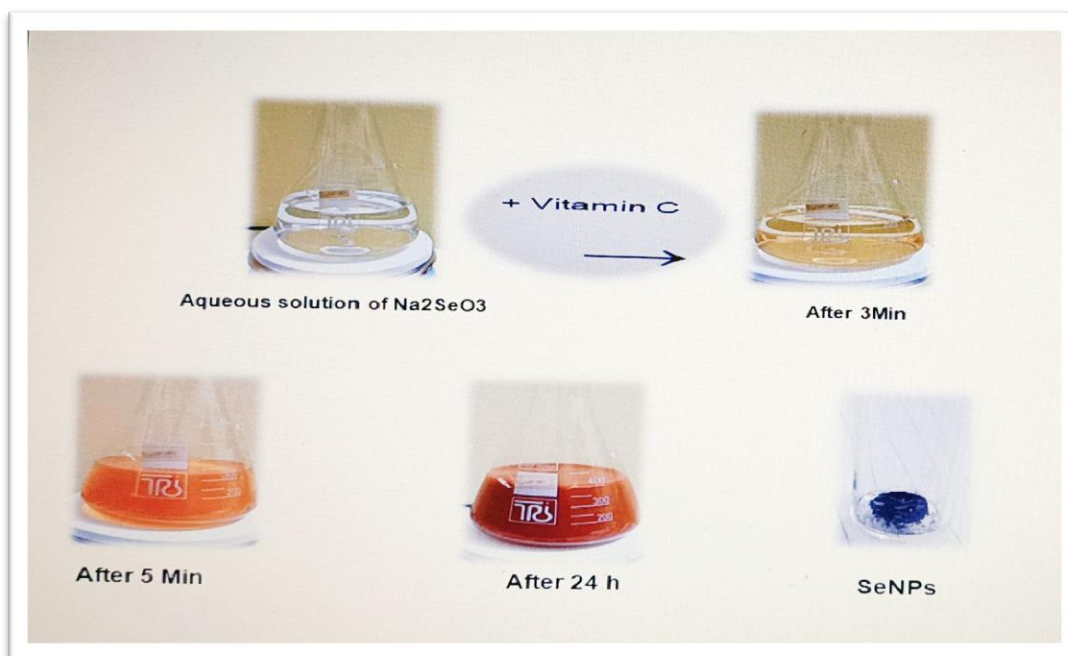


Figure (1) show preparation selenium nanoparticale

New Modified of Selenium nanoparticle

To synthesize Nano-selenium, 300 mL of vitamin C (Ascorbic acid 0.1 mol/L) was added drop wise into the 600 mL of SeO_2 (5 mmol/L). With the same steps above, the nanoparticles were prepared and the results were identical between the two synthesize methods.

λ max Determining of MB dye in different media

The wavelength of methylene blue dye was measured at different media using a device Shimadzu UV-1700 spectrophotometer where the maximum absorbance of methylene blue at 664nm. As shown in the figure (2).

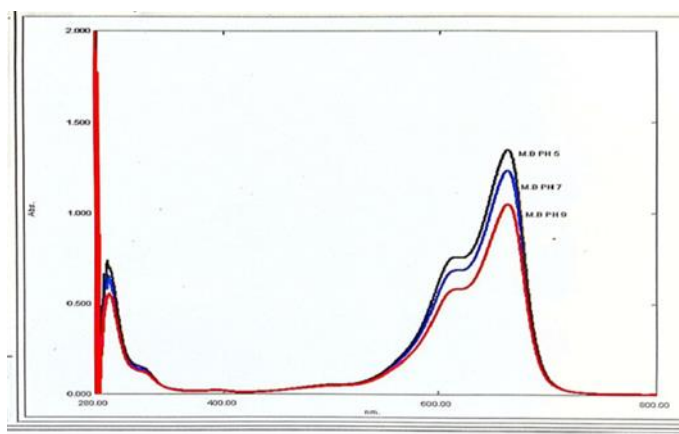


Figure (2) Determine the wavelength of maximum absorption of a dye(M.B) in different media.

Adsorption Batch Studies

The optimal methylene blue dye adsorption performance was achieved by adjusting the selenium nanoparticle dosage, contact time, and methylene blue dye concentrations. After combining a weighed sample of selenium nanoparticles with 1 mL of methylene blue dye solution, Equation (1) was used to calculate the dye removal percentage (%R)

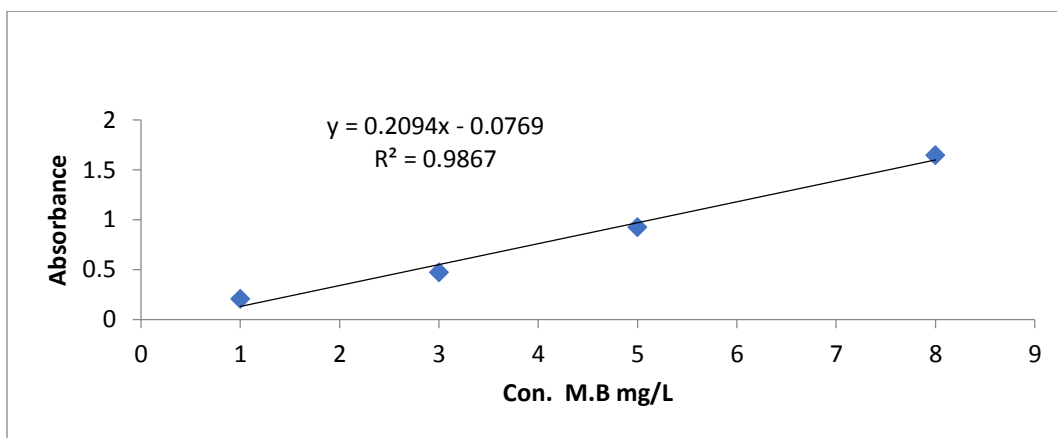
$$\%R = \frac{C_1 - C_2}{C_1} \dots\dots(1)$$

where C_1 , C_2 , refers the MB dye concentration in the initial and at the equilibrium (measured in mg/L).(21,22)

Results and Discussion

Calibration Curve of M.B before adsorption

The calibration curve for MB dye at wavelength 664nm was prepared before the adsorption process by preparing and measuring the absorbance for a series of concentrations(1-8) mg/L as shown in Figure(3).



Figure(3)Calibration curve of M.B dye before the adsorption process

Characterizing Selenium Nano particle

FTIR Spectroscopy

FT-IR analysis was performed on selenium nanoparticles prepared by two methods, and the results were identical. A peak for the hydroxide group(OH) was shown for the two methods prepared from sodium selenite and selenium oxide, respectively were (3429.43 , 3454.51) cm⁻¹. The A group C=O appeared in (1735.93 , 1766.80)cm⁻¹, and the peak indicates the bond between selenium and oxygen in(468.70 , 472.56)cm⁻¹ (23), as shown in Figures (4, 5).

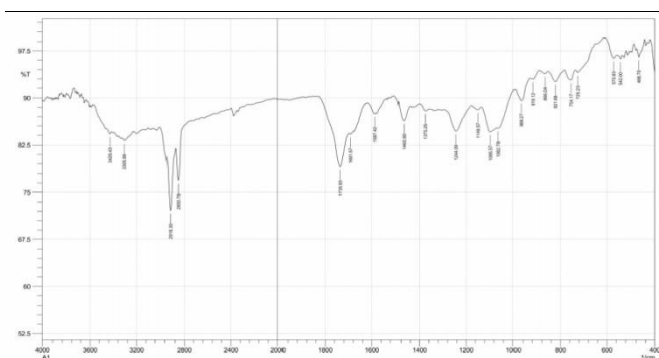


Figure (4)FTIR of SeNPs prepared from Na₂SeO₃

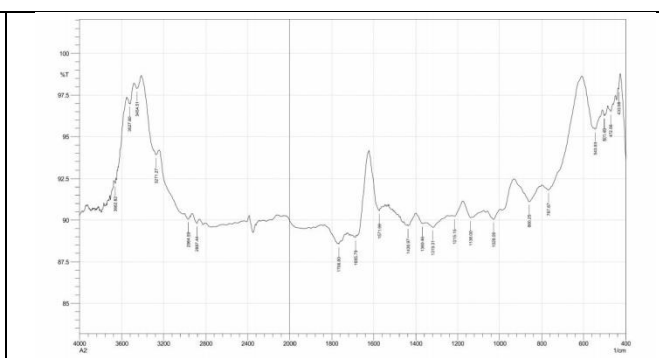
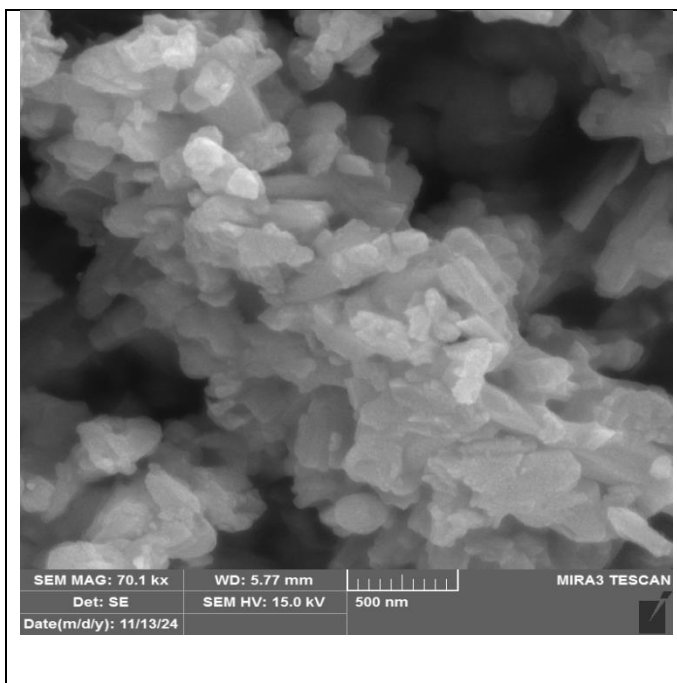
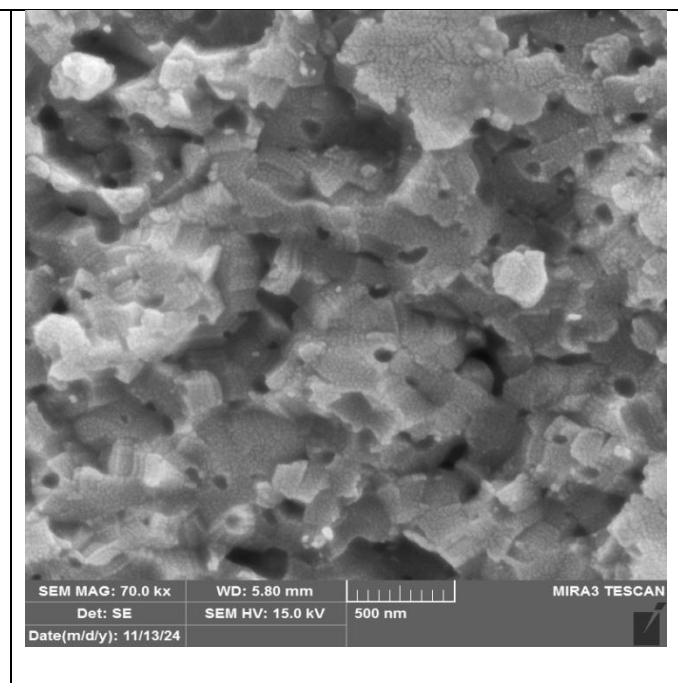


Figure (5)FTIR of SeNPs prepared from SeO₂

Field Emission Scanning Electron Microscopy (FE-SEM)

To study the properties of the outer surface of Selenium nano particles , the field emission scanning electron microscope technique was used , as show in the two figure (5,6) , the analysis is confirmed to be compound of nanoparticales.

	
Figure (6)FE-SEM of SeNPs prepared from Na ₂ SeO ₃	Figure (7)FE-SEM of SeNPs prepared from SeO ₂

Energy dispersion X-ray (EDX)

EDX analysis can be used for determine the elements present in the sample .Figure (7)show EDX analysis of SeNPs preparation by Na₂SeO₃.5H₂O the samples includes only selenium , carbon and oxygen .And the figure (8) show EDX of SeNPs preparation by SeO₂.

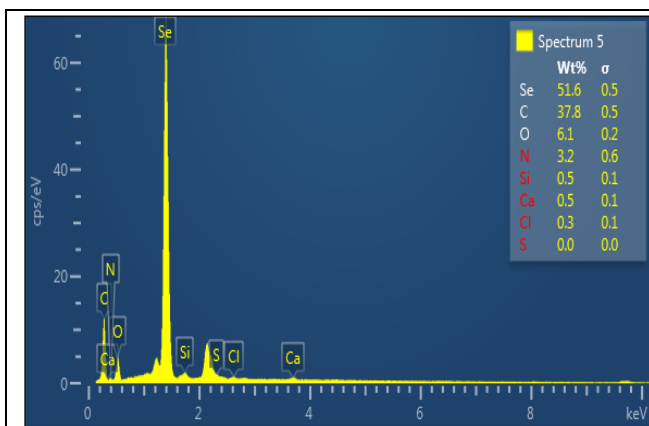


Figure (7)EDX of SeNPs prepared from Na₂SeO₃

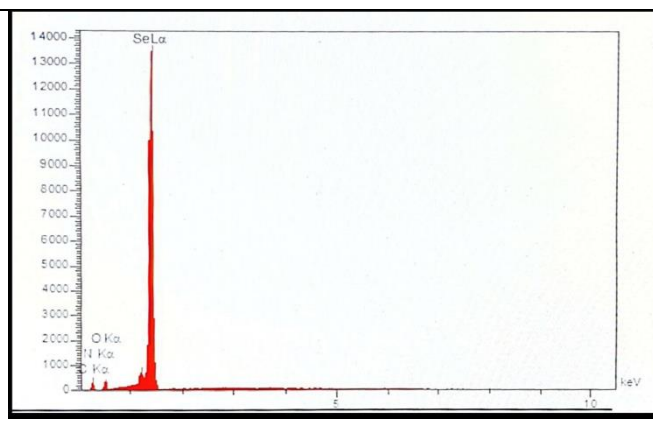
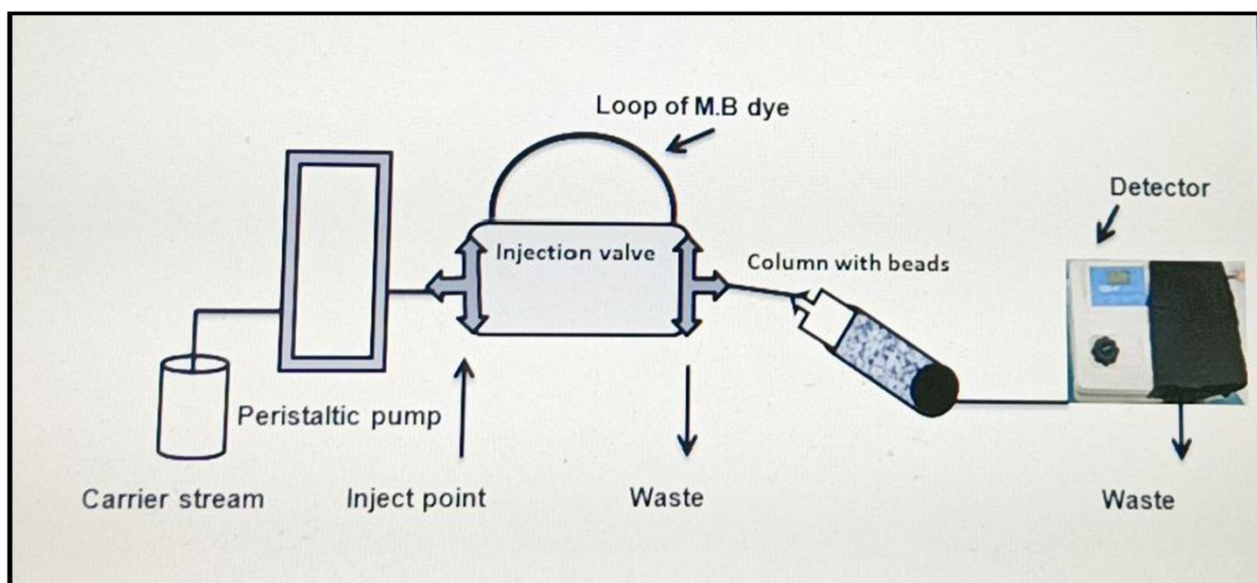


Figure (8)EDX of SeNPs prepared from SeO₂

The best design

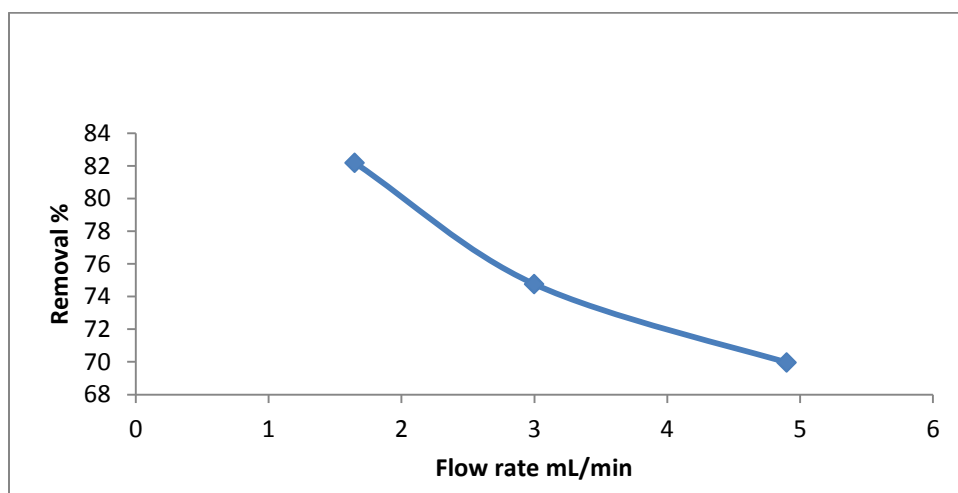
Several designs were studied for the success of the injection system, based on studying these designs by spectroscopic method and verifying the percentage of M.B dye removal. The proposed design includes injecting the dye into the loop and filling the column with silicon balls made within a specific mold whose surface is covered with a layer of nano-selenium as show the figure(9). This design was chosen because it gave better and more accurate results for removing the M.B dye .



Figure(9) The beads injection system

Effect flow rate on the removal M.B dye

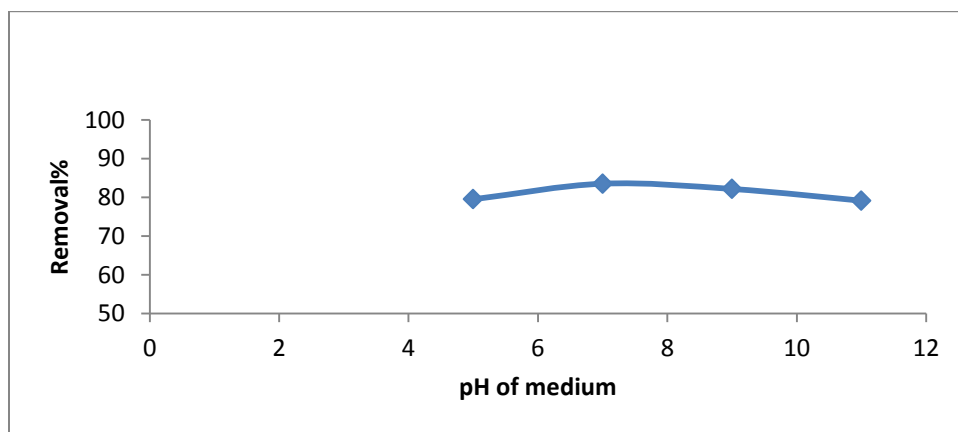
The effect of the flow rate, which is considered one of the important changes that affect the removal rate of M.B dye, was studied. Different flow rates from (1.65-4.90 ml/min) were studied at M.B concentration = 20 mg/L , The Selenium nano particle mass = 0.004 g ,dye Volume = 157 μ l (20 cm) , Reaction coil length = 3 cm and the pH= 9. The results showed that the removal rate was the highest at a flow rate of 1.65 ml/min because it gave enough time for adsorption and removal of the dye As in the figure(10).



Figure(11) The Influence of flow rate on the removal percentage

Effect pH value on the removal M.B dye

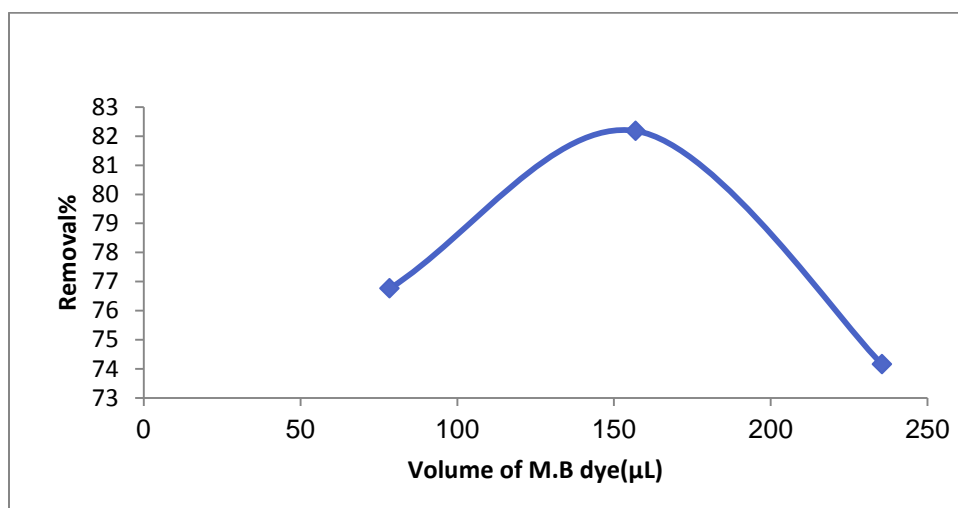
The effect of the acidity function on the removal rate of M.B dye was studied after choosing the appropriate flow rate, where the acidity function was studied from (5-9) as shown in the figure(11). The optimum acidity function for removing M.B dye was = 7. In this test, M.B concentration = 20 mg/L , The Selenium nano particle mass = 0.004 g , dye volume = 157 μ l (20 cm) , Reaction coil length = 3 cm and flow rate =1.65 ml/min.



Figure(11) The Influence of pH value on the removal M.B dye

The effect the M.B dye volume

Effect of M.B dye volume on the removal rate was studied by injecting different volumes (78.50-235.50) μL at, M.B concentration = 20 mg/L , The Selenium nano particle mass = 0.004 g, Reaction coil length = 3 cm, flow rate=1.65ml/min, and pH= 7 . The volume of 157.00 μL (20cm of loop) was chosen because it gave the highest dye removal rate as shown in the figure(12).

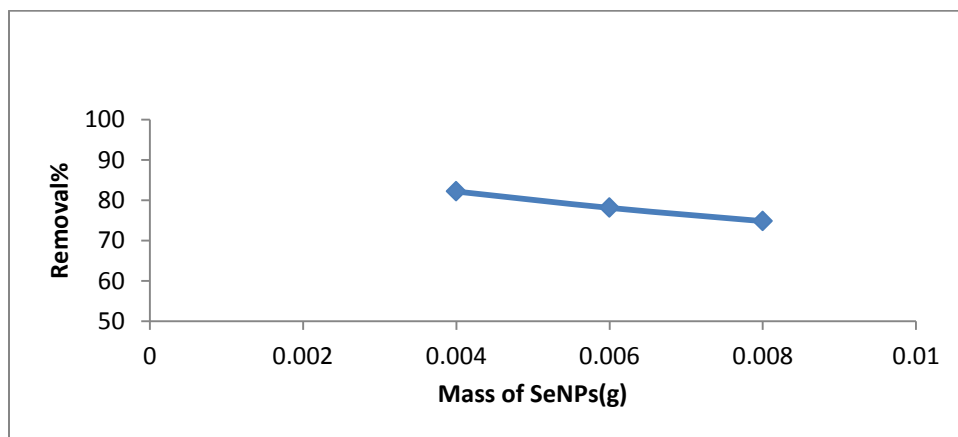


Figure(12) The Influence of M.B dye volume(μL) on the removal percentage

Effect mass of Selenium nanoparticle on the removal M.B dye

The effect of changing the mass of selenium nanoparticles on the removal rate of M.B dye was studied. The mass was studied from (0.004-0.008)g and the mass of nano

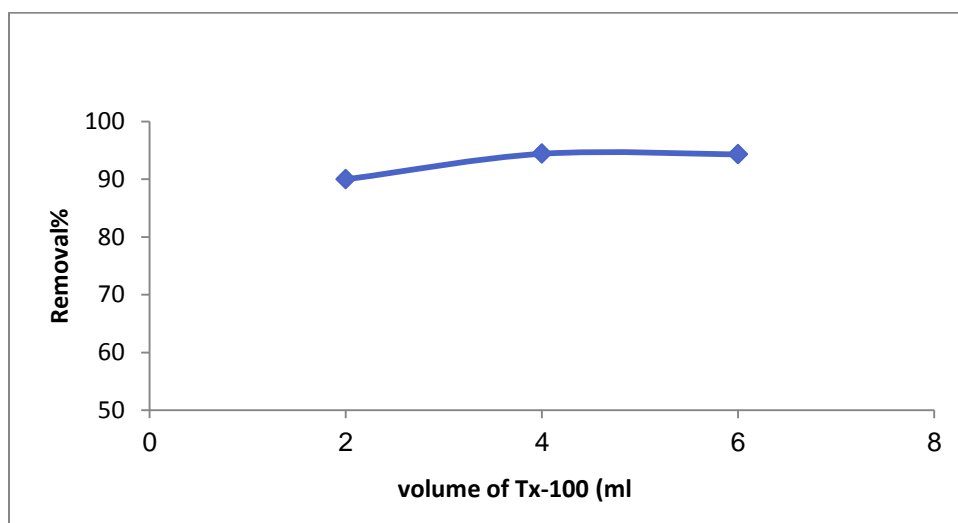
Selenium was chosen as 0.004 g because it gave the highest removal rate of the dye at M.B concentration = 20 mg/L , dye volume = 157 μ l (20 cm),flow rate=1.65 ml/min , Reaction coil length = 3 cm, and PH =7 as show figure (13).



Figure(13) The Influence of mass of SeNPs (g) on the removal percentage

Higher removal percentage of M.B dye by using Tx-100(poly(ethylene glycol) as surface modifier SeNPs

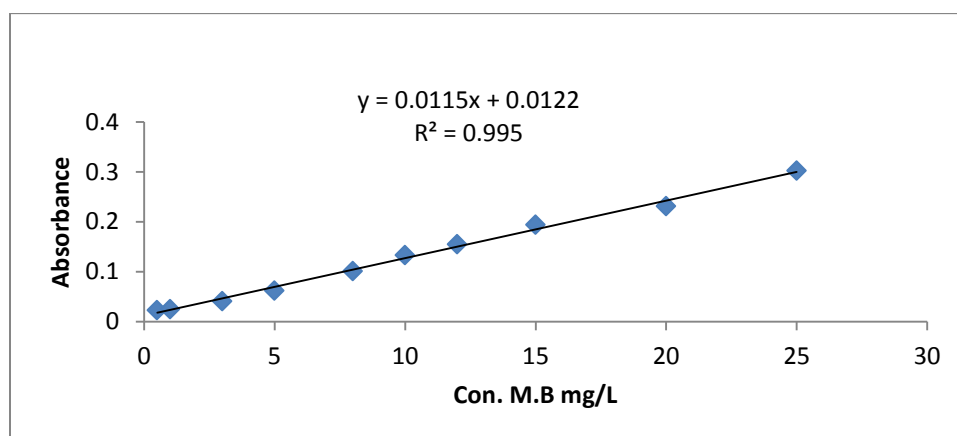
The surface modification of Selenium nanoparticles with Tx-100 was studied to increase their ability to absorb M.B dye from aqueous solutions. The removal rate was higher compared to unmodified Selenium nanoparticles, which suffer from particle agglomeration, which reduces the dye absorption capacity, different volumes were studied of Tx-100 from(2-6)ml as shown in Figure (14)



Figure(14) The Influence of Tx-100 (ml) volume on removal percentage

Calibration curve of methylene blue dye

The calibration curve was prepared at the optimum conditions for M.B dye (Figure 15) show The calibration curve is linear in the range (0.5-25) mg/L, the correlation coefficient value $R^2 = 0.995$ and the Sandell's sensitivity Calculated and was = $8.695 \times 10^{-2} \mu\text{g} \cdot \text{cm}^{-2}$



Figure(15) The calibration curve of M.B dye (mg/L)

Repeatability

The experiment was repeated ten times to measure the accuracy of the bead injection unit for M.B dye at a concentration of 20 mg/L, dye volume = 157 μl (20 cm), flow rate=1.65 ml/min , Reaction coil length = 3 cm, and PH =7 and the SeNPs mass =0.004 g . As shown in the figure(16)., the results were identical, indicating the accuracy of the study of the bead injection system for dye removal using Selenium nanoparticles.

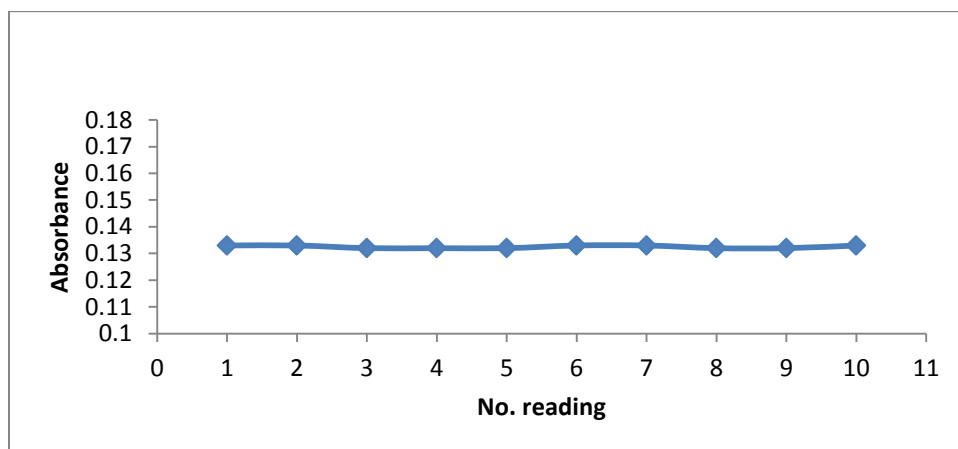


Figure (16) the Repeatability of M.B dye

Dispersion coefficient

The dispersion coefficient (D) has been widely studied as an empirical parameter to determine the degree of dilution from the injection point to the dye. The results in Table (1), show that the type of dispersion in this study is limited dispersion(21,22). The value of dispersion (D) from this experiment can be calculated from this equation(1)

$$D = \frac{A^\circ}{A_{max}}$$

A° Absorption without dilution (outside BI system)

A_{max} Absorption with dilution (inside BI system)

Table(1)The Dispersion coefficient of BI system

Conc. M.B dye mg/L	Response		Dispersion $D = A^\circ / A_{max}$
	A°	A_{max}	
10			2.383
	0.317	0.133	

Application

Samples were prepared by stabilizing the acid function of the (tap water and beach water) at PH = 7, and the dye was added and the removal is applied using the selenium nanoparticles in the bead injection system as shown in the Table 2.

Table 2: Recovery value of a new BI system

Sample	Taken value mg/L	Found value mg/L	R.E%	Recovery%
Tap water	5	5.322	0.064	100.064
Tap water	10	10.15	0.015	100.015
Tap water	15	14.613	-0.025	99.975
Tap water	20	18.441	-0.077	99.922
Beach water	10	8.796	-0.120	99.879
Beach water	20	19.22	-0.039	99.961

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