



Gold nanoparticles encapsulated alginate microspheres as an adsorbent for the separation of the dye safranin orange from the aqueous solutions through batch method

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Abstract

Gold nanoparticles encapsulated alginate microspheres were synthesized and evaluated as a nanoadsorbent for removing Safranin Orange from aqueous solutions. Gold nanoparticles were prepared and characterized by X-Ray Diffraction (XRD), Transmission Electron Microscopy (TEM) and FT-IR. The adsorption of Safranin Orange was examined by batch technique. The effects of pH, initial Safranin Orange concentration, adsorbent dosage and contact time on the efficiency of Safranin Orange removal were studied for the batch method. The equilibrium data analyzed by using Langmuir and Freundlich isotherm models showed better agreement with the latter model. Kinetic studies were conducted and the resulting data were analyzed using first- and second-order equations; pseudo-second-order kinetic equation was found to provide the best correlation. Repeated adsorption and desorption cycles were performed to examine the stability and reusability of the nanoadsorbent. The result of this study proved high stability and reusability of Gold nanoparticles encapsulated alginate microspheres as an adsorbent for Safranin Orange dye.

Keywords: Microspheres, Nanoparticles, Adsorption, Isotherm models, Desorption.

Introduction

The random increase in the human needs lead to the overexploitation of the nature and hence, its damage. The scientific fraternity has to prioritise and rectify the destruction caused till date so that life gets secured. In this respect, one of the major contributions of the pollutants constitutes the dyes; that has been widely used in industries, such as textile, paper, printing, cosmetics, plastics and rubber^{1,2}. Generally they have a synthetic origin and are based on complex aromatic structures; which render them stable and hard to be biodegraded¹. Even a meagre amount of dye can color large water bodies affecting not only the aesthetic merit but also hampers light penetration and photosynthesis, thereby affecting aquatic flora and fauna. Besides, numerous dyes are toxic in nature with suspected carcinogenic and mutagenic effects that hamper aquatic biota and also human beings^{3,4}. Out of the various dyes, basic dyes are amongst the brightest class of soluble dyes which is generally used by the textile industry, as their tinctorial value is very high. Safranin(O) is a basic dye which is widely used in textile, trace, biological laboratory purpose. These biological stains are analysed to be toxic to human and animals. Contamination of Safranin-O in water can cause allergic dermatitis, skin irritation, cancer and mutation in human beings⁵.

According to the Color Index (C.I.), which is managed by the Society of Dyers and Colorists and the American Association of

Textile Chemists and Colorists, currently almost more than 10,000 various types of dyes are synthesized in the world. Though no latest data is available on worldwide dye production, annual production of over 700,000 tonnes has been often reported in the literature⁶⁻⁸. Dyes are the organic compounds consisting of two main groups of compounds, chromophores (primarily responsible for the color of the dye) and auxochromes (responsible for the color intensity)⁹. The degradation of the dye has been attributed to both photosensitized oxidation and reduction mechanisms¹⁰.

Hence, the decolorization and remediation of dye-containing effluents is considered compulsory prior to discharge into the water bodies according to the environmental regulations in most of the countries^{11,12}. Various processes have been reported by various investigations for the removal of dyes from water and wastewater exhibited by biological processes, combined chemical and biochemical processes, chemical oxidation, adsorption, coagulation, and membrane treatments; each possessing its own specific advantages and disadvantages. Out of these several conventional chemical and physical methods, the adsorption process is one of the effective techniques that have been successfully employed for dye removal from wastewater. Adsorption is a classical technique which involves a variety of highly porous adsorbents having adequate surface area for adsorption process¹³. Based upon this, many porous adsorbent materials have been tested for the possibility of dye removal such as activated carbon¹⁴, peat, chitin, and silica¹⁵.

But, intraparticle diffusion involved with porous adsorbents may reduce the adsorption rate and capacity¹⁶. Therefore, it is a requisition to develop alternative novel adsorbents with both large surface area and small diffusion resistance properties. Current advances in nanotechnology provide a class of promising adsorbents that are ultrafine and characterized by their large surface area⁵.

Nanoparticles have added advantage of treating water in depths and any location which is generally uncarved out by other conventional technologies¹⁷. Since gold nanoparticles absorb light in the visible region, their interference with these assays should be considered. Gold nanoparticles can adsorb molecules (such as indicator dyes) from the surrounding media and thus quench their fluorescence¹⁸.

Nanosized metal nanoparticles have received considerable attention due to the simple procedure involved in its synthesis. A wide number of methods have been used to prepare nanoparticles like Gas Phase Elaboration method, Matrix metal-vapour co-deposition method, Reverse Micellar Techniques and sol-gel processes¹⁹⁻²¹. In comparison to the various stated preparation techniques, sol-gel technique represents one of the rapid growing fields of contemporary chemistry and this preparation technique was utilized for synthesis of Au nanoparticles. This is due to the fact that this preparation technique offers several advantages such as being easy, fast, and able to deform materials into complex geometries in a gel state with high purity²². Since these are difficult to be handled in the adsorption techniques due to its small size and hydrophobic nature, it was suggested to get them incorporated with organic polymers and immobilise it. In this way, several investigators have introduced organic-inorganic hybrid blocks consisting of inorganic sorbent materials and organic binding matrices^{23,24}. So, the major thrust was to select a suitable support polymeric material for the immobilization of the synthesized Au nanoparticles. Several polymer compounds have been employed as immobilized matrix such as alginate, agar, polyacrylamide, chitosan, carrageenan, cellulose acetate, and polyvinyl alcohol²⁵. Alginate is a polysaccharide biopolymer constituted of anionic blocks of (1→4) linked -l-gluronic acid (G) and -d-mannuronic acid (M). Alginate (alginate salts) shows high affinity to metal ions.

Materials and methods

Materials: Tetrachloro auric acid, Safranin Orange, Sodium Alginate, Trisodium Citrate and Calcium Chloride of A.R. grade were purchased from Molychem, Mumbai, India. Double distilled water was used throughout the experiment.

Preparation of Adsorbent: Beads of Sodium Alginate is prepared by dissolving it in required amount of double distilled water. It is left overnight for deaeration. The uniform sized beads are prepared by adding the solution dropwise in Calcium Chloride solution with the help of a syringe. The beads so

prepared get crosslinked with calcium ions. Such beads are mixed with tetrachloro auric acid and trisodium citrate dihydrate to produce in-situ gold nanoparticles. Gold nanoparticles formation is based on the well documented Turkevitch process i.e. by adding tetrachloro auric acid or gold chloride trihydrate with trisodium citrate dihydrate. The colour transition from colourless to dark red beads during brisk boiling in magnetic stirrer indicates the formation of gold nanoparticles. It is washed several times thoroughly with double distilled water and stored for further experiment (Figure-1(a) and 1(b)).



(A)



(B)

Figure-1: A photograph showing the swollen (A) Alginate and (B) Gold encapsulated Alginate polymeric beads.

Preparation of stock solution: 0.1 g. of Safranin Orange (AR) was dissolved in 100 ml. distilled water to prepare the stock solution of Safranin Orange (1000 mg dm^{-3}). Further dilutions of the stock solution with deionized distilled water were made to prepare suitable concentrations of working solutions.

Other solutions prepared are: 0.001 M HAuCl_4 solution, 1% Trisodium Citrate solution, 0.5 M Calcium Chloride solution).

Adsorption experiments: Batch method was adopted for the adsorption experiment. The contact time, pH and initial metal ion concentration parameters were studied for the above

method. The swollen biopolymeric beads (0.1 g) contained in the conical flask with 10 ml solution of Safranin Orange (10 mg dm⁻³ concentration) at constant pH 5 and room temperature (25°C) was rapidly stirred using mechanical shaker for 3 hrs. The amount of Safranin Orange present in the solution was assayed spectrophotometrically using VISISCAN 167. The amount of adsorbed Safranin Orange was calculated by the following mass balance equation (1).

$$\text{Adsorbed amount (mg/g)} = \frac{(C_i - C_f)V}{M} \quad (1)$$

Where: C_i and C_f being the initial and final concentrations of Safranin Orange solution (mg ml⁻¹), V being the volume of adsorbate solution and m is the weight of swollen beads.

Factors affecting adsorption: Effect of concentration: No sooner than the concentration of Safranin Orange was elevated in the domain 5.0 to 20.0 mg dm⁻³, the amount of adsorbed Safranin Orange was also seen to get elevated. It can be well elucidated that such an increase is due to the greater number of the solute approaching the adsorbent interface and getting adsorbed. This phenomenon has been largely cited in the literature²⁶. The highest adsorption of Safranin Orange by the adsorbent was found at 10.0 mg dm⁻³ initial Safranin Orange concentration. The adsorption was further found to decrease at higher concentrations probably due to the ultimate saturation of binding sites.

Effect of pH: The effect of pH has been observed by varying the pH of suspension in the range 2.0 to 9.0, using 0.1 M HCl and 0.1M NaOH solution. The results clearly point out that the optimum adsorption is noticed at pH 5.0 while the adsorption of Safranin Orange shows a decrease on both sides of the optimum pH.

Effect of Time: When the shaking time was increased in the range from 5 min to 180 min, the adsorbed amount is seen to increase. This can be explained on the basis that as the shaking time of solute gets increased, more solute particles tend to arrive at the adsorbent interface. The highest uptake of the dye by the adsorbent was found at 30 min., which was found to decrease at larger time span, might be due to the consecutive saturation of binding sites.

Desorption experiments: Desorption studies of Safranin Orange were performed by batch method under similar conditions. In order to desorb the Safranin Orange, the beads loaded with Safranin Orange were exposed to 10 ml of 0.1 M HNO₃ for 15 minutes, centrifuged and washed with double distilled water. The beads were then again exposed to HNO₃ to strip off any remaining Safranin Orange and then used again for further experiments. The desorbed beads were verified by the above adsorption process.

Adsorption isotherms: The data analysis for the adsorption for various ranges of adsorbate pH, contact time, concentration and

adsorbent dosage was performed using the classical Langmuir and Freundlich isotherms.

Langmuir isotherm: A saturated monolayer of adsorbate molecules on the adsorbent surface forms the basis of maximum adsorption of the Langmuir isotherm model. Langmuir isotherms were evaluated by batch method. An initial adsorbent dosage (0.1 g) at a constant pH 5, time (30 minutes) and 25°C temperature was studied by varying the adsorbate concentration of Safranin Orange. The Langmuir isotherm represents the equilibrium condition of Safranin Orange between solute (solid) and solution (liquid) phase. The Langmuir adsorption isotherm is given by equation (2).

$$\frac{C_e}{a} = \frac{1}{a_s} K + \frac{C_e}{a_s} \quad (2)$$

Where: 'a' is the adsorbed amount of Safranin Orange (mg g⁻¹) at equilibrium concentration C_e, a_s (mg dm⁻³) is the adsorption capacity and K is the adsorption coefficient.

Freundlich isotherm: The Freundlich isotherm has the following equation (3)

$$a = K_f C_e^{1/n} \quad (3)$$

Where: 'a' is the adsorbed amount of Safranin Orange, C_e represents the equilibrium concentration; K_f and n are Freundlich constants.

The linearised form of Freundlich adsorption isotherm was used to evaluate the sorption data, represented as in equation (4)

$$\log a = \log K_f + (1/n) \log C_e \quad (4)$$

The values of K_f and n were calculated from the slope and intercept of the Freundlich plots by plotting log C_e vs. log a.

Modified Freundlich: The presence of multiple functional groups in the biopolymeric beads might have caused the adsorption process heterogeneous, i.e. not mono energetic. Hence, the following modified Freundlich equation may be applied as in equation (5)

$$\log (as/a) = \beta \log C_e + \log (A/as) \quad (5)$$

Where: β and A are empirical constants.

Adsorption kinetics: The progress of adsorption process was monitored at various time intervals (5 - 180 minutes). A constant value of the adsorbed amount of the dye was acquired after 30 minutes. The adsorption and desorption equilibrium is reached with time. The kinetic model suggested by Bajpai et.al.²⁷ may be assumed to explain the dynamic nature of the process as in equation (6).

$$\frac{1}{c} = k_1 \frac{t}{c_0} + \frac{1}{c_0} \quad (6)$$

Where: C and C_0 represents the concentration of adsorbate solution at any time t and the initial concentration of adsorbate solution and k_1 is the rate constant for adsorption. By plotting $1/C$ vs. t , the value of k_1 was calculated.

Pseudo first order: Pseudo first order equation as given by Lagergreen for studying the kinetics of sorption of the dye is as follows (7)

$$\frac{da}{dt} = K_{ad} (a_s - a) \quad (7)$$

Where: a_s and a represent the adsorption capacity at equilibrium and at time t respectively, K_{ad} is Lagergreen rate constant. On applying boundary conditions, the integrated form of equation becomes as follows (8)

$$\log (a_s - a) = \log a_s - \frac{K_{ad}}{2.303} t \quad (8)$$

The value of K_{ad} can be calculated when the value of $\log (a_s - a)$ is linearly correlated with t and a plot of $\log (a_s - a)$ against t gives a straight line.

Pseudo second order: The Pseudo second order adsorption kinetics rate equation is expressed as in equation (9)

$$\frac{da_t}{dt} = K_2 (a_s - a_t)^2 \quad (9)$$

Where: K_2 is the rate constant of Pseudo second order adsorption. The boundary condition $t = 0$ to $t = t$ and $a_t = 0$ to $a_t = a_t$, the integrated form may be written as equation (10)

$$(1/a_s - at) = 1/a_s + Kt \quad (10)$$

This gives the integrated rate law for Pseudo second order kinetics reaction.

Characterization of microspheres: TEM Analysis: The particles size was determined using the TEM image. Transmission electron microscopy (TEM) was performed by using a TECNAI-G20 transmission electron microscope having an acceleration voltage of 200 KV. The sample was prepared by dispersing a drop of the sample solution onto glass grids (AIIMS, Delhi).

XRD Analysis: The crystalline nature of alginate alone and composite beads of Gold nanoparticles encapsulated alginate microspheres were studied on a rotating X-ray diffractometer (NIT, Raipur).

FTIR Analysis: FTIR spectra of unadsorbed and adsorbed Safranin-Orange biopolymeric beads were recorded on a Perkin Elmer Spectrophotometer (Dr. M. K. Deb, PRSU, Raipur).

Results and discussions

TEM Analysis: The TEM image shows the spherical structure and minute size of the Au particles. Based on the image, the

average size of Au nanoparticles was estimated at 11.77 nm. (Figure-2).

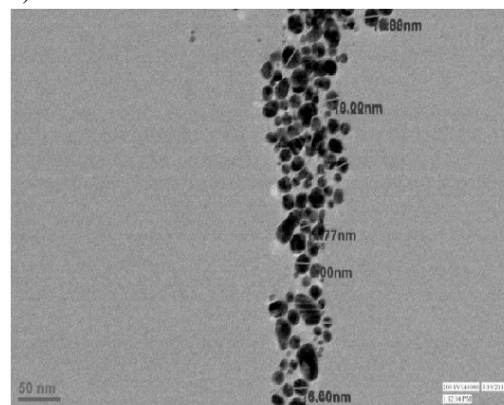
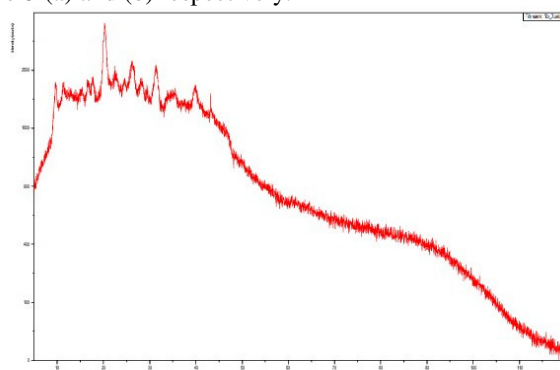
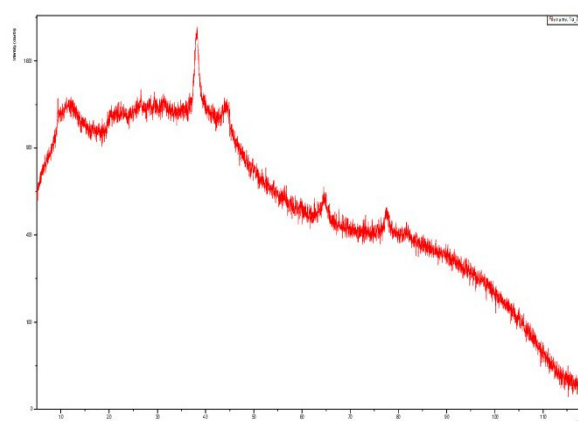


Figure-2: TEM images of bare nanoparticles of Gold nanoparticles encapsulated alginate microspheres.

XRD analysis: The XRD patterns of composite beads of Gold nanoparticles encapsulated alginate microspheres are shown in Figure-3 (a) and (b) respectively.



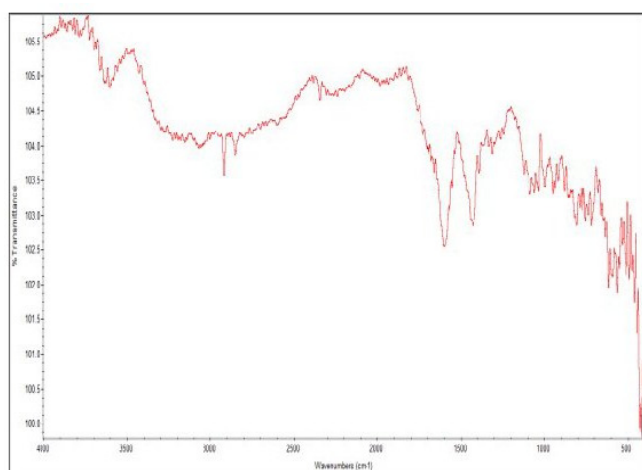
(A)



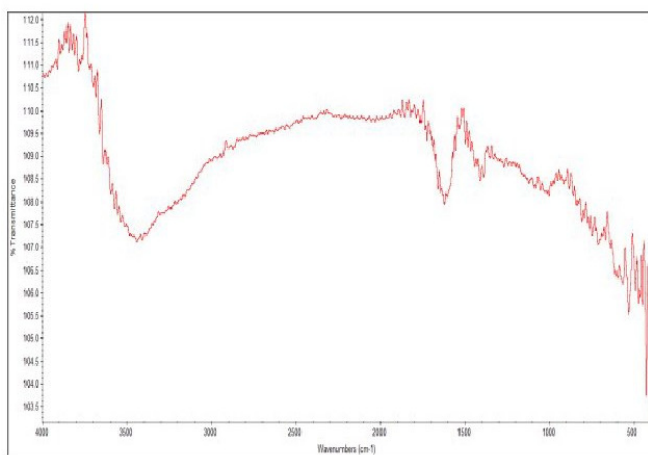
(B)

Figure-3: XRD pattern of Alginate and nano particles of Gold nanoparticles encapsulated alginate microspheres.

FTIR analysis: Fourier transformed infrared (FTIR) spectra of unadsorbed and dye adsorbed beads are depicted in Figure-4 (a) and (b) respectively. The FTIR analysis indicated the band at 2923.61 cm^{-1} that is due to the C-H bond of methylene group. The almost sharp peak at 1652.73 cm^{-1} may be designated to $>\text{C}=\text{O}$ group. The absorption peak around 3446.24 cm^{-1} may be assigned to $-\text{OH}$ stretching, while a peak around 1070.32 cm^{-1} may be due to the C-O stretching. The characteristic peak at 561.19 cm^{-1} indicates the coating of Au nanoparticles on alginate because the surface of alginate with negative charges has an affinity towards Au nanoparticles by the electrostatic interaction and chemical reaction through glutaraldehyde crosslinking. Following adsorption, the specific band at 1070.32 cm^{-1} (C-O str.) was shifted to 1072.24 cm^{-1} and a peak appearing at 2991.1 cm^{-1} (C-H str.) shifted to 2998.82 cm^{-1} , which may be attributed to the binding of the dye to the adsorbent surface.



(A)



(B)

Figure-4: FTIR spectra of (a) nanoparticles of Gold nanoparticles encapsulated alginate microspheres (b) Cr (VI) adsorbed nanoparticles of Gold nanoparticles encapsulated alginate microspheres.

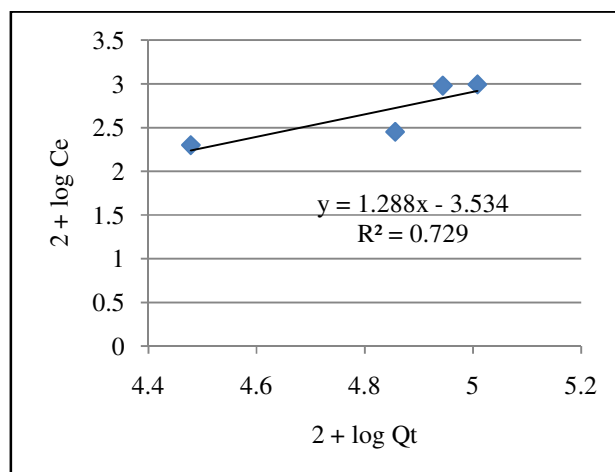


Figure-5: Freundlich adsorption isotherm drawn between adsorbed amount of Cr (VI) ions and equilibrium concentration of potassium dichromate solution showing the adsorption of Cr (VI) ions onto Gold nanoparticles encapsulated alginate microspheres = 0.1 g, pH = 8.0 at room temp.

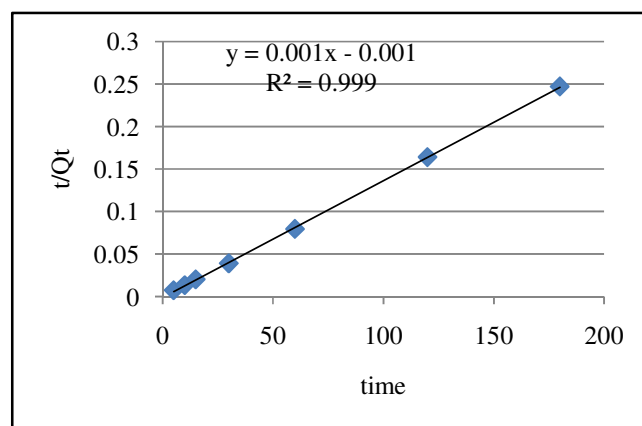


Figure-6: Variation in the adsorbed amount of Cr (VI) ions with time for fixed amount of Gold nanoparticles encapsulated alginate microspheres = 0.1 g, pH = 8.0 at room temp.

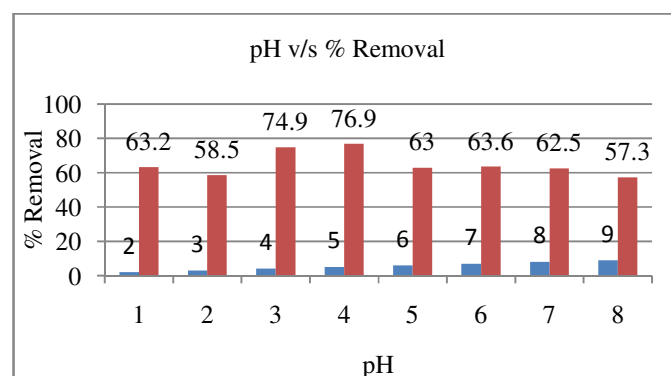


Figure-7: Effect of time on the adsorption of Cr (VI) ions onto Gold nanoparticles encapsulated alginate microspheres composite beads = 0.1 g. at room temp.

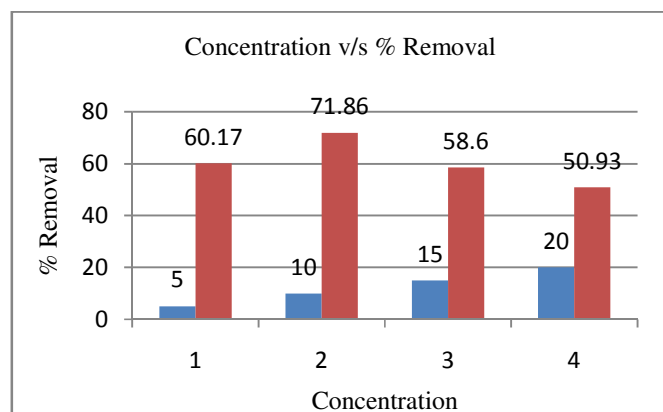


Figure-8: Effect of pH on the adsorption of Cr (VI) ions onto Gold nanoparticles encapsulated alginate microspheres composite beads = 0.1 g. at room temp.

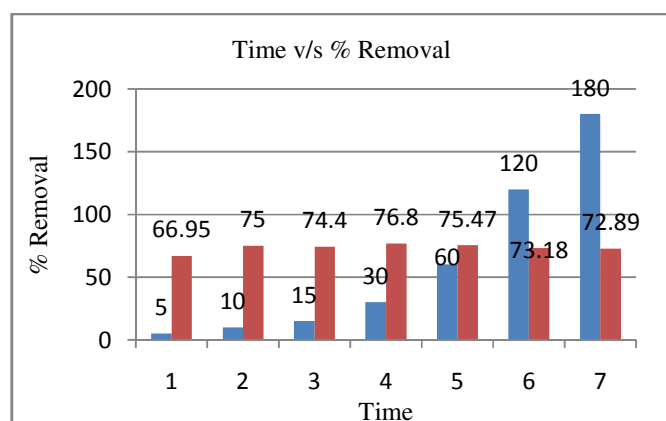


Figure-9: Effect of concentration on the adsorption of Cr (VI) ions onto Gold nanoparticles encapsulated alginate microspheres composite beads = 0.1 g. at room temp.

Conclusion

Biopolymeric beads composed of Gold nanoparticles encapsulated alginate microspheres seem to be an effective adsorbent for the removal of Safranin Orange from their contaminated solutions. The adsorption of Safranin Orange is significantly affected by factors like pH, time and concentration of the solution. It was found that the maximum adsorption was obtained at 30 min. for 10 ppm solution at pH 5 in room temperature. The polymeric adsorbent beads composed of Gold nanoparticles encapsulated alginate microspheres could be used time and again in the adsorption studies by adsorption and desorption recycle process without an appreciable loss in their initial adsorption capacities.

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