



Superparamagnetic PVA-Alginate Microspheres as Adsorbent for Cu^{2+} ions Removal from Aqueous Systems

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Abstract

The sorption efficiency of superparamagnetic nano iron oxide loaded Polyvinyl Alcohol-Alginate (PVA-A) was investigated for the removal of Cu^{2+} ions from aqueous solution. Various effects i.e. adsorbent dose, contact time, pH, initial metal ion concentration and temperature were studied. The PVA-A microspheres were magnetized insitu and the size and structure of magnetic nano particles were characterized by XRD, FTIR and TEM analysis. The equilibrium experimental results were analyzed in terms of Langmuir, Freundlich, Temkin and Dubinin-Radushkevich isotherms to obtain the appropriate model and found that all the isotherms well represented the measured sorption data for Cu^{2+} and various static parameters were evaluated showing the sorption to be feasible, spontaneous and exothermic in nature. The superparamagnetic PVA-A microspheres have been found to be the efficient adsorbent for removal of toxic Cu^{2+} ions from industrial wastewater (>99% removal) and could be regenerated efficiently (>98%) and used repeatedly for further experiments.

Keywords: Superparamagnetic nano iron oxide, polyvinyl alcohol, alginate, adsorption Isotherm.

Introduction

Industrial effluents loaded with heavy metals are a cause of hazard to humans and other forms of life. Heavy metals have been excessively released into the environment due to rapid industrialization and have created a major global concern¹. The environmental impact due to their toxicity has led to the enforcement of stringent standards for the maximum allowable limits of their discharge into open landscapes and water bodies. Industrial and mining wastewaters are important source of pollution of heavy metals². Copper and its compounds are widely used in metal finishing, plating, dyeing and petroleum industries. These industries produce large quantities of toxic wastewater effluents. Since copper is an essential metal in a number of enzymes for all forms of life, problem arises when it is deficient or in excess. However the carcinogenic character of copper is accepted and epidemiological evidence, such as the higher incidence of cancer among coppermiths, suggests a primary carcinogenic role of copper³. Moreover in Wilson disease and Indian Childhood Cirrhosis (ICC), copper accumulates in the liver, resulting in poor hepatocyte regeneration and fibrosis⁴. According to Environmental Quality Act 1974, the permitted concentration for Cu^{2+} discharged in effluents was 0.05 mg/dm^3 . Treatments for such metal bearing effluents are chemical precipitation, membrane separation and electrodeposition, though such treatments are effective for the removal of heavy metal ion in higher concentrations. Ion exchange and reverse osmosis have showed some promising results in treating diluted metal solutions but at a higher operating cost. Thus adsorption has become an alternative technique for the removal of heavy metal ions from diluted solutions.

Many materials of biological origin like papaya seed⁵, pine sawdust⁶, green alga, grafted cellulosic fabrics⁷ and some natural polymers such as pectin⁸, sodium alginate⁹, carboxy methyl cellulose¹⁰ and chitosan¹¹ have been reported as adsorbents to remove heavy metal ions from water and industrial effluents. The adsorption mechanism of heavy metals is theorized to be an active or passive transport. The active mode is a metabolism dependent and slow process. The metal uptake by synthetic adsorbent will take place by the passive mode, which is a metabolism independent mechanism that essentially involves adsorption process such as ionic, chemical and physical adsorption. The passive mode is very rapid and occurs in a short time after the adsorbent comes into contact with the metal solution¹². Advances in nanoscale science and engineering suggest that many of the current problems involving water quality could be resolved or greatly diminished by using nano materials. They could be classified to adsorbent, nanocatalysts, bioactive nanoparticles, nanostructured catalytic membranes, submicron, nanopowder, nanotubes, magnetic nanoparticles, granules, flakes and high surface area metal particle supramolecular assemblies. They have characteristic length scales of 9-10 nm including clusters, micromolecules, nanoparticles and colloids¹³. Nanotechnology, now considered as one of the most important advancements in science and technology of the past decade, is related to the manipulation of materials and systems at the nanometer scale. At this length scale materials exhibit new properties for novel applications¹⁴⁻¹⁵.

Novel invention in adsorption technology is the use of magnetic nanoparticles as an adsorbent. Currently many methods exist to remove copper such as coagulation, ion exchange and sorption with iron oxides. However, these methods can produce large

amounts of waste, the use of magnetic nanoparticles for separation and preconcentration in analytical chemistry is opening a new methodology that is faster, simpler and more precise than those used traditionally. The greatest advantage of this method is that desired materials are separated from solution by a simple and compact process while fewer secondary wastes are produced. Other advantages are large active surface area for given mass of particles and the ability to process solution that contains suspended solids¹⁶. Iron oxides in various forms such as magnetite (Fe₃O₄), maghemite (gamma Fe₃O₄), iron oxide-coated materials^{12,17} and magnetite exchanger resin have been used for treatment of radioactive and heavy metals from water and wastewater solutions¹⁸.

The objective of the present study is to investigate the role and the effectiveness of the adsorbent composed of PVA-Alginate and magnetite nano particles (Fe₃O₄) in the removal of Cu²⁺ ions from synthetic industrial wastewater. Superparamagnetic nano magnetite loaded PVA-Alginate microspheres were synthesized by sol-gel method and then different experimental conditions such as amount of adsorbent dose, initial pH, adsorption time, shaking rate, concentration of Cu (II) ions and adsorption isotherm equation ions have been studied.

Material and Methods

Materials: The polyvinyl alcohol, sodium alginate, sodium hydroxide pellets, calcium chloride (cross linker), anhydrous ferric chloride and ferrous chloride tetrahydrate were purchased from Molychem, Mumbai, INDIA. Triple distilled water was used throughout the experiments.

Synthesis of Superparamagnetic PVA-A microspheres: The adsorbent microspheres were prepared in three steps. The first step involves the preparation of viscous gel of polyvinyl alcohol (PVA) by dissolving at 90°C in hot triple distilled water and was mixed thoroughly with the sodium alginate to get 1:1 ratio, stirred for an hour for homogeneity and kept aside to obtain a bubble free solution. In second step the microspheres were prepared by drop wise addition of the above mixture in CaCl₂ solution (0.5M) for cross linking. The microspheres so produced were allowed to harden by leaving them in solution for 24h then filtered and washed several times with distilled water. In the third step for insitu magnetization, these microspheres were kept in an aqueous solution of ferrous chloride tetrahydrate and ferric chloride in 1:3 ratio, for 24h. The nano iron-oxide loaded microspheres were then added into ammonia solution and kept for 2h, so that the Fe²⁺/Fe³⁺ ions get precipitated into iron-oxide within the PVA-A matrix. These superparamagnetic PVA-Alginate microspheres were then thoroughly washed several times and stored for adsorption studies (figure 1).

Preparation of Stock Solution: Stock solution of Cu (II) ions of 1000 mg/dm³ was prepared by dissolving 0.393g of CuSO₄.5H₂O (AR) in 100 ml triple distilled water. Suitable concentrations for Cu (II) ions for batch experiments were

prepared by diluting the stock solution with distilled water. Fresh dilutions were used in each experiment.

Analytical Techniques: The concentration of Cu²⁺ ions was determined using Atomic Absorption Spectrophotometer [Varian AA-24-OFS model]. Each experiment was carried out in triplicate under identical conditions to get the mean values.

Adsorption Experiments: The adsorption experiments were carried out by batch method by varying contact time, pH, adsorbate concentration, adsorbent dose and temperature. For adsorption experiments, the superparamagnetic PVA-A microspheres 0.2g and 20 ml CuSO₄.5H₂O solution of 1.0 mg/dm³ concentration at pH 4 and room temperature (27°C) was stirred in an orbital shaking machine at 200 RPM for 2h, which was found to be a sufficient time to attain equilibrium sorption. The amount of Cu²⁺ ions present in solution (before and after equilibrium adsorption) was determined by Atomic Absorption Spectrometer. The sorption degree (percentage removal) and sorption capacity of the sorbent was calculated by the following equations:

$$\text{Sorption degree} = \frac{C_i - C_e}{C_i} \times 100 \% \quad (1)$$

$$\text{Sorption Capacity} = C_i - C_e \times V / m \quad (2)$$

Where C_i and C_e (mg/dm³) are the initial and equilibrium concentration of Cu²⁺ ions respectively, V (Litre) is the volume of the copper solution (adsorbate) subjected to sorption and m (gram) is the weight of adsorbent (swollen microspheres).

Desorption Studies: Desorption studies indicate the nature of adsorption and recovery of valuable metals from wastewater and sorbent. In order to desorb Cu²⁺ ions from the magnetic PVA-Alginate adsorbent the microspheres were collected, washed and then treated with nitric acid of various strengths ranging from 0.02 to 0.2N. Desorption efficiency was calculated by using following equations.

$$\text{Desorption efficiency} = \frac{\text{Amount of Cu (II) desorbed}}{\text{Amount of Cu (II) sorbed}} \times 100 \quad (3)$$

Characterization of superparamagnetic PVA-A Microspheres: The adsorbent was characterized by XRD, FTIR and TEM analysis, which are given below.

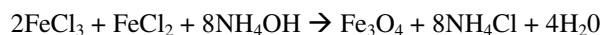
XRD Analysis: The crystalline nature of superparamagnetic PVA-A microspheres was studied on a Bruker D8 advanced X-ray Diffractometer with scanning range of 20°-80° (2theta) using Cu Ka radiation with wavelength of 1.5406 Å (UGC-DAE, Indore, INDIA).

FTIR Analysis: The FTIR spectra of adsorbent was recorded using Varian Vertex FTIR Spectrometer (UGC-DAE, Indore, INDIA).

TEM Analysis:-The average particle size, morphology and size distribution of iron-oxide nanoparticles were examined using TECNAI-G-20 TEM at a voltage of 200 KV. The solvent dispersion of the particles was drop cast onto a carbon coated copper grid and the grid was air dried at ambient conditions ($25 \pm 1^\circ\text{C}$) before loading into the microscope (AIIMS, New Delhi, INDIA)

Results and Discussion

X-ray diffraction (XRD) analysis:-The XRD pattern of superparamagnetic PVA-A microspheres showed five characteristics peaks (2 Theta =26.93, 31.89, 38.87, 41.23 and 45.55). The position and relative intensities of all diffraction peaks in match well with those from the JCPDS file number 89-5984 for magnetite (Fe_3O_4) and reveal that the prominent phase formed is Fe_3O_4 with resultant nanoparticles of pure magnetic with cubic structure. Magnetite particles are obtained according to the following reaction:



Powder XRD was carried out to identify the nanocrystalline structure of the iron-oxide and the amorphous nature of PVA-A. The particle sizes can be quantitatively evaluated from XRD data using the Debye-Scherrer equation, which gives a relationship between peak broadening in XRD and crystallite size.

$$D = K \lambda / \beta \cos \theta \quad (4)$$

Where D is the crystal thickness, K is Scherrer constant (0.89), λ is the wave length of X-ray (0.15406 nm) β is the peak width of half maximum and θ is the Bragg angle of the XRD peak (1,1,1). The calculated average crystallite size of superparamagnetic PVA-A was found to be 26.93 nm¹⁹ (figure 2).

Fourier transform infrared spectroscopy (FTIR) analysis:-Numerous chemical groups have been proposed to be responsible for the adsorption of metals. They include carboxyl, hydroxyl, sulphonate and amino²⁰. Their relative importance in

metal sorption may depend on factor such as the quantity of sites, accessibility, chemical state and affinity between site and metal²¹. The FTIR is an important tool to identify the functional groups. The vibrancy signals of superparamagnetic PVA-A microspheres before and after adsorption of copper were different, indicates bands close to 3406 cm^{-1} due to -OH stretching in carboxyl group and near 1609 cm^{-1} due to C=O asymmetrical stretching of -COOH group and near 1415 cm^{-1} due to C=O symmetrical stretching vibration in carboxylic group. The band at 1086 cm^{-1} is attributed to the -C-O stretching²². There is an obvious absorption band at the low frequency zone of $450\text{-}750 \text{ cm}^{-1}$, which is assigned to the stretching vibration of the Fe-O band in iron oxide. The characteristic peak at 479.56 cm^{-1} relates to Fe-O group, which indicates the loading of nano iron oxide particles on PVA-Alginate because the surface of iron oxide with negative charges has an affinity towards PVA-Alginate microspheres, hence the magnetite nanoparticles could be loaded onto protonated copolymer by the electrostatic interaction and chemical reaction through crosslinker. A general explanation is that the polyvinyl alcohol and alginate is attached to iron-oxide via the interaction between the alcoholic and carboxylic groups respectively and surface hydroxyl groups of PVA to iron oxide²³. By comparing the spectra of magnetic beads before adsorption and after adsorption, the following conclusions could be drawn. The shifting of -OH stretching band from 3380 to 3406 cm^{-1} suggests the attachment of adsorbate Cu^{2+} ions. The shifting of the C-O band to the lower frequency from 1034 to 1027 cm^{-1} can be attributed to the association of the hydroxyl group with adsorbate. A slight shift of Fe-O band from 465 to 479 cm^{-1} shows the adsorption of some of the adsorbate ions onto the nano iron -oxide surface (figure 3).

Transmission electron microscopy (TEM) analysis:- The shape, size and morphology of nano iron-oxide particles were determined through TEM imaging. The TEM images of nanoparticles show almost cubic iron-oxide particles with an average size of (1-7 nm) as shown in figure-4. It should be noted however, that the majority of particles were scattered, a few of them showing aggregates indicate stabilization of the nanoparticles.

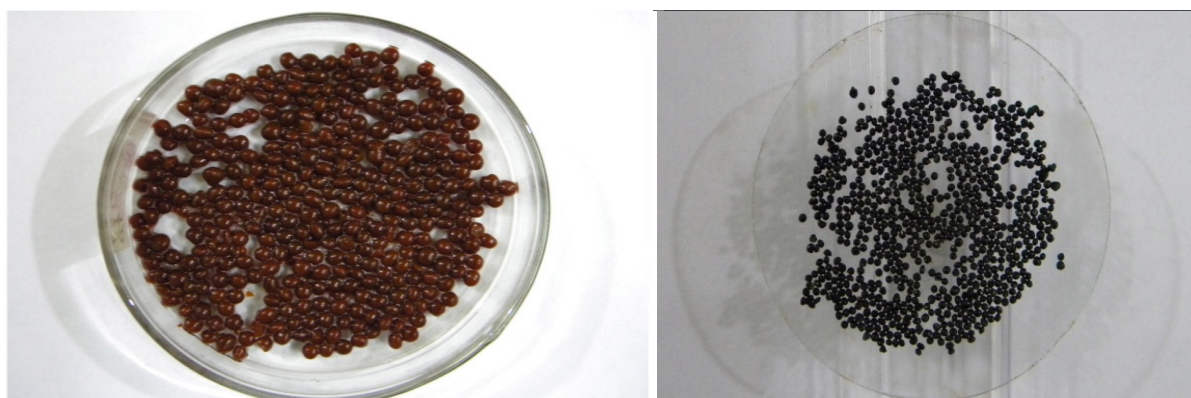


Figure-1
Superparamagnetic PVA-Alginate microspheres Swollen and Dry

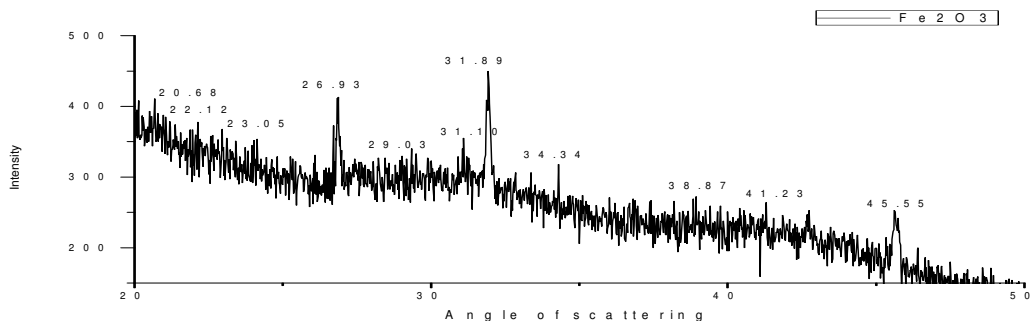


Figure-2
 The XRD pattern of Superparamagnetic PVA-A microspheres

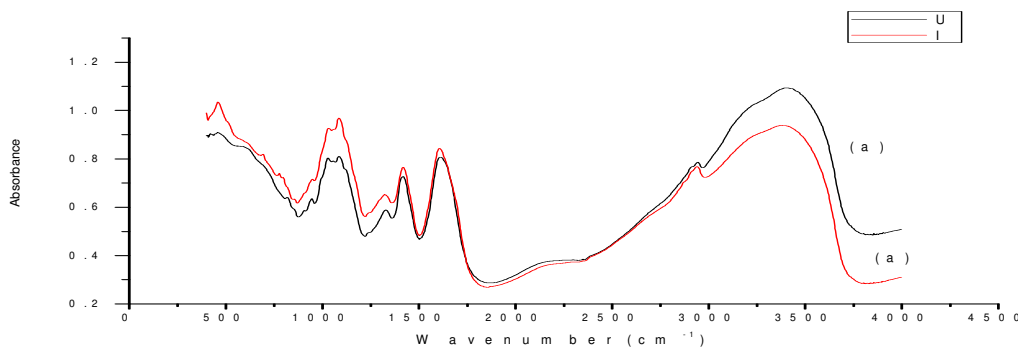


Figure-3
 FTIR Pattern of Superparamagnetic PVA-Alginate before and after adsorption respectively

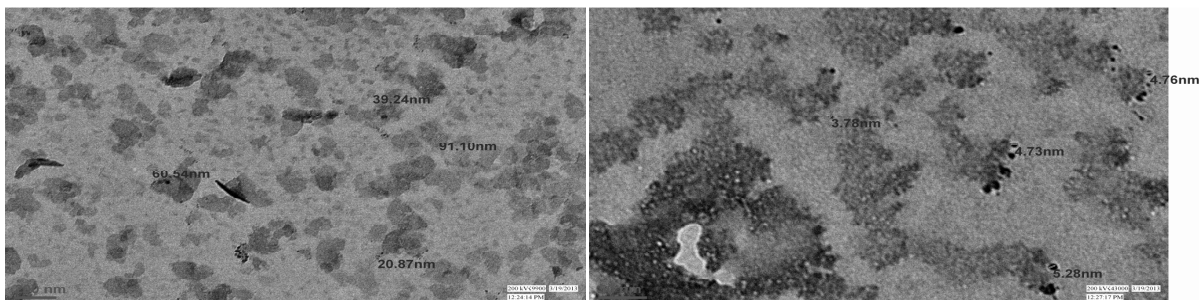


Figure-4
 Transmission Electron Micrograph of Fe₃O₄ nanoparticles

Adsorption Isotherm: The equilibrium relationships between adsorbent and adsorbate which is the ratio between quantities adsorbed and that remaining in solution at a fixed temperature is described by adsorption isotherm. The experimental data for the uptake of Cu²⁺ ions by adsorbent, over the studied concentration range were processed in accordance with the four most widely used adsorption isotherms: Langmuir, freundlich, Temkin and Dubinin-Radushkevich isotherm.

Langmuir isotherm: The most widely used isotherm equation for modeling equilibrium is the Langmuir equation based on the assumption that there is an infinite number of binding sites which are homogeneously distributed over the adsorbent

surface, these binding sites have the same affinity for adsorption of a single molecular layer and there is no interaction between adsorbed molecules. The isotherm follows the typical Langmuir adsorption pattern as shown in figure-5. The linear form of Langmuir isotherm may be represented as:

$$C_{eq}/q_{eq} = 1/K_a q_{max} + 1/q_{max} \times C_{eq} \quad (5)$$

Where q_{eq} is the amount of solute adsorbed per unit weight of adsorbent (mg/g), C_{eq} is the equilibrium concentration of solute in the bulk solution (mg/dm³), q_{max} is the monolayer adsorption capacity (mg/g) and K_a is sorption equilibrium constant related to the free energy of adsorption, q_{max} represent a practical limiting adsorption capacity and when the surface is fully

covered with heavy metal ions and assists in the comparison of adsorption performance, particularly in case where the sorbent did not reach its full saturation in experiments. The values of q_{max} and K_a can be calculated from the slope and intercept of the plot of C_{eq}/q_{eq} versus C_{eq} . The values of K_a and q_{max} are given in table-1.

Freundlich Isotherm: Freundlich equation was applied to describe the analytical results on adsorption. The Freundlich equation proposes an empirical model that is based on sorption on heterogeneous surface and has the form:

$$\ln q_e = \ln K_f + 1/n \ln C_e \quad (6)$$

Where C_e is the equilibrium concentration (mg/dm^3) and q_e is the amount adsorbed per unit mass of adsorbent (mg/g). When $\ln q_e$ was plotted against $\ln C_e$, a straight line was obtained, which shows a favourable adsorption of Cu^{2+} ions following the Freundlich Isotherm. The values of K_f and n are given in table-1

Modified Freundlich Isotherm: The superparamagnetic PVA-A microspheres are multifunctional in nature, they may be considered as responsible for the heterogeneity of the adsorption processes. Thus in the present case the modified Freundlich equation (equation 7) may be applied.

$$\log(a/a_s - a) = \beta \log C_e + \log(A/a_s) \quad (7)$$

Where β and A are empirical constants, which can be determined through linear regression analysis and the values of β and A are tabulated in table-1. The values of β and A indicate that distribution of Cu^{2+} ions is not even over the active sites of adsorbent surfaces, rather it is widely spread, thus indicating the heterogeneity of the beads' surfaces (figure-7).

Temkin Isotherm: The Temkin isotherm is often used to represent the equilibrium adsorptive behavior between two phases composing the adsorption system. The Temkin isotherm model is given by the following equation:

$$q_{eq} = a_s + b \ln C_e \quad (8)$$

Where q_{eq} is the amount of metal adsorbed per unit weight of adsorbent (mg/g), C_e is the concentration of adsorbate at

equilibrium (mg/dm^3), a_s and b are constants related to adsorption capacity and intensity of adsorption respectively. The correlation coefficient ($R^2=0.972$), showed that adsorption of Cu^{2+} ions also follows Temkin model. This suggests that Cu^{2+} ions adsorption may be chemical sorption or chemisorptions. The values of a_s , b and R^2 are tabulated in table-1 (figure 8).

Dubinin-Radushkevich isotherm: This equation is used to estimate the porosity value of adsorbent and the apparent energy E of sorption for Cu^{2+} ions from aqueous solution. This equation is represented as:-

$$Q_e = Q_D [\text{Exp} - B_D RT \ln(1+1/C_e)] \quad (9)$$

Where Q_e is the amount of Cu^{2+} ions sorbed by the adsorbent, Q_D is the Dubinin-Radushkevich constant, a measure of the porosity characteristics of adsorbent, B_D is used to calculate the apparent energy E of Cu^{2+} sorption and C_e is the initial concentration of the $Cu(II)$ ion solution. The linear form of equation (9) is given as

$$\ln Q_e = \ln Q_D [\text{Exp} - 2B_D RT \ln(1+1/C_e)] \quad (10)$$

The experimental data obtained from the sorption studies was fitted into equation 10 by plotting the values of $\ln Q_e$ against the values of $RT \ln(1+1/C_e)$ at temperature of $25^\circ C$. The slope gives Q_D and intercept yields the value of porosity B_D . The apparent energy E is obtained as follows:-

$$E = 1/\sqrt{2BD} \quad (11)$$

The values of Q_D and E at given temperature are given in Table-1. The Dubinin-Radushkevich plot figure- 9 shows, the porosity value Q_D equal to 6.701 g/l and the apparent (sorption) energy E is 3.2971 cal/mole , which proves that the sorption of Cu^{2+} ions onto superparamagnetic PVA-A microspheres which is energy dependent.

In conclusion all the above parameters have to be taken into consideration whenever these adsorbents are to be used as metal ion sorbent from aqueous systems like waste waters, industrial effluents and agricultural waters.

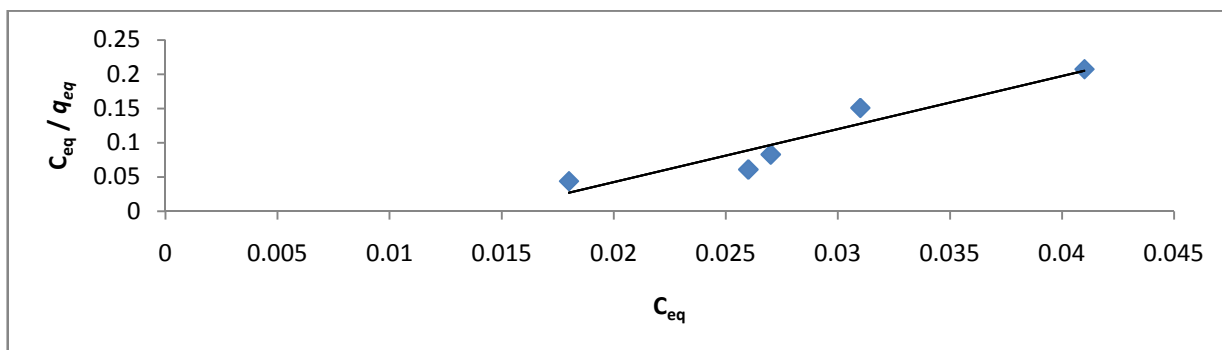


Figure-5
 Langmuir adsorption isotherm of Superparamagnetic PVA-A for $Cu(II)$ ions

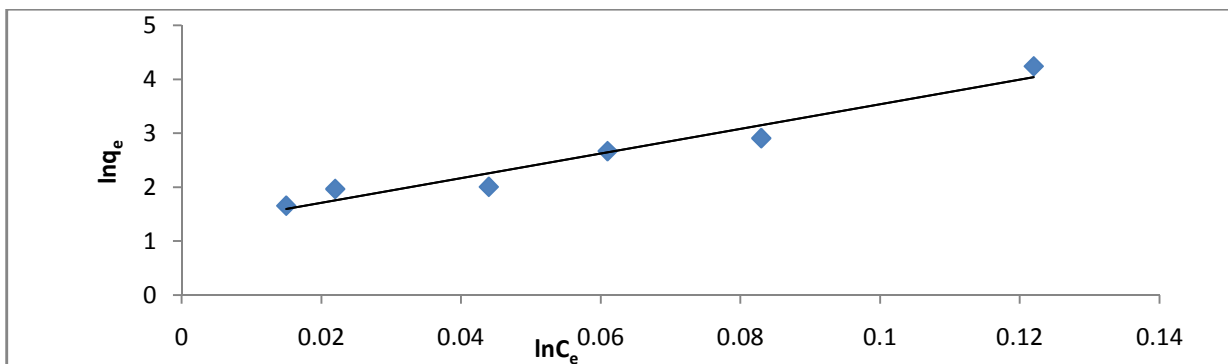


Figure-6
 Freundlich adsorption isotherm of Superparamagnetic PVA-A for Cu (II) ions

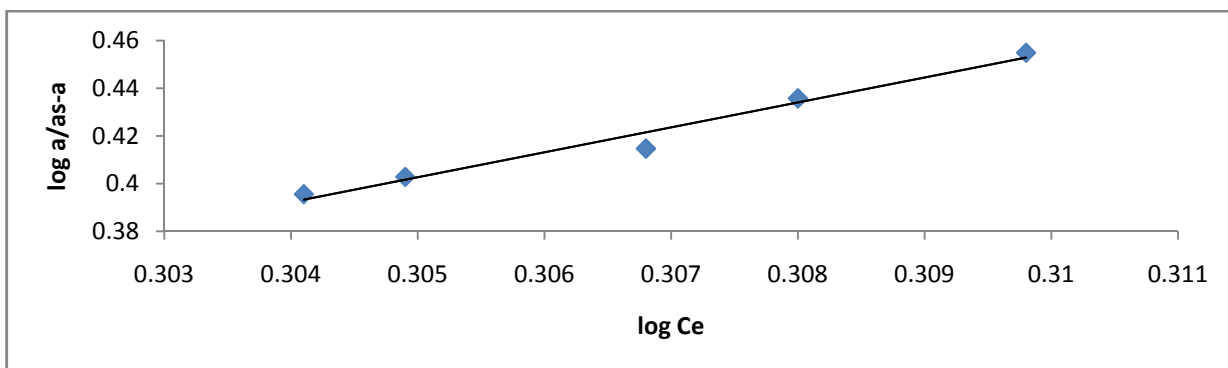


Figure-7
 Modified Freundlich adsorption isotherm of Superparamagnetic PVA-A for Cu (II) ions

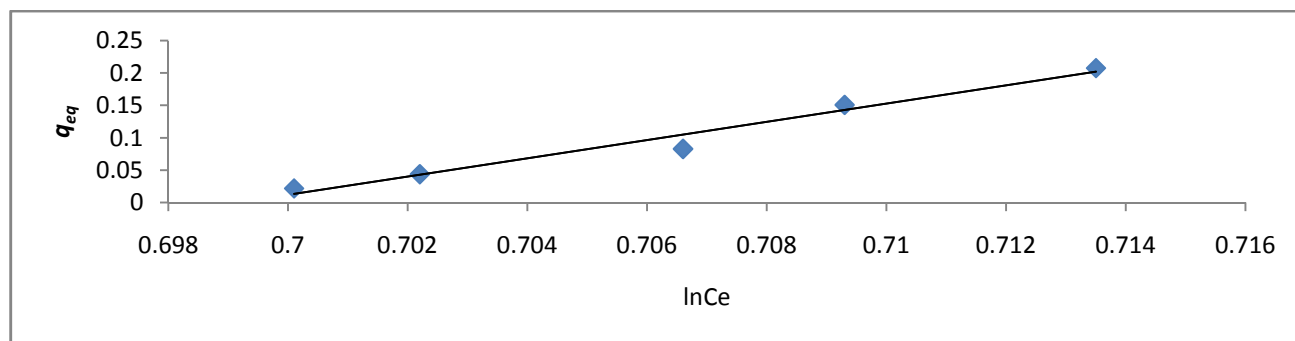


Figure-8
 Temkin adsorption isotherm of Superparamagnetic PVA-A for Cu (II) ions

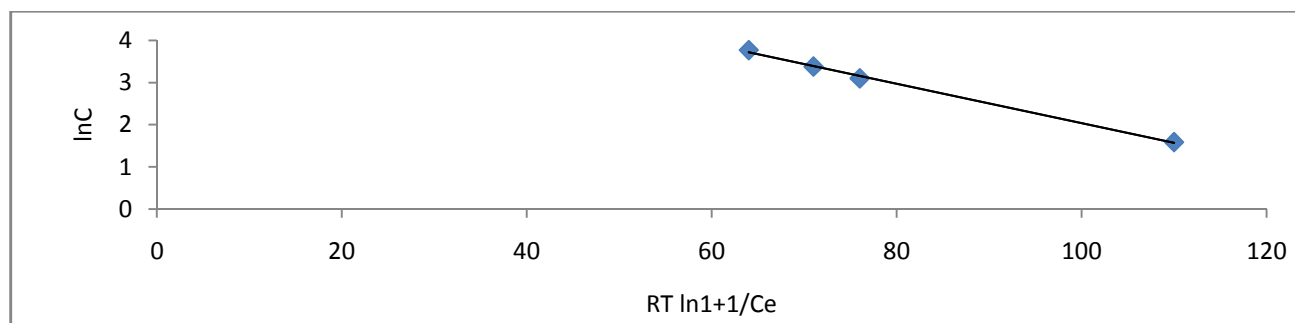


Figure-9
 Dubinin-Radushkevich adsorption isotherm of Superparamagnetic PVA-A for Cu (II) ions

Table-1
Estimated isotherm models and their Constants values for Cu²⁺ ions

Langmuir Isotherm			Freundlich Isotherm			Modified Freundlich Isotherm			Temkin Isotherm			Dubinin-Radushkevich Isotherm		
q _{max}	K _a	R ²	K _f	n	R ²	A	β	R ²	a _s	b	R ²	Q _D	E	R ²
8.928	0.129	0.903	9.913	0.796	0.952	0.0605	10.44	0.974	6.105	4.27	0.972	6.701	3.297	0.997

Factors Affecting Adsorption: Effect of Adsorbent Dose: The dependence of Cu²⁺ ions sorption on adsorbent dose was studied by varying the amount of adsorbent dose from 0.05 to 0.5 g with fixed volume of adsorbate (20 ml) keeping other parameters like temperature, pH and contact time constant. It was observed that maximum removal of Cu²⁺ ions was obtained with 0.2 g adsorbent. This is due to the increased availability of active adsorption sites arising due to the increase effective surface area resulting from the increases in dose of adsorbent or due to conglomeration of the adsorbent (figure-10).

Effect of pH: The pH level is one of the most important parameter on adsorption of heavy metal ions from aqueous solutions, since it determines the surface charge of the adsorbent, the degree of ionization and speciation of the adsorbate. In order to establish the effect of pH on the sorption of Cu²⁺ ions, the batch equilibrium studies at different pH values were carried out in the range of 3 to 8, using 0.1 M HNO₃ and 0.1 M NaOH. It was found that the highest uptake of Cu²⁺ ions was obtained at pH 4 and at higher pH levels, the adsorption was found to decrease. At higher pH values, Cu ions precipitated as hydroxide which decreased the rate of adsorption, subsequently the percent removal of metal ions²⁴. Less sorption at lower pH may be due to the competition of H⁺ ions with metal ions at sorption sites. This means that at higher H⁺ ion concentration, the adsorbent surface becomes more positively charged, thus reducing the attraction between adsorbent and the metal ions. In contrast, as the pH increases, more negatively charged surface becomes available, thus facilitating greater metal ion uptake (figure-11).

Effect of Contact Time: The adsorption of Cu²⁺ ions increased with increasing contact time and attains equilibrium after 120 min. From figure 12, depicts that the Cu²⁺ ions removal percentage is higher at the beginning, which may be due to a larger surface area of the adsorbent being available at the beginning of adsorption process. As the surface adsorption sites become exhausted, the uptake rate is controlled by the rate at which the adsorbate is transported from the exterior to the interior sites of the adsorbent particles. So taking the optimum adsorbent dose and varying contact time, it is found that up to 120 min, the uptake of metal ions increases and remain constant in further increasing the time. Therefore the optimum time for maximum removal 98.76% was 120 minutes. For the further optimization of other parameters, the contact time was considered as the equilibrium time corresponding to the adsorbent and adsorbate.

Effect of Temperature: Temperature plays an important role on the retention of metal ions by adsorbent. Effect of temperature on removal of Cu²⁺ ions was studied by conducting adsorption experiment at different temperatures in the range from 10 to 50°C and it was observed that the adsorption of Cu²⁺ ions increases from 10 to 25°C, while beyond 25°C, it decreases, which may be explained by the fact that by the increase in temperature, a greater number of active sites may be generated on the adsorbent surface due to the enhanced rate of protonation and deprotonation of functional groups present on the adsorbent surface thus increasing the adsorption of Cu²⁺ ions. At much higher temperatures the observed decrease in adsorption may be due to the weakening of binding forces between Cu²⁺ ions and active sites on the copolymer (figure-13).

Effect of Initial Concentration: The adsorbate and adsorbent interaction was studied by performing the adsorption experiments with different copper ion concentrations in the range of 0.01-1.0 mg/dm³ and it was observed that with the increase in initial Cu²⁺ ion concentration, the percent removal of metal ions also increased. The highest uptake of Cu²⁺ ions onto magnetite PVA-A was obtained at 1.0 mg/dm³ initial ion concentration, which was found to decrease at higher concentrations, may be due to the progressive saturation of binding sites. The observed increase is quite obvious, as on increasing the concentration of solute, greater number of metal ions arrives at interface and thus get adsorbed (figure-14).

Desorption studies: Figure-15, depicts the desorption studies of Cu²⁺ ions, which were removed from the surface of the sorbent containing 0.0991 mg/g of Cu (II) using 0.01, 0.02, 0.04, 0.06, 0.08 and 0.1 M HNO₃ strength respectively at room temperature (27°C). The percentage recoveries of copper found 98.64% Complete desorption of Cu²⁺ ions from the sorbent took place by 0.06 M HNO₃ and the superparamagnetic PVA-A microspheres showed almost the same metal ion adsorption capacity after the repeated regeneration. It may be stated that, in the acidic medium, protons compete with Cu²⁺ ions and displace the maximum amount of adsorbed Cu²⁺ ions. Hence, ion exchange mechanism is important in connection with adsorption / desorption process for adsorbent.

Conclusion

The superparamagnetic polyvinyl alcohol-alginate microspheres has been found to be very effective adsorbent for the removal of Cu²⁺ ions from aqueous solution. The maximum removal of metal ions occurs at the pH 4, between temperature range 25-

27°C within 120 minutes. The superparamagnetic PVA-A microspheres could be repeatedly used in the adsorption studies by adsorption-desorption cycle without detectable losses in their initial adsorption capacities. The maximum removal of

Cu²⁺ ions from aqueous solution was observed to be 99.27%, which proves this adsorbent to be superior among other adsorbents.

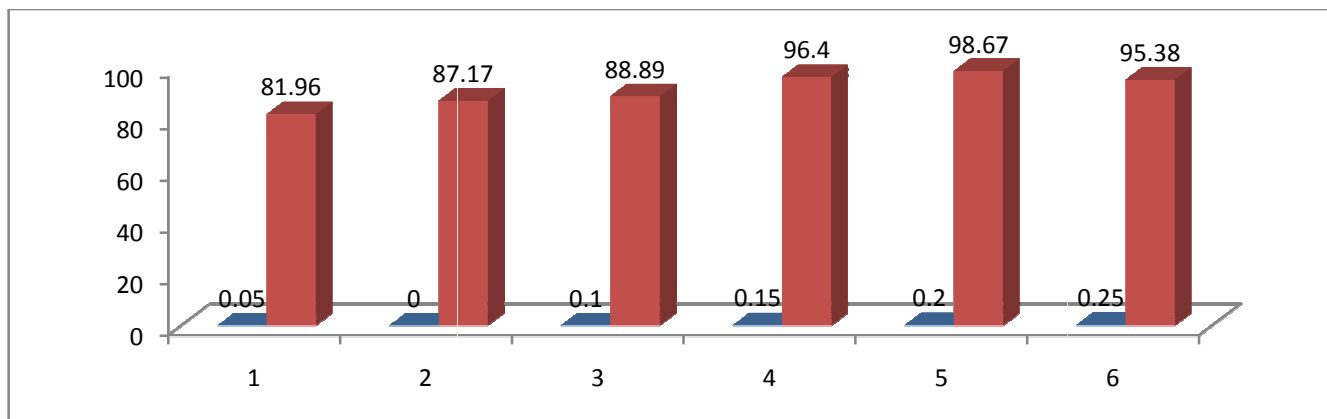


Figure-10
 Effect of adsorbent dose on Cu (II) ions removal through Superparamagnetic PVA-A Microspheres
 pH = 4, temp = 25 ± 0.5°C, time = 120min

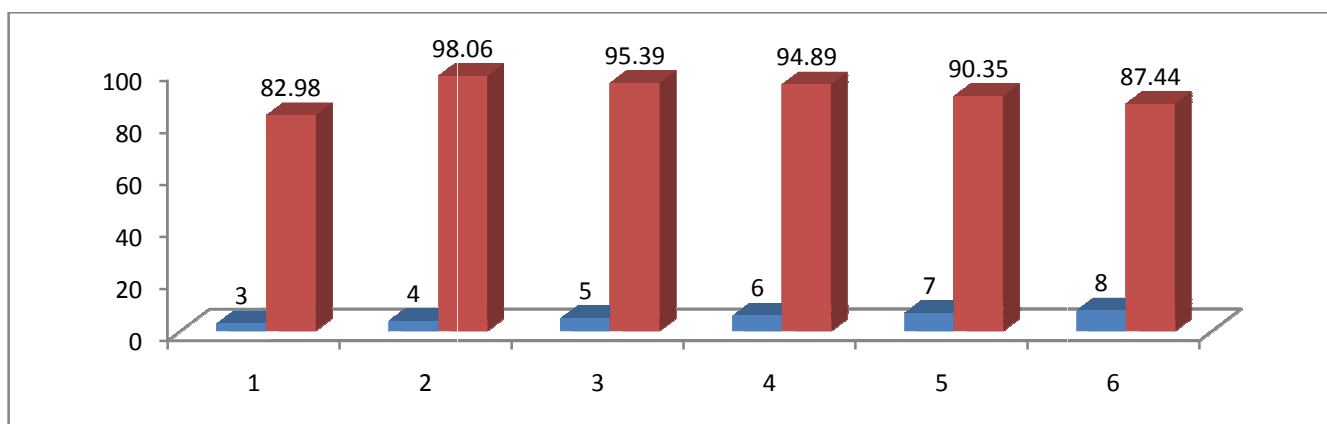


Figure-11
 Effect of pH on Cu (II) ions removal through Superparamagnetic PVA-A Microspheres =0.2g,
 temperature = 25 ± 0.5°C, time = 120min

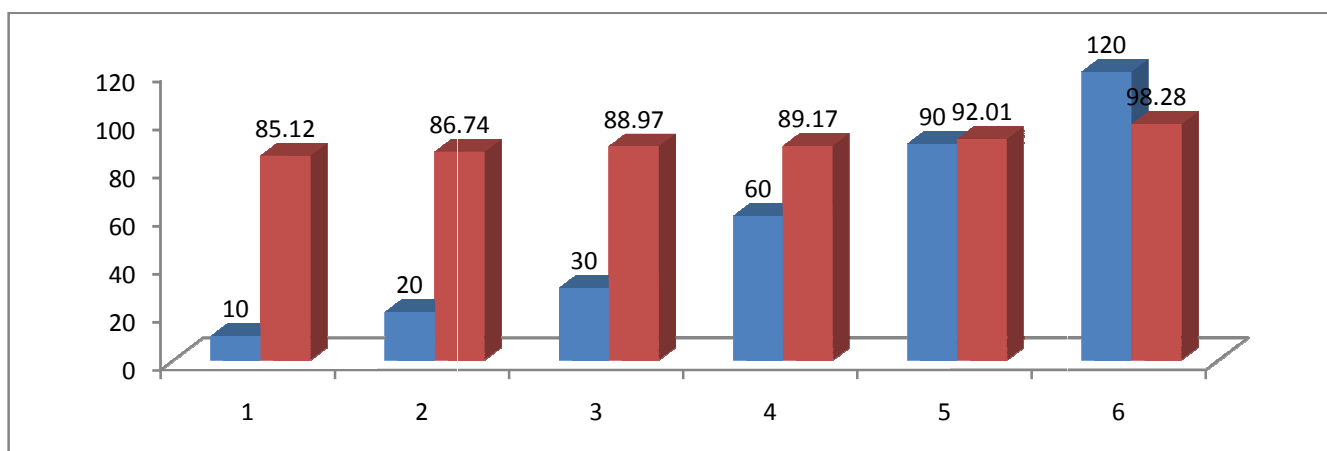


Figure-12
 Effect of Contact Time on Cu (II) ions removal through Superparamagnetic PVA-A Microspheres=0.2g,
 temperature = 25 ± 0.5°C, pH = 4.

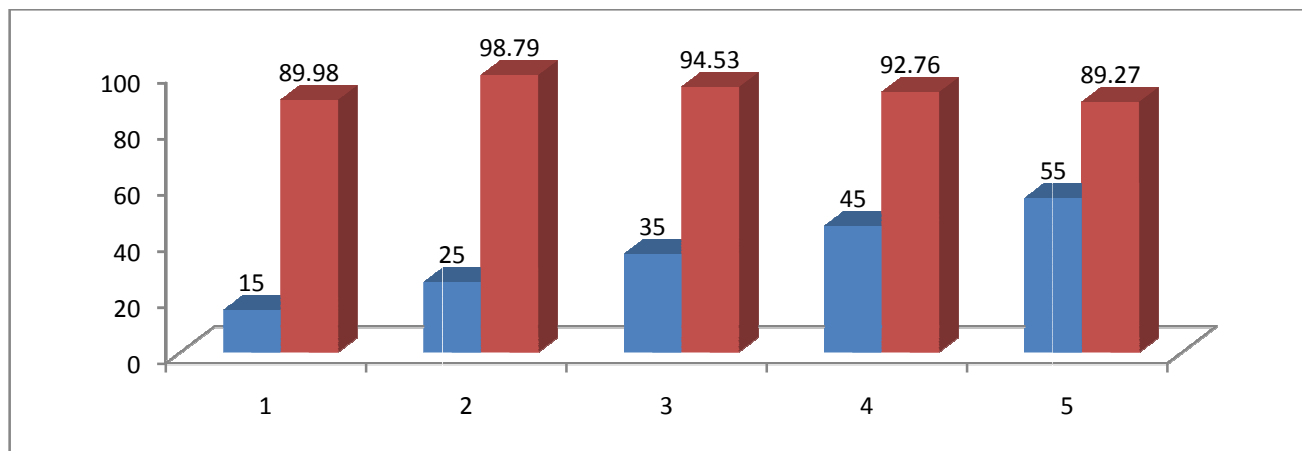


Figure-13
 Effect of Temperature on the adsorption of Cu (II) ions removal through Superparamagnetic PVA-A
 Microspheres=0.2g, time = 120min., pH = 4.

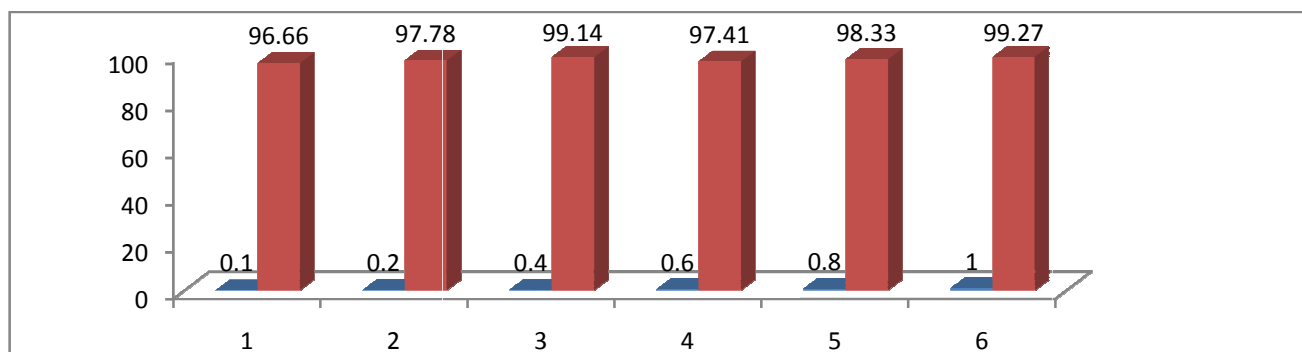


Figure-14
 Effect of different concentration on Cu (II) ions removal through Super paramagnetic PVA-A
 Microspheres = 0.2 g, pH =4, time = 120 min., temperature = 25 ± 0.2°C.

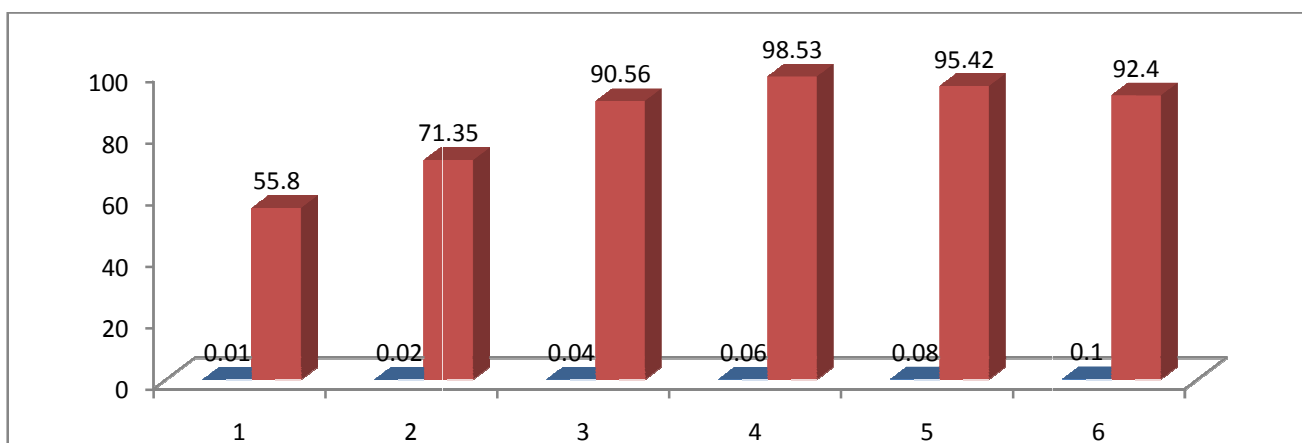


Figure-15
 Desorption studies of Cu (II) ions using varies strengths of HNO₃ with Superparamagnetic PVA- A Microspheres

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