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Removal of As(V) from aqueous solutions using Cu(II)-loaded 4-vinyl pyridine grafted polymeric ligand exchanger

4-Vinil piridin aşılanmış Cu(II)-yüklenmiş polimerik ligand değiştiriciler kullanılarak sulu çözeltilerden As(V) uzaklaştırılması

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Research Article

ABSTRACT

In order to prepare fibrous polymeric ligand exchanger (PLE) adsorbent for the removal of As(V), 4-vinyl pyridine (VP) monomer was first grafted onto polyethylene/polypropylene nonwoven fabrics (NWF) made of polypropylene coated by polyethylene (PE/PP) in emulsion medium by using radiation induced graft polymerization (RIGP). 4-Vinyl pyridine grafting conditions were optimized and about 150% VP grafted samples were used for further experiments. For the preparation of the suitable polymer ligand exchanger (PLE) for the removal of As(V), VP grafted NWF were loaded with Cu(II) ions. Copper loading capacity of PLE was determined to be 0.5 mmol Cu(II)/g polymer. As(V) adsorption experiments were performed in batch mode at different contact time, pH (3-9) and initial As(V) concentrations. The As(V) adsorption rate onto PLE adsorbent was rapid and adsorption equilibrium was established within 4 hours. It was found that As(V) adsorption by Cu(II) loaded VP grafted NWF did not change significantly over a wide pH range. The effect of initial concentration of As(V) on the adsorption behaviour of PLE was determined for different As(V) concentrations (0.1-500 ppm) at pH 7. The new PLE showed high affinity for As(V), the maximum adsorption capacity was found to be 51 mg As(V)/g PLE from Langmuir isotherm. It was found that the theoretical capacity found from Langmuir isotherm is very good accordance with experimental capacity 47 mg As(V)/g PLE.

Key Words
4-vinyl pyridine, radiation induced graft polymerization, Cu(II)-loaded VP grafted adsorbent, As(V) adsorption.

ÖZET

As(V) uzaklaştırılmasında kullanılmak üzere polimerik ligand değiştirici (PLE) fiber adsorbent hazırlamak amacıyla, 4-vinil piridin (VP) monomeri radyasyonla başlatılan aşı polimerizasyonu (RIGP) tekniği kullanılarak, polietilen (PE/PP) ile kaplanmış polipropilen (PE/PP) dokumasız kumaşlar (NWF) üzerine emülsiyon ortamında aşılanmıştır. 4-vinil piridin aşılama koşulları optimize edilmiş ve yaklaşık % 150 VP aşılanan örnekler adsorpsiyon deneylerinde kullanılmıştır. As(V) uzaklaştırılması için uygun polimer ligand değiştirici (PLE) hazırlanması için, VP aşılanmış dokumasız kumaş fiberler Cu(II) iyonları ile yüklenmiştir. PLE'nin bakır yükleme kapasitesinin 0.5 mmol Cu(II)/g polimer olduğu belirlenmiştir. As(V) adsorpsiyon deneyleri, kesikli yöntemde farklı adsorpsiyon zamanı, pH (3-9) ve başlangıç As(V) konsantrasyonlarında gerçekleştirilmiştir. PLE adsorbent üzerine As(V) adsorpsiyonunun hızlı olduğu gözlenmiş ve adsorpsiyon dengesine 4 saat içinde ulaşılmıştır. Cu(II) yüklenmiş VP aşılanmış NWF tarafından adsorplanan As(V) miktarının geniş pH aralığında önemli bir değişiklik göstermediği tespit edilmiştir. PLE'nin adsorpsiyon davranışı üzerine başlangıç As(V) konsantrasyonunun etkisi, farklı As(V) konsantrasyonlarında (0.1-500 ppm) pH 7'de belirlenmiştir. Yeni PLE adsorbentinin, As(V) için yüksek afinite gösterdiği gözlenmiştir. Langmuir izoterminden maksimum adsorpsiyon kapasitesi, 51 mg As(V)/g PLE olduğu bulunmuştur. Langmuir izoterminden bulunan teorik adsorpsiyon kapasitesinin, 47 mg As(V)/g PLE olarak bulunan deneysel adsorpsiyon kapasitesi ile uyumlu olduğu bulunmuştur.

Anahtar Kelimeler
4-vinil piridin, radyasyonla başlatılan aşı polimerizasyonu, Cu(II)-yüklenmiş VP aşılanmış adsorbent, As(V) adsorpsiyonu.

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INTRODUCTION

Arsenic is one of the most toxic and ubiquitous element for human health and the environment [1-2]. Arsenic exists in natural waters both as inorganic and organic arsenic. In natural waters, arsenic mainly exists as arsenate, As (V) and arsenite, As (III) [3]. Arsenate is predominat under oxidizing conditions in water, while arsenite becomes predominant under nonoxidizing conditions. At about neutral pH, the predominant species are $H_2AsO_4^-$ and $HAsO_4^{2-}$ for arsenate, and uncharged H_3AsO_3 for arsenite. Arsenic toxicity is dependent on its chemical form. Arsenic can originate either from anthropogenic activities such as agricultural pesticides, wood preservatives, mining activities, and electronic industry or from natural erosion of arsenic containing rocks. Arsenic is toxic and carcinogenic element that exists primarily as oxyanion forms in the water sources and has become a worldwide environmental issue. The World Health Organization (WHO) guideline value, the European Community's (EC) maximum admissible concentration, and the United States Environmental Protection Agency (USEPA) limit value for As in drinking water is 10 μg/L [4]. Therefore, the removal of arsenic from water sources is one of the most essential issues, with regard to environmental protection and conservation. The major treatment technologies for the removal of arsenic include chemical precipitation, membrane filtration, adsorption and ion exchange processes. Recently, adsorbents loaded with a transition metal having polymeric ligand exchanger (PLE) properties have been applied to remove arsenic from water sources. A PLE consists of a polymeric support with chelating functional groups that can bind tightly to a transition metal ion, which can remove variety of ions from aqueous systems by complex formation. It is known that Cu(II), Fe(III), Al(III), Y(III), La(III), Mo(VI) Ti(IV) and Zr(IV) have specific affinity for oxoanions [5-13]. Various transition metal-loaded synthetic or natural adsorbent materials such as Fe(III)-loaded Uniselec UR-10 resin (bearing o-hydroxybenzylnitrilodiacetic groups) [14], Fe(III)-loaded (lysine-N$^\alpha$,N$^\alpha$-diacetic acid) resin [15], Fe(III)-loaded Chelex-100 (iminodiacetic acid) resin [16], Fe(III)-loaded Lewatit TP 207 (iminodiacetic acid) resin [17], Fe(III)-loaded poly(hydroxamic) acid resin [18], Fe(III)-loaded Dow XFS-4195 (bis(2-picolylamine)) resin [19], Fe(III)-doped alginate gels [20], Cu(II)-loaded Dow 2N, Cu(II)-loaded Dow 3N [21], Cu(II)-loaded poly (4-vinylpyridine) [22], Zr(IV)-loaded Amberlite XAD-7 (poly(methylmethacrylate)) [23], Zr(IV)-loaded (lysine-N$^\alpha$,N$^\alpha$-diacetic acid) resin [24], Zr(IV)-loaded 2-hydroxyethyl-methacrylate phosphoric acid fiber [25], Zr(IV)-loaded phosphoric acid chelating resin [26], La(III)-loaded Amberlite IRC-718 (iminodiacetic acid) resin [27], La(III)-loaded poly(hydroxamic) acid resin [28], Ce(IV)-loaded Amberlite IRC-718 (iminodiacetic acid) resin [29], Ti(IV)-loaded poly(hydroxamic acid) resin [30], Ti(IV)-loaded Amberlite XAD-7 resin [31], Mo(VI)-loaded chitosan gel beds [32], Fe(III)-loaded cellulose [33] have been developed and used for the removal of arsenic from aqueous solutions.

In this study, grafted nonwoven fabric was prepared by radiation induced graft polymerization of vinyl pyridine on the polyethylene/polypropylene (PE/PP) nonwoven fiber and then VP grafted PE/PP nonwoven fabric was loaded with Cu(II) ions. The optimum degree of grafting was found to be 150% at 30 kGy irradiation dose, 5% monomer concentration, 0.5% tween 20 concentration in water and 3 h reaction time. The effect of solution pH, contact time, and the initial As(V) ion concentration on the adsorption capacity of the Cu(II) loaded VP grafted nonwoven fibers were investigated. Desorption of As(V) ions from the PLE fibers was also examined using 4% NaCl solution.

Experimental

Materials and Methods

PE/PP nonwoven fabric was supplied by Kurashiki Senl Kako Co. Okayama, Japan. 4-Vinyl pyridine (VP) was purchased from Kanto Chemical, Tokyo, Japan and used without purification. Other reagents were of analytical or higher grade and used as received.

Preparation of Cu(II) Loaded VP Grafted NWF Adsorbent

The PE/PP nonwoven fabrics were cut into pieces of 10 cm by 5 cm and packed into polyethylene bags in nitrogen atmosphere. The trunk polymer was irradiated by electron beam at a voltage of 2 MeV and a current of 3 mA in nitrogen atmosphere at dry ice temperature (-20°C). After irradiation, nonwoven fabrics were immersed in VP emulsion medium. The detailed experimental conditions of VP grafting were given in our previous paper [34].

For the preparation of Cu(II) loaded adsorbent, first, VP grafted nonwoven fabrics were conditioned by successive washings with 1.0 M HCl and 1.0 M NaOH solutions. Then, VP grafted nonwoven fabrics was treated twice with 500 ppm Cu(II) solution at pH 5 for 10 h at room temperature. Finally, Cu(II) loaded-VP grafted nonwoven fabrics were washed several times with ultrapure water until all the non-chelated Cu(II) was removed and dried at 40°C for 6 h.

Determination of Cu(II) loading capacity of the prepared fabric was carried out by desorbing Cu(II) ions from a known amount of Cu(II)-loaded VP grafted nonwoven fabric with 3M NH_3 solution and determining the concentration of Cu(II) ions in the collected solution by ICP-MS (Thermo Fisher Scientific, XSeries 2, Germany).

As(V) Adsorption Experiment

As(V) adsorption studies at varying pH

The effect of pH on As(V) removal by using polymeric ligand exchanger was investigated at different pH values. The pH was adjusted by NaOH and HCl solutions. 0.03 g of Cu(II)-loaded VP grafted nonwoven fabric were treated with 10 ppm of As(V) solution at different pH values ranging from 3.00 to 9.00. As(V) concentrations remaining in solution after adsorption were determined by ICP-MS. The adsorbed amounts were calculated by using an Equation 1.

$$q_e = \frac{(C_0 - C_e) \times V}{m} \qquad (1)$$

where, q_e is the amount of As(V) ions adsorbed onto unit dry mass of VP grafted NWF (mg/g), C_0 and C_e are the concentrations of As(V) in solution (mg/L) initially and after treatment for a certain period of time, respectively. V, is the volume of aqueous solution (L) and m is the amount of dry VP grafted NWF (g).

As(V) Adsorption Studies At Different Contact Time and Initial As(V) Concentrations

0.03 g of Cu-loaded VP grafted NWF adsorbent was treated with As(V) solution (100 mL) in order to get information on the relative performance of newly prepared PLE. The adsorption kinetics of As(V) from 10 ppm As(V) solution was followed at pH 7.00. For this purpose the amount of adsorbed As(V) was checked at different time intervals.

Batch adsorption experiments with ~ 0.03 g of Cu(II)-loaded VP grafted nonwoven fabrics for As(V) removal were also carried out in 30 mL of As(V) of desired concentrations both at low As(V) concentrations (0.1 –5 ppm) and at high As(V) concentrations (50 – 500 ppm). As(V) concentrations remaining in the solution after every adsorption stage were determined by ICP-MS. The amounts of As(V) ions adsorbed per unit mass of the Cu-loaded VP grafted NWF were also evaluated by using Eq. 1. Desorption of As(V) was performed by 4 % NaCl solution.

Results and Discussion

Preparation of the Cu(II) Loaded VP Grafted PE/PP Nonwoven Fabric

Radiation induced grafting method was used to prepare VP grafted PE/PP nonwoven fiber by initially grafting of VP onto inert nonwoven polyethylene/polypropylene fibers by using accelerated electrons. 30 kGy irradiation dose, 5% monomer concentration, 0.5% tween 20 concentration in water and 3 h reaction time were selected as optimum conditions for the preparation of VP grafted nonwoven fabrics. The detailed preparation conditions of VP grafted NWF were given in our previous paper [34]. The preparation Scheme of PLE adsorbent was given in Figure 1.

To prepare the PLEs for the removal of As(V), VP grafted PE/PP nonwoven fabrics were loaded with Cu(II) ions. VP grafted PE/PP nonwoven fabrics exhibited a high affinity for Cu(II) ion with the highest uptake value of 0.5 mmol Cu(II) ion/g of VP grafted dry fabric from 500 ppm Cu(II) ion solution at pH 5.00 in twice. These fabrics

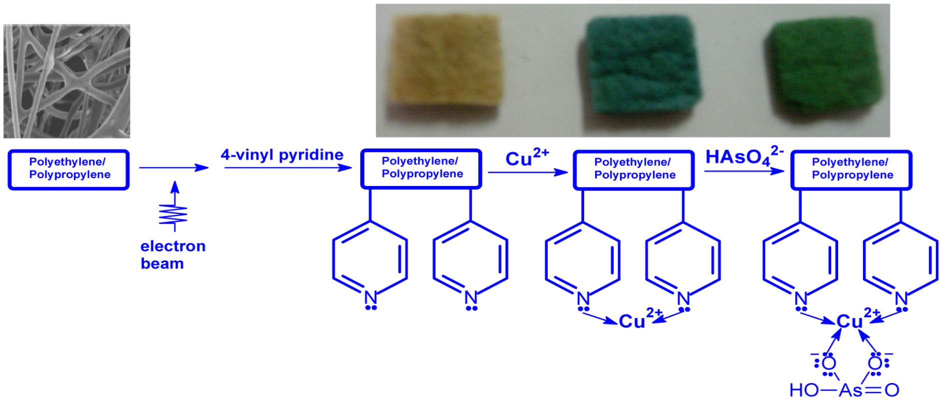

Figure 1. Preparation scheme of Cu(II) loaded VP grafted NWF.

were used as PLEs for further As(V) adsorption experiments.

As(V) Adsorption Studies

Effect of pH on As(V) adsorption

The pH value of the aqueous solution plays a major role on the arsenic adsorption capacity. The pH of the aqueous solution is an important variable that influences the adsorption process especially in ion exchangers. Knowledge of the speciation of arsenic, the partition of the arsenic species as a function of pH, is fundamental to understand the sorption process. In the typical pH range of natural waters, arsenate ions are present as $H_2AsO_4^-$ and $HAsO_4^{2-}$. Figure 2 shows the relationships between As(V) adsorption and solution pH. The As(V) adsorption was studied from pH 3.00 to 9.00 with an initial aqueous As(V) concentration of 10 mg/L. It was found that As(V) adsorption did not change virtually within pH values from 3.00 to 9.00. This result shows that adsorbent material can effectively remove different forms of arsenate ions.

Adsorption kinetics

Kinetics of the adsorption represents the speed with which reaction takes place. Figure 3 shows the adsorption kinetics of As(V) onto Cu(II) loaded VP grafted NWF. High adsorption rate was observed within 2 hours and the plateau value (i.e., adsorption equilibrium) was reached approximately at 12 mg As(V)/g PLE from 10 ppm initial As(V) solution within 4 h.

Two different kinetic models (the pseudo-first-order kinetic model and pseudo-second-order kinetic model) were used to fit the experimental data to explain the mechanism of As(V) adsorption onto Cu(II) loaded VP grafted NWF.

The formula of pseudo-first-order kinetic model for the adsorption of solid/liquid systems is given as the following equation [35]:

$$\frac{dq_t}{dt} = k_1 (q_e - q_t) \qquad (2)$$

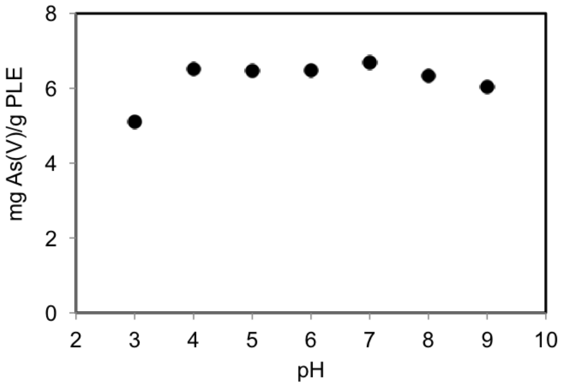

Figure 2. The effect of pH on As(V) adsorption onto Cu(II) loaded VP grafted NWF.

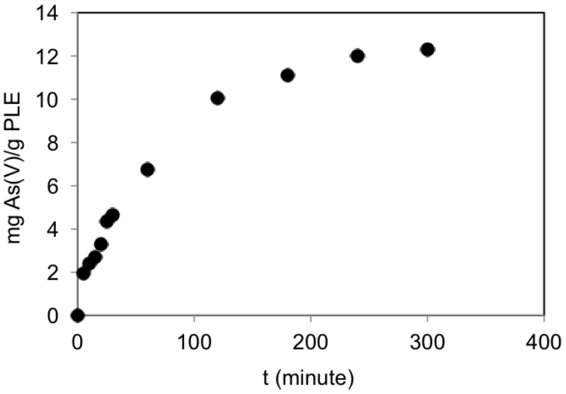

Figure 3. Adsorption kinetics of As(V) adsorption onto Cu(II) loaded VP grafted NWF.

rearranged as follows:

$$q_t = q_e\,(1 - e^{-k_1 t}) \qquad (3)$$

The linear form of this equation is expressed as follows:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \qquad (4)$$

first-order reaction where q_t is the adsorption capacity at time t (mg.g^{-1}) and k_1 (min^{-1}) is the rate constant of the pseudo-first order adsorption, was applied to the present study of As(V) adsorption. The rate constant, k_1 and correlation coefficients were calculated from the linear plots of $\ln(q_e - q_t)$ versus t in Figure 4 and listed in Table 1. The low correlation coefficient for pseudo-first-order kinetic model was observed, indicating a poor pseudo first-order fit to the experimental data.

The kinetic data were also analyzed using Ho's pseudo-second-order kinetics model. This model is based on the assumption the adsorption follows second order chemisorption from liquid solutions [36]. It can be expressed as Equation 5.

$$\frac{dq_t}{dt} = k_2\,(q_e - q_t)^2 \qquad (5)$$

Integrating this for the boundary conditions *t* = 0 to *t* = *t* and $q_t = 0$ to $q_t = q_t$, gives:

$$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t} \qquad (6)$$

The linear form of this equation is expressed as follows:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad (7)$$

where k_2 (g.mg^{-1}·min^{-1}) is the rate constant of the pseudo-second-order adsorption. The rate constant k_2, the q_e value and the corresponding linear regression correlation coefficient r^2 were calculated from the linear plots of t/q_t versus t in Figure 5 and given in Table 1. The values of q_e (cal), and k_2 were 15.11 mg·g^{-1} and 0.00102 min^{-1}, respectively. The straight lines with extremely high correlation coefficients (r^2 = 0.9966) were obtained. In addition, the calculated q_e values also agreed with the experimental data in the case of pseudo-second-order kinetics. These results suggested that the adsorption data were well represented by pseudo-second-order kinetics model and the rate-limiting step of As(V) onto Cu(II) loaded VP grafted NWF adsorbent may be chemical sorption or chemisorption.

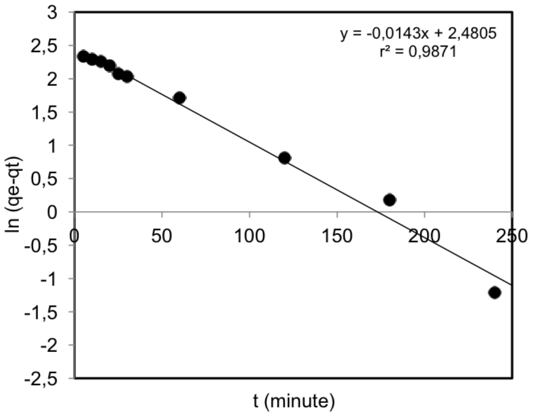

Figure 4. Linear model of pseudo-first-order reaction.

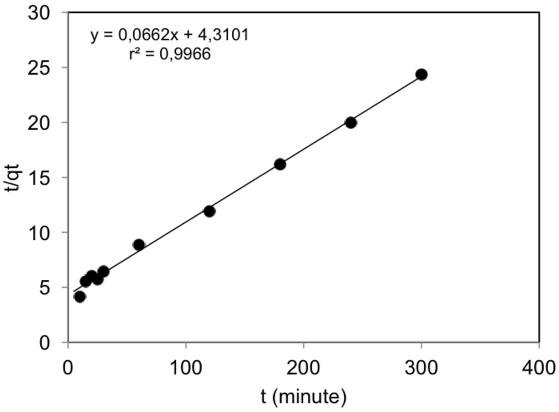

Figure 5. Linear model of pseudo-second-order reaction.

Table 1. Comparison of the pseudo-first and pseudo-second-order constants.

q_{eq} (exp) (mg.g^{-1})	Pseudo-first-order model			Pseudo-second-order model		
	k_1 (min^{-1})	q_e (cal) (mg·g^{-1})	r^2	k_2 (g.mg^{-1}·min^{-1})	q_e (cal) (mg·g^{-1})	r^2
12.3	0.0143	12.0	0.9871	0.001017	15.11	0.9966

Effect of initial As(V) concentration on adsorption

The effect of initial concentration of As(V) on the adsorption behavior of Cu(II) loaded-VP grafted nonwoven fabrics was determined at low (0.1 – 5 ppm) and high (50 – 500 ppm) As(V) concentrations level at pH 7.00 and given in Figures 6 and 7, respectively. These results showed that the adsorption of As(V) ions increases linearly with increasing initial As(V) concentration especially at low As(V) concentration and adsorption equilibrium was reached after 250 ppm initial As(V) concentration. Adsorbed As(V) amounts were found to be 4.07 mg As(V)/g PLE and 47 mg As(V)/g PLE for low As(V) concentration (1 ppm) and high As(V) concentration (500 ppm), respectively. These results show that the developed adsorbent material is quite effective in removing As(V) in wide concentration range.

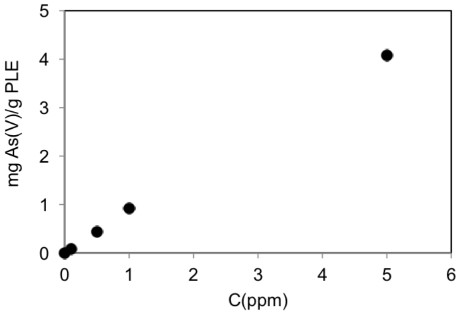

Figure 6. As(V) adsorption onto PLE at low concentration levels.

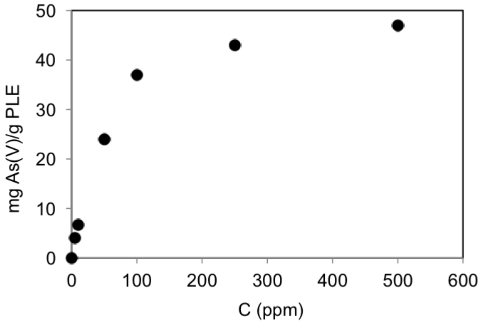

Figure 7. As(V) adsorption onto PLE at high concentration levels.

Adsorption isotherms of Cu(II) loaded VP grafted NWF was analyzed according to the linear form of Langmuir isotherms for As(V) by using Equation 8,

$$\frac{C_e}{q_e} = (1/K_L q_{mon}) + (1/q_{mon})C_e \qquad (8)$$

where C_e is the equilibrium concentration of adsorbate in solution, q_e represents the adsorbed As(V) per unit mass of adsorbent at equilibrium. q_{mon} denotes the amount of adsorption corresponding to complete monolayer coverage. K_L is the Langmuir constant. A plot of C_e/q_e versus C_e would give K_L and q_{mon} [37].

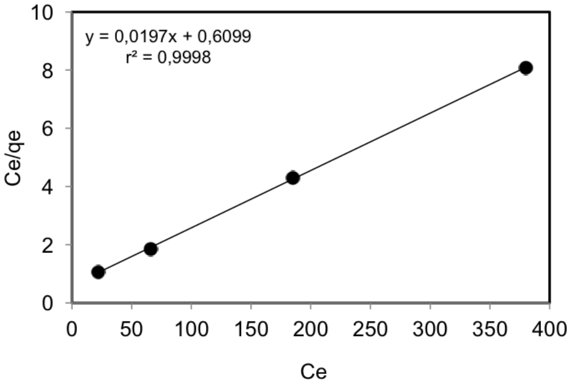

Figure 8. Langmuir isotherm for As(V) adsorption onto PLE.

Table 2. K_L and q_{mon} value determined from Langmuir equation for adsorption of As(V)

K_L (L.mg^{-1})	3.2 x 10^{-2}
q_{mon} (mg.g^{-1})	51

The plot of isotherm is shown in Figure 8 and observed to be linear over the whole concentration range studied. K_L and q_{mon} values which were calculated from Langmuir equation are given in Table 2. The constant, K_L, contains enthalphic interaction of the binding of As(V) with PLE, and can be found from the intercept of the lines given in Figure 8. As can be seen from the Table 2, K_L value of PLE indicate the favorable interaction of accessible As(V) sites on the surface of the polymer. q_{mon} is a quantity representing adsorption capacity, also known as monolayer coverage of the surface. q_{mon} value of PLE from the Langmuir equation for As(V) was found to be 51 mg/g, respectively. This is well-matched with experimental result previously found and reported above. This result show that theoretical adsorption capacity is good accordance with the experimental capacity.

Table 3. As(V) adsorption capacities onto various PLE adsorbents.

Polimeric ligand exchanger	mg As(V)/g polymer	Ref.
Fe(III) loaded chelating resin (lysine-N^{α},N^{α}-diacetic acid)	55.44	[38]
Zr(IV) loaded chelating resin (lysine-N^{α},N^{α}-diacetic acid)	88.73 (from spring water)	[39]
Zr(IV) loaded chelating resin (phosphoric acid grafted fiber)	149.9 (column capacity)	[25]
Mo(VI) loaded citosan gel sphere	200 (column capacity)	[11]
Fe(III) loaded chelating resin	60	[40]
Cu (II) loaded –Dow 2N resin (picolyl amine group containing resin)	44	[41]
Cu(II)-Loaded 4-Vinyl Pyridine	47	This study

The comparison of maximum As(V) adsorption capacities on various adsorbents are listed in Table 3. The As(V) adsorption capacities by other adsorbents are in the range of 55 - 200 mg As(V)/g polymer. Higher As(V) adsorption values were shown in column mode experiment. These values were not exactly comparable with our data. It can be seen that compared to the results published in the literature, Cu(II)-loaded VP grafted nonwoven fabrics used in this study shows a comparable As(V) adsorption capacity of 47 mg As(V)/g PLE. Cu(II)-loaded VP grafted nonwoven fabrics has a potential for As(V) removal from wastewater.

Desorption studies

4% NaCl solution was used for regeneration of As(V) adsorbed Cu(II) loaded-VP grafted nonwoven fabrics. High regeneration efficiencies were achieved with a As(V) recovery of nearly 100%.

Conclusion

In order to introduce specific functional groups to the trunk polymer, VP was first grafted onto pre-irradiated fabrics in emulsion medium and then VP adsorbent were conducted with Cu(II) ions for the preparation of PLE. The Cu(II) ion load capacity was found to be 0.5 mmol/g polymer. As(V) removal capacity was obtained 47 mg As(V)/g PLE from 500 ppm As(V) initial solution at pH 7.00. 4% NaCl solution was used for regeneration of As(V) adsorbed Cu(II) loaded VP grafted NWF with 100% regeneration efficiency. Langmuir type of adsorption isotherm was found to be linearly fitted with adsorption data of As(V) with correlation coefficient of $R^2 > 0.999$. It was concluded that Cu(II) loaded VP grafted adsorbent can be considered as a promising adsorbent for the removal of As(V).

Acknowledgements

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