

Combined Use of Chitosan and Alginate in the Treatment of Wastewater

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ABSTRACT: This study examined the combined use of chitosan and sodium alginate in the treatment of wastewater containing heavy-metal ions and dye. Wastewater samples were divided into two equal parts before chitosan and sodium alginate solutions were added to each part. When these two solutions were mixed together, the heavy-metal ions and dye molecules were separated from the water as the positively charged chitosan and the negatively charged sodium alginate precipitated each other. The effects of the

concentration and ratio of chitosan and sodium alginate, the treatment temperature, and the time on the efficiency of metal-ion and dye removal were investigated. The results showed that when used in combination, sodium alginate and chitosan were effective in removing copper, cadmium, lead, and silver ions as well as acid dye molecules © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 3581–3587, 2007

Key words: chitosan; dyes/pigments; waste

INTRODUCTION

Heavy-metal ions and waste dye are two major industrial pollutants, and many methods have been developed to remove them from wastewater.^{1–4} In recent years, with heavy-metal ions, researchers have worked on a number of inexpensive materials, such as chitosan, zeolites, and other absorbents, that have high absorption capacities and are locally available.^{5–8} These low-cost absorbents have demonstrated good removal capabilities for certain metal ions. Similarly, many attempts have also been made to use biomass to absorb waste dyes. Chandran et al.⁹ studied the use of agricultural residues in treating textile effluents. They found that agricultural residues such as barley husk, sugarcane bagasse, and wheat straw were effective in dye removal.

Chitosan is an outstanding absorbent capable of absorbing 815, 273, and 250 mg/g Hg(II), Cr(VI), and Cd(II), respectively, and its absorption capacity can be further enhanced by chemical modification.^{6,7} As a natural, hydrophilic polymer, chitosan has also been used for waste-dye removal. Chitosan is particularly suited for this purpose because it has primary amine groups on the polymer chain, which help with dye absorption. Research has shown that one effective way of using chitosan to remove waste dye

is to convert it into beads because this helps to increase the surface area.^{10,11} The adsorption mechanism is electrostatic interactions between the dye and chitosan beads. The adsorption capacity for dyes at 30°C with swollen chitosan beads is around 5 times greater than that with common chitosan flakes.

Similar to chitosan, alginate is also a natural polymer with abundant natural resources.¹² As a polymeric acid, alginate can form an insoluble salt with metal ions, so it can precipitate heavy-metal ions from aqueous solutions. Alginate has polar groups such as —OH and —COO[−] in its chemical structure, which can absorb dye molecules.

As a polymeric amine, chitosan is positively charged when dissolved in aqueous solutions. On the other hand, as a polymeric acid, alginate is negatively charged in solution. When chitosan and alginate solutions are mixed, the positively charged chitosan and the negatively charged alginate can precipitate each other and separate from the solution. At the same time, the heavy-metal ions and waste-dye molecules are absorbed onto the precipitate and removed from the water.

This work assesses the feasibility of using the ionic interactions of chitosan and alginate and studies the combined use of chitosan and alginate in removing heavy-metal ions and dye from wastewater.

EXPERIMENTAL

Treatment of wastewater containing heavy-metal ions

The sodium alginate and chitosan powders were commercial-grade materials supplied by Bright

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Moon Group (Qingdao City, China) and Xindie, Ltd. (Dalian City, China), respectively. The sodium alginate had a viscosity in a 1% solution of about 40 cps and had a mannuronate content of about 40%. The chitosan had a degree of deacetylation of about 85%.

Sodium alginate and chitosan powders were dissolved in water and 1% aqueous acetic acid solutions, respectively, to form the treatment solutions. The concentrations were both 10 g/L.

CuSO₄ was dissolved in water to prepare a solution containing ~ 1000 ug/mL Cu(II) ions. When sodium alginate or chitosan solutions were used alone, 100-mL CuSO₄ solutions were measured into 250-mL beakers, and 0, 10, 25, 50, or 100 mL of either a chitosan or sodium alginate solution was added. After thorough mixing, the mixture was left standing for 24 h at room temperature. The solutions were then filtered and diluted (1 : 200) before the Cu(II) concentration was measured with an atomic absorption spectrometer.

When the sodium alginate and chitosan solutions were used in combination, to a 100-mL CuSO₄ solution was first added 0, 10, 25, 50, or 100 mL of either a chitosan or sodium alginate solution; after mixing, a 20-mL solution was taken from the chitosan or sodium alginate mixture, and they were mixed together. After being left standing for 24 h at room temperature, the solution was filtered and diluted (1 : 200) before the Cu(II) concentration was measured with the atomic absorption spectrometer.

When we studied the effect of the ratio of chitosan to sodium alginate, a 100-mL CuSO₄ solution and a 20-mL chitosan solution were first measured into five 250-mL beakers; to the mixtures were then added 2-, 4-, 6-, 10-, and 20-mL sodium alginate solutions. Separately, a 100-mL CuSO₄ solution and a 20-mL sodium alginate solution were first measured into five 250-mL beakers; to the mixtures were then added 2-, 4-, 6-, 10-, and 20-mL chitosan solutions. After being left standing for 24 h at room temperature, the solutions were filtered and diluted (1 : 200) before the Cu(II) concentration was measured with the atomic absorption spectrometer.

When we studied the effect of the temperature, a 12.5-mL chitosan solution and a 12.5-mL sodium alginate solution were added to a 100-mL CuSO₄ solution, and the mixture was stored at 25, 30, 35, 40, 45, 50, 55, and 60°C for 24 h before the Cu(II)-ion concentration was measured.

When we studied the effect of the reaction time, a 12.5-mL chitosan solution and a 12.5-mL sodium alginate solution were added to a 100-mL CuSO₄ solution; after 0.25, 0.5, 1, 1.5, 2, 2.5, 3, 3.5, 4, 5, 6, 7, 8, 9, and 10 h, the treatment was terminated, and the Cu(II) concentration was measured.

When we studied the treatment efficiency for cadmium, lead, and silver ions, CdCl₂, Pb(NO₃)₂, and

AgNO₃ were used to prepare aqueous solutions containing ~1000 ug/mL metal ions. The treatment with cadmium, lead, and silver ions was carried out in a similar way to that used for the Cu(II) ions.

Treatment of wastewater containing dye

An acid dye [trade name Chrome Blue K; the chemical structure is 3-(2-OHC₆H₃SO₃N : N)4,5(OH)₂C₁₀H₃-2,7(SO₃Na)₂] was used to prepare sample wastewater. Aqueous solutions containing 1 g/L Chrome Blue K were first prepared. They were then diluted (1 : 50) to produce a wastewater sample containing 20 ug/mL dye.

The chitosan and alginate were dissolved to produce solutions containing 10 g/L chitosan and alginate, respectively. Chitosan was dissolved in a 1% aqueous acetic acid solution, whereas alginate was dissolved in pure water.

The 20 ug/mL dye solution was further diluted to 1.25, 2.5, 5, 10, and 20 ug/mL before the light absorption and transmission of these solutions were measured on a spectrometer to establish a calibration curve.

The treatment of wastewater with chitosan and alginate solutions was carried out under room temperature. One hundred milliliters each of the 20 ug/mL Chrome Blue K wastewater was measured into two beakers. Chitosan solutions were added to one beaker, whereas alginate solutions were added to the other beaker. Both solutions were mixed thoroughly before they were brought together and stirred at 100 rpm on a magnetic stirrer. The solution and the precipitate were separated, and the light absorbency and transmission were analyzed for the solution before the dye concentration was calculated from the calibration curve.

RESULTS AND DISCUSSION

Removal of heavy-metal ions from wastewater

After chitosan and sodium alginate solutions were added to CuSO₄ solutions, clear differences could be observed with the chitosan and sodium alginate when they were used alone. As shown in Figure 1, although both resulted in the precipitation of the polymer, the alginate solution produced a gel-like precipitate, whereas the chitosan produced a loose colloid. Phase separation between the precipitate and water was not clear when chitosan and sodium alginate were used alone. However, when chitosan and alginate were used in combination, because of the neutralization of the electric charge, there was a clear separation of the precipitate from the solution.

The absorption of heavy-metal ions by chitosan and sodium alginate can be quantified in two ways,

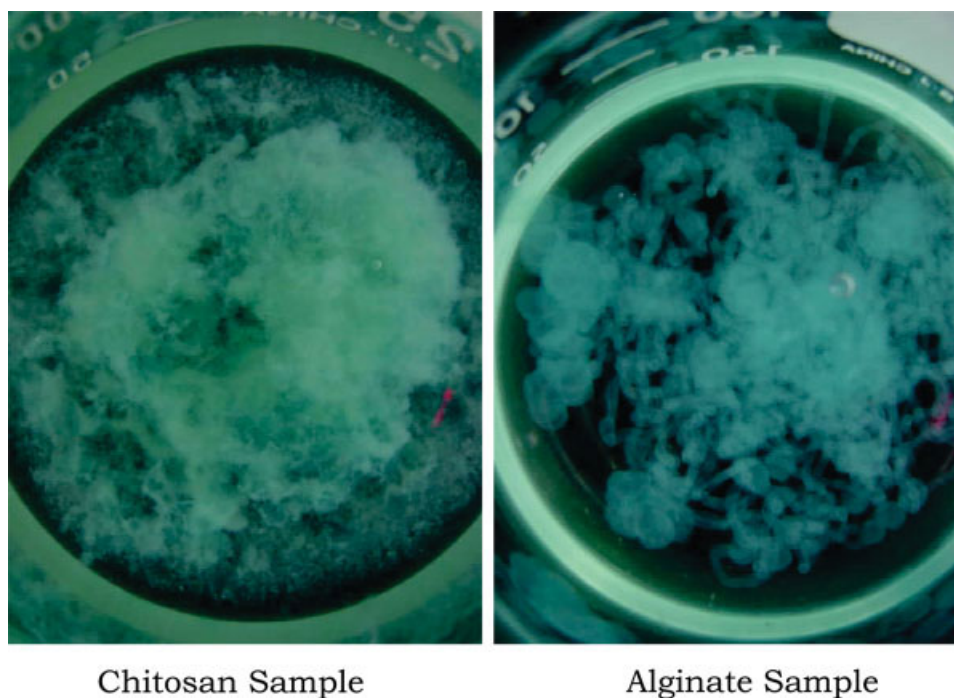


Figure 1 Photographs of CuSO_4 solutions after the addition of chitosan and sodium alginate solutions. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

that is, the absorption capacity and rate of removal. The rate of removal measures the quantity as a percentage of the heavy-metal ions removed from the original solution, whereas the absorption capacity measures the amount of heavy-metal ions absorbed per unit of weight of the absorbent. The rate of removal and absorption capacity can be calculated with the following equations:

$$R(\%) = (C_0 - C_1)/C_0 \times 100\%$$

$$Q'(C_0 - C_1) \times V/1000m$$

where R is the rate of removal (%), C_0 is the concentration of heavy-metal ions in the original solution ($\mu\text{g}/\text{mL}$), C_1 is the concentration of heavy-metal ions

in the treated solution ($\mu\text{g}/\text{mL}$), Q is the absorption capacity (mg of heavy-metal ions removed/g of the absorbent), V is the volume of the solution being treated (mL), and m is the weight of the absorbent used (g).

Effect of the chitosan and sodium alginate concentrations on heavy-metal-ion removal

Table I shows the $\text{Cu}(\text{II})$ concentration after different amounts of chitosan and sodium alginate solutions were added to 100-mL CuSO_4 solutions. The same amount of chitosan and sodium alginate produced remarkably different results. Sodium alginate had a much better removal rate than chitosan. The removal

TABLE I
Effects of Chitosan and Sodium Alginate Concentrations on Heavy-Metal-Ion Removal

Amount added (mL)		0	10	25	50	100
Cu(II) concentration ($\mu\text{g}/\text{mL}$) ^a	Sodium alginate	4.180	2.868	1.813	0.806	0.000
	Chitosan	4.338	3.593	2.468	1.560	1.465
	1 : 1 mixture	4.226	3.439	2.319	1.365	0.735
Removal rate (%)	Sodium alginate	0	31.39	56.63	80.72	100.00
	Chitosan	0	17.17	43.11	64.04	66.23
	1 : 1 mixture	0	18.62	45.13	67.70	82.61
Absorption capacity [mg of $\text{Cu}(\text{II})/\text{g}$ of polymer]	Sodium alginate	0	262.40	189.36	134.96	83.60
	Chitosan	0	149.00	149.60	111.12	57.46
	1 : 1 mixture	0	206	118.24	114.44	69.70

^a For filtered solutions after 1 : 200 dilution.

TABLE II
Effect of the Ratio of Chitosan to Sodium Alginate on the Treatment Results

Chitosan (mL)	Sodium alginate (mL)	Cu(II) concentration ($\mu\text{g}/\text{mL}$) ^a	Removal rate (%)	Absorption capacity [mg of Cu(II)/g of polymer]
0	0	4.312	0	0
20	2	2.834	34.28	134.36
20	4	2.723	36.85	132.42
20	6	2.596	39.80	128.7
20	10	2.468	42.76	122.92
20	20	1.987	53.92	116.25
10	20	2.278	47.17	135.6
6	20	2.416	43.97	142.18
4	20	2.532	41.28	148.33
2	20	2.627	39.08	153.19

^a For filtered solutions after 1 : 200 dilution.

rate was 80.72% when a 50-mL sodium alginate solution was added, and the Cu(II) ions in the original solution could be completely removed when 100-mL sodium alginate solution was added.

The removal rate for chitosan was below 70%. It reached an equilibrium when a 50-mL chitosan solution was added; more chitosan did not produce a better removal rate. When chitosan and sodium alginate were used in combination, the removal rate was not as good as when sodium alginate was used alone, but it was better than when chitosan was used alone.

When the concentrations of chitosan and sodium alginate were low, the polymeric molecules could fully combine with the heavy-metal ions, so the absorption capacity was high. From results shown in Table I, it can be calculated that 1 g of sodium alginate can absorb up to 262.40 mg of Cu(II) ions. When the concentration increased, the rate of removal increased; however, the absorption capacity showed a small decline.

Effect of the ratio of chitosan to sodium alginate

Table II shows the effect of the ratio of chitosan to sodium alginate on the treatment results. In general, the removal rate is better when the amount of sodium alginate is more than that of chitosan. As pointed out earlier, sodium alginate combines heavy-metal ions through the formation of an insoluble salt, and gelation occurs when a sodium alginate solution is added to a solution containing Cu(II) ions. For chitosan, it combines with heavy-metal ions through chelation, and a loose colloid is formed. When the amount of alginate is more than that of chitosan, the alginate combines with heavy-metal ions to form an insoluble gel, and the chitosan is attached to the gelled structure through electrostatic

forces. On the other hand, when chitosan is in excess, the excess amount of chitosan that is not coagulated with the sodium alginate is dispersed in the solution, which can stabilize some of the heavy-metal ions in the solution, hence reducing the amount of heavy-metal ions absorbed onto the polymeric absorbent.

Effect of the treatment time

Figure 2 shows that at the beginning of the treatment, there was a rapid rise in the removal rate. The process then slowed down and reached an equilibrium after about 7 h. The absorption capacity for the sodium alginate/chitosan complex was about 66.40 mg/g at 25 min before it reached 147.52 mg/g at 10 h.

Effect of the temperature

Figure 3 shows the effect of the temperature on the removal rate. When the temperature was in the 25–45°C range, the absorption capacity was relatively

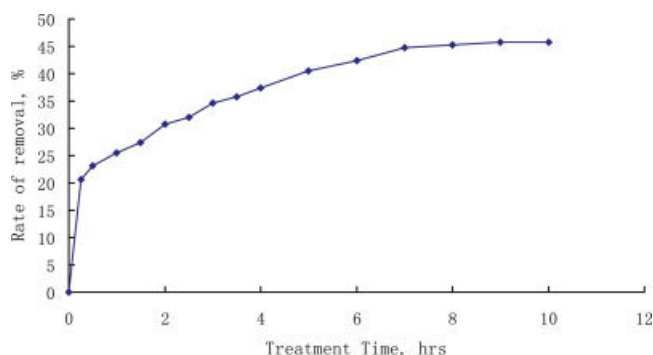


Figure 2 Effect of the time on the removal rate for Cu(II) ions. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

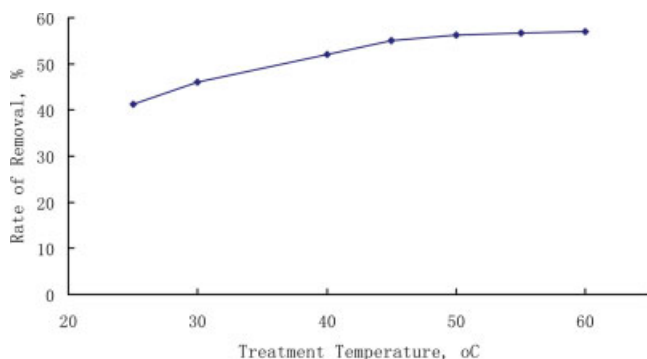


Figure 3 Effect of the temperature on the removal rate for Cu(II) ions. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

low. However, as the temperature rose, there was a significant rise in the absorption capacity. The absorption capacity for the sodium alginate/chitosan complex was 133.12 mg of Cu(II) per g of the polymer at 25°C. It rose to 177.28 mg/g at 45°C.

Treatment efficiency for different types of heavy-metal ions

In addition to Cu(II) ions, sodium alginate and chitosan were used to treat solutions containing Pb(II), Cd(II), and Ag(I) ions. Except for the silver ions, sodium alginate alone was able to produce precipitates when added to the solutions. The chitosan solution was able to produce a colloid precipitate only in the Cu(II) solution.

Because silver ions are monovalent metal ions, when the silver ions are in contact with sodium alginate, the resultant silver alginate is water-soluble. Although the literature suggests that chitosan can chelate silver ions, when a chitosan solution was in

contact with silver ions, no precipitation was observed in this study.

When sodium alginate and chitosan solutions were first dispersed into silver-containing solutions separately and then the two solutions were mixed together, the sodium alginate and chitosan formed an insoluble polymeric network. The structure of this network was similar to that of ethylenediamine-tetraacetic acid because it had both the primary amine and carboxylic acid groups. When sodium alginate and chitosan precipitated each other, the silver ions that were absorbed by them also separated from the solution.

Similarly to the results observed for the Cu(II) ions, the use of sodium alginate and chitosan in combination also produced enhanced treatment results for Cd(II) and Pb(II) ions. The separation of the polymeric precipitate from the solution was much better than when either sodium alginate or chitosan solutions were used alone.

Table III shows the removal rate and absorption capacity when the sodium alginate and chitosan solutions were used to treat wastewater containing Ag(I), Pb(II), and Cd(II) ions. For the Ag(I) ions, the absorption capacities for sodium alginate and chitosan were 122.08 and 69.28 mg/g, respectively. Sodium alginate had an excellent removal rate for Pb(II) ions, and it could completely remove the Pb(II) ions from wastewater, with an absorption capacity of 254.88 mg/g. Although the addition of a chitosan solution did not produce a visible precipitate, after filtration, 58.63% of the Pb(II) ions were removed from the wastewater.

Both the sodium alginate and chitosan had poor treatment efficiency against Cd(II) ions; the removal rates were 39.03 and 9.6%, respectively. The absorp-

TABLE III
Treatment Efficiencies for Different Types of Heavy-Metal Ions

	Heavy-metal-ion concentration ($\mu\text{g/mL}$) ^a	Removal rate (%)	Absorption capacity (mg of heavy-metal ions/g of polymer)
Ag(I)	Original solution	0	0
	+25-mL sodium alginate solution	1.926	44.21
	+25-mL chitosan solution	2.586	25.09
	+12.5-mL each of sodium alginate and chitosan solutions	2.480	28.16
Pb(II)	Original solution	0	0
	+25-mL sodium alginate solution	0	100
	+25-mL chitosan solution	1.318	58.63
	+12.5-mL each of sodium alginate and chitosan solutions	0.334	89.52
Cd(II)	Original solution	0	0
	+25-mL sodium alginate solution	1.267	39.03
	+25-mL chitosan solution	1.878	9.6
	+12.5-mL each of sodium alginate and chitosan solutions	1.585	23.72

^a For filtered solutions after 1 : 200 dilution.

tion capacities were 64.88 and 2.98 mg/g for sodium alginate and chitosan, respectively.

Removal of dye from wastewater

Although there have been many reports on the use of chitosan to remove waste dye, in this study, it was found that when the chitosan solution was used alone, it had no effect on waste-dye removal. After being added to the effluent, the chitosan solution quickly dispersed into the solution, resulting in a uniform mixture of chitosan and waste dye. There was no evidence of phase separation

Similarly, when an alginate solution was dispersed into the effluent, it also quickly dispersed, forming a transparent solution. Because both the chitosan and alginate were added in a solution form, their dispersion into the effluent was rapid, ensuring very good contact between the polymeric molecules and the waste dye. After the two solutions were brought together, the chitosan and alginate precipitated each other very quickly. Because the polymer concentration was low, the solution viscosity was low, and mixing was not difficult.

Effect of the chitosan and alginate concentrations on dye removal

Table IV shows the effect of the amount of the additive on dye removal when the weight/weight ratio of chitosan to alginate was 1 : 1. As the amount of the polymer increased, more and more dye was removed from the solution. A 86.2% removal rate was obtained when 3-mL chitosan and alginate solutions were added to a 100-mL 20 mg/L Chrome Blue K solution. The amount of the polymer was about 60 mg, whereas the amount of the dye removed was about 1.72 mg. The absorption capacity was 28.6 mg of dye/g of the polymer.

Effect of the ratio of chitosan to alginate on dye removal

Table V shows the effect of the ratio of chitosan to alginate on dye removal under room temperature.

TABLE IV
Effects of the Chitosan and Alginate Concentrations on Dye Removal

Alginate (mL)	Chitosan (mL)	Absorbency	Transmission	Dye removal rate (%)
0	0	1.38	4	0
1	1	0.57	27	58.7
2	2	0.23	59	83.3
3	3	0.19	65	86.2
4	4	0.20	63	85.5
5	5	0.23	60	83.3

TABLE V
The effect of the ratio between chitosan and alginate on dye removal

Amount of Alginate (ml)	Amount of Chitosan (ml)	Ratio Between Chitosan and Alginate	Absorbency	Dye Removal Rate
0	0		1.38	0%
1	10	1 : 10	1.20	13.0%
2	10	1 : 5	1.15	16.7%
5	10	1 : 2	1.25	9.4%
7.5	10	3 : 4	1.10	20.3%
10	7.5	4 : 3	0.28	79.7%
10	5	2 : 1	0.19	86.2%
10	2	5 : 1	0.28	79.7%
10	1	10 : 1	0.80	42.0%

The dye removal was more efficient when the amount of alginate exceeded that of chitosan. On the other hand, the removal rate deteriorated when the amount of chitosan exceeded that of alginate. The best ratio appeared to be 2 parts of alginate to 1 part of chitosan.

It was observed in the experiment that when the ratio of chitosan to alginate was about 1 : 1, the positive and negative charges could be neutralized the best. When chitosan exceeded alginate in solution, the excess amount of chitosan did not form a precipitate and was dispersed in the solution. It could stabilize some of the dye molecules in the solution through the amine groups. On the other hand, when the amount of alginate exceeded chitosan, the positively charged chitosan became fully precipitated in the presence of excess alginate. The amine groups helped to absorb dye molecules onto the precipitate, resulting in a good dye-removal rate.

Effect of the temperature and time on dye removal

Table VI shows the effect of the temperature on dye removal. In this experiment, 3-mL chitosan and alginate solutions were separately added to two 100-mL 20 mg/L Chrome Blue K solutions. After the two solutions were mixed together, the mixture was conditioned at different temperatures. Although there was a slight increase in the dye-removal rate with the increase in the temperature, the results in Table VI indicate that the temperature had little effect on dye removal. Similarly, because the dye molecules had

TABLE VI
Effect of temperature on dye removal

Temperature (°C)	Absorbency	Transmission	Dye Removal Rate
30	0.15	70	89.1%
50	0.12	76	91.3%
80	0.14	73	89.8%
100	0.29	52	79.0%

TABLE VII
Dye Removal Under Acidic and Alkali Conditions

Additive	Amount	pH	Absorbency	Transmission	Dye removal rate (%)
None	—	6	0.55	28	60.1
Acetic acid	1 mL	4	0.43	38	68.8
NaOH	1 g	13	0.80	15	42.0

sufficient contact with chitosan and alginate before the two solutions were mixed, the removal process was fairly rapid, and the time had little effect on dye removal.

Effect of pH

Table VII shows the dye-removal results under acidic and alkali conditions. In this experiment, 1-mL chitosan and alginate solutions were added to two sets of 100-mL 20 mg/L Chrome Blue K solutions before they were mixed together. It seems that dye removal was more effective in the acidic environment. This is because under acidic conditions, chitosan molecules are more positively charged and are effective in removing negatively charged acidic dye molecules. Under alkali conditions, the alginate is soluble, and this reduces its ability to precipitate chitosan.

CONCLUSIONS

This study has shown that both sodium alginate and chitosan can absorb significant amounts of heavy-metal ions. When placed in contact with heavy-metal ions, sodium alginate tends to form an insoluble gel structure, whereas chitosan forms a loose colloid structure. When sodium alginate and chitosan are used in combination, the separation of the polymers

containing the heavy-metal ions from the solution is much better than when the sodium alginate and chitosan solutions are used alone, and this improves the process for the removal of heavy-metal ions. The results of this study further indicate that for monovalent metal ions such as silver ions, it is difficult for either sodium alginate or chitosan solutions to precipitate the metal ions; however, when they are used in combination, there is a clear separation of the polymeric absorbent from the wastewater, resulting in the removal of the heavy-metal ions.

The combined use of chitosan and alginate is also effective in removing dye from wastewater. Because the chitosan and alginate are added to the waste solution in a liquid state, they can mix very well with the dye molecules. This makes the removal process fairly rapid, and it can be carried out at a low temperature. For the process to be more effective, the amount of alginate should preferably exceed that of chitosan.

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