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Spectrophotometric Studies on The Removal of Some Metal Ions and Methylene Blue Dye from Their Aqueous Solutions Using New Absorbents

Manal A. El-Sheikh[1,2,*], Ghadeer Almulhim[1], Hanan Alenazi[1], Yasah Al ruwaili[1], Haya Al ruwaili[1], Tahani Al enazi[1]

[1]*Chemistry Department, College of Science and Arts, AlQurayyat, Jouf University, Kingdom of Saudi Arabia*
[2]*Pretreatment and finishing of Cellulosic Fibers Department, Textile Research Division, National Research Centre, Egypt.*

HEAVY metal pollutants can be found in marine, ground, industrial and even treated waste waters. Although some heavy metals such as copper, selenium, and zinc are essential to human life and health, they can be toxic to living species when taken in excess. Metals, such as copper and nickel tend to accumulate in organs, disturbing important biochemical processes, and posing a serious health threat.

In the current work, carboxy methyl starch graft copolymerized with acrylamide (CMS-g-PAAm) and CMS-g-PAAm silver nanoparticles composite (CMS-g-PAAm-AgNPs) prepared in previous works were used as novel absorbents for the removal of Cu^{2+}, Co^{2+}, Ni^{2+} ions and methylene blue dye from their aqueous solutions. Reaction kinetics and % removal of the metal ions and methylene blue using CMS-g-PAAm and CMS-g-PAAm-AgNPs were studied. Metal ions and MB removal were determined by measuring the absorbance of the colored solution of Cu^{2+}, Co^{2+}, Ni^{2+} ions and methylene blue dye before and after treatment with CMS-g-PAAm and CMS-g-PAAm-AgNPs using spectrophotometer.

Results showed that the % removal of Cu^{++}, Co^{++}, and Ni^{++} is very high at the first 30 min then slowly increased. The % removal of ion for Cu^{++}, Co^{++}, and Ni^{++} reached up to 81.2%, 79.88, 77.97 respectively. Study also showed that the % of MB removal using both CMS-g-PAAm-AgNPs and CMS-g-PAAm reached up to 99.7 and 99.33% respectively. The novel absorbents are promising for use in waste-water treatments applications.

Keywords: Copper, Cobalt, Nickel, Methylene blue, Removal, CMS-g-PAAm, CMS-g-PAAm-AgNPs

Introduction:

Heavy metal ions constitute some of the most dangerous water-soluble pollutants. Exposure to low concentrations of heavy metal ions may provoke loss of weight, auditory disorders, diarrhea, muscular weakness, growth retardation, cardiovascular abnormalities, cancers, renal insufficiency and sleeping disturbances [1]. The importance of water, sanitation and hygiene for health and develop- ment has been reflected in the outcomes of a series of international policy forums. This phenomenon has yielded increasingly stricter environmental laws and regulations that require lower metal releases from all branches of industry [2]. Numerous treatment technologies to eliminate or reduce environmental problems have been developed, such as biodegradation, adsorption, and photocatalysis. Photocatalysis is an environmentally friendly process that utilizes irradiation energy for

catalytic reactions. Thus, the photocatalysis technology has been widely investigated for pollutant eradication and nano-photocatalysts including nano-TiO$_2$, nano-SrTiO$_3$, and nano-Fe$_2$O$_3$ have been intensively studied [3]. Adsorption also is an environmental treatment technology, and the adsorption process has been extensively examined for the elimination of organic substances or heavy metal ions from water and wastewater. The most common absorbents are porous materials, such as activated carbon, quartz sand, activated alumina, and zeolite. The development of nanotechnology at the end of the 20th century has widened the variety of adsorbents. The removal of heavy metals by nanoparticles has shown promising results with nanocrystalline titanium dioxide, nanoscale zero-valent iron, and so on [3]. Chemically modified cellulose, starch and chitosan was effectively used as absorbents for metal ion and dye removal [4-14]. Chemical modification of starch via grafting of vinyl monomers is one of the most effective methods to incorporate desirable properties into starch without sacrificing its biodegradable nature. Grafting of acrylamide onto starch or starch derivatives [6, 15] has been investigated. Starch graft copolymers have been used as hydrogels, flocculants, and ion exchangers [6]. In recent years, the study of organic–inorganic nanocomposites has become a very important field. Silver nanoparticles (AgNPs) doped TiO$_2$ nanoparticles was found to have catalytic activity for the degradation of some dyes. Increasing amounts of silver in Ag-doped TiO$_2$ significantly increases the rate of degradation of a model dye [16].

In the current work, carboxy methyl starch graft copolymerized with acrylamide (CMS-g-PAAm) and CMS-g-PAAm silver nanoparticles composite (CMS-g-PAAm-AgNPs) prepared according to reported method [15, 17] were utilized as novel absorbents used for the first time in the removal of Cu^{2+}, Co^{2+}, Ni^{2+} ions from aqueous colored solutions of CuSO$_4$.5H$_2$O, CoCl$_2$.6H$_2$O and NiCl$_2$.6H$_2$O in addition to the removal of methylene blue (MB) dye from its aqueous colored solution as well. The spectrophotometric curve of each colored metal ion and MB solution was performed to detect the l each. Depending of the color strength of these aqueous solution, the concentrations of their ions were recorded before and after treatment by measuring the absorbance of their solutions using spectrophotometer. Reaction kinetics for the absorption of Cu^{2+}, Co^{2+}, Ni^{2+} and MB dye was studied by taking samples at time intervals from 0.5:3 h at 70°C; 0.3 g of

CMS-g-PAAm or CMS-g-PAAm-AgNPs; Material: liquor ratio 1:500.

Experimental

Materials

Copper sulphate Pentahydrate (CuSO$_4$.5H$_2$O), cobalt chloride hexahydrate (CoCl$_2$.6H$_2$O), nickel chloride hexahydrate (NiCl$_2$.6H$_2$O) and methylene blue (MB) were of analytical grade chemicals.

CMS-g-PAAm and CMS-g-PAAm-AgNPs prepared according to reported methods [15, 17].

Equipment

Single beam spectrophotometer Camspec M 105 was used to measure the absorbance of the colored aqueous solutions of the Cu^{++}, Co^{++}, and Ni^{++} and MB dye.

Method

Samples preparation

Aqueous solutions with concentrations of 5% (w/v) of CuSO$_4$.5H$_2$O, CoCl$_2$.6H$_2$O and NiCl$_2$.6H$_2$O and aqueous solution with concentration of 0.1% (w/v) of MB dye were prepared.

Removal of metal ion and MB by CMS-g-PAAm and CMS-g-PAAm-AgNPs

A 0.3 g CMS-g-PAAm or CMS-g-PAAm-AgNPs was placed in a sealable 150 ml glass bottle followed by adding 30 ml of 5% CuSO$_4$.5H$_2$O, CoCl$_2$.6H$_2$O or NiCl$_2$.6H$_2$O aqueous solution and diluted to 150 ml. Same for 0.1% MB aqueous solution. The samples under test were placed in a thermostatic water bath at 70°C and left for 3 h. Samples were picked at different time intervals namely: 0.5, 1, 1.5 2, 2.5 and 3 h. Picked samples were placed in a sealed bottle and allowed to cooldown and filtered through Whatman filter paper. The filtrate was used to measure the absorbance at the determined λ_{max} using spectrophotometer then calculating the % metal removal.

Characterization

Absorbance of the aqueous solutions was determined by using a single beam Spectrophotometer after determination of λ_{max} of each solution.

Aqueous solutions with concentrations of 5% (w/v) of CuSO$_4$.5H$_2$O, CoCl$_2$.6H$_2$O and NiCl$_2$.6H$_2$O were diluted twice of the original sample before determination of the λ_{max}.

Aqueous solution with concentrations of 0.1% (w/v) of MB was diluted 100 times of original sample before determination of the λ_{max}.

Determination of the λ_{max} was performed at wavelength range from 320-900 nm. A blank sample of distilled water was first scanned at the same wavelength followed by scan of the diluted samples of $CuSO_4.5H_2O$, $CoCl_2.6H_2O$, $NiCl_2.6H_2O$ and MB. The λ_{max} was recorded at the highest absorbance of the aqueous solution of a given sample.

Calibration curves were performed using five known concentrations of each metal ion and MB dye versus the absorbance at l each. The equation of the calibration curve was applied to measure the concentrations and hence the % of metal ion and MB dye removal.

Percentage of metal ion or dye removal could be calculated according to the following Equation:

% metal ion or MB removal = [1- (C(0)-C(t)) x 100(1)

Where:

C0 is the concentration at 0 time (before treatment)

Ct is the concentration after t time (during treatment)

Results and Discussions

Preparation of CMS-g-PAAm and CMS-g-PAAm-AgNPs

Carboxymethyl starch (CMS) was prepared and graft copolymerized with acrylamide using UV/photoinitiator system to obtain CMS-g-PAAm. The latter was treated with silver nitrate and sodium hydroxide to obtain CMS-g-PAAm-AgNPs. All the preparations were performed according to a previous reported work [15, 17, 18].

Determination of λ_{max} of metal ions and methylene blue
Determination of λ_{max} of $CuSO_4.5H_2O$
Fig.1 shows that λ_{max} of $CuSO_4.5H_2O$ is 720 nm

Determination of λmax of CoCl2.6H2O
Fig.2 shows that λmax of CoCl2.6H2O is 520 nm

Determination of λmax of NiCl2.6H2O
Figure 3 shows that λmax of $NiCl_2.6H_2O$ is 400 nm

Determination of λmax of Methylene Blue
Figure 4 shows that λ_{max} MB dye is 660 nm

Calibration Curves
Calibration curves of the metal ions and MB solution were performed in order calculate the unknown concentration after absorption using CMS-g-PAAm and CMS-g-PAAm-AgNPs. To do so, the absorbance of five known concentration of $CuSO_4.5H_2O$, $CoCl_2.6H_2O$, $NiCl_2.6H_2O$ namely, 1, 2, 3, 4 and 5 g/100 was measured at λ_{max} each metal ion solution whereas the five known concentrations of MB were 0.0001, 0.0002, 0.0003, 0.0004 and 0.0005 g/100 ml at λ_{max} of MB. From each calibration curve, the equation of the straight line was displayed at which the concentration could be calculated with the knowledge of the absorbance.

Calibration curve of CuSO4.5H2O
Figure 5 shows the calibration curve of $CuSO_4.5H_2O$

Fig.1: λ_{max} of $CuSO_4.5H_2O$

λ_max of CoCl₂.5H₂O

Fig. 2: λ_{max} of $CoCl_2.6H_2O$

λ_max of NiCl₂.5H₂O

Fig. 3: λ_{max} of $NiCl_2.6H_2O$

λ_max of Methylene Blue
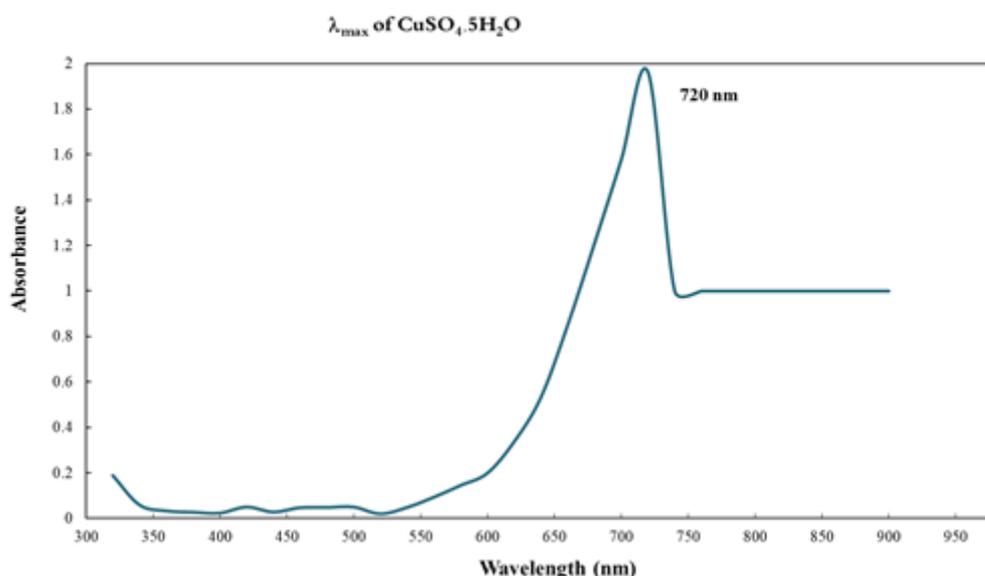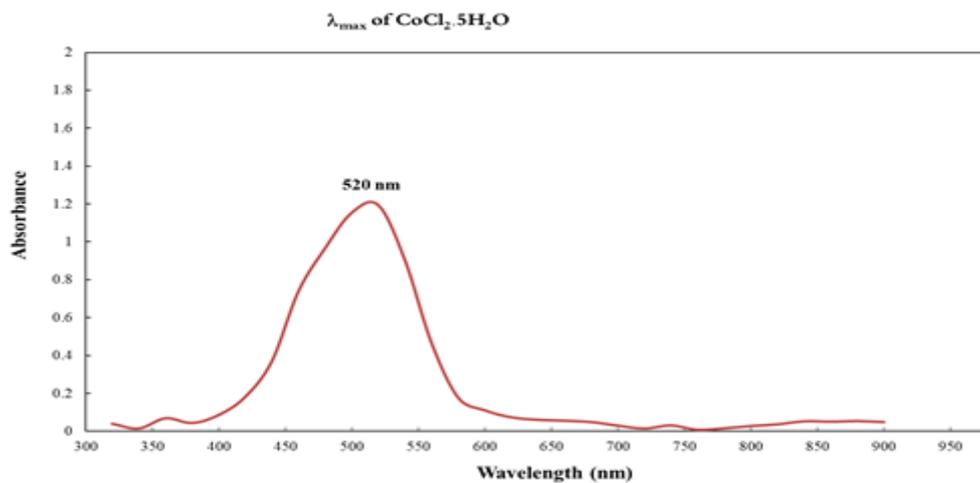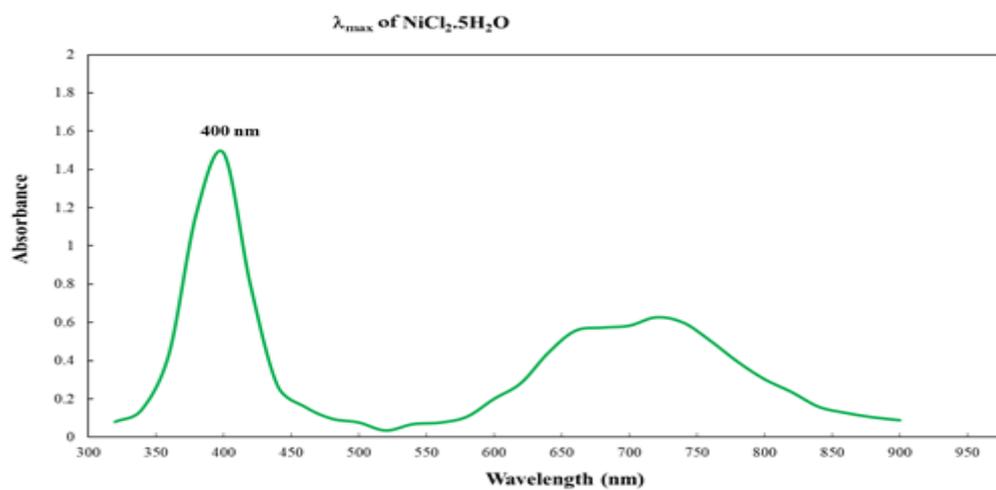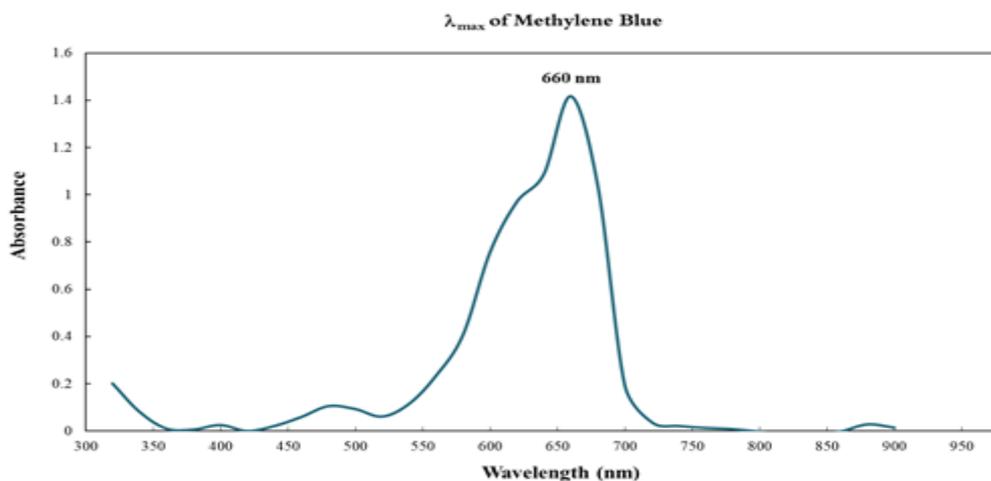
Fig.4: λ_{max} MB dye
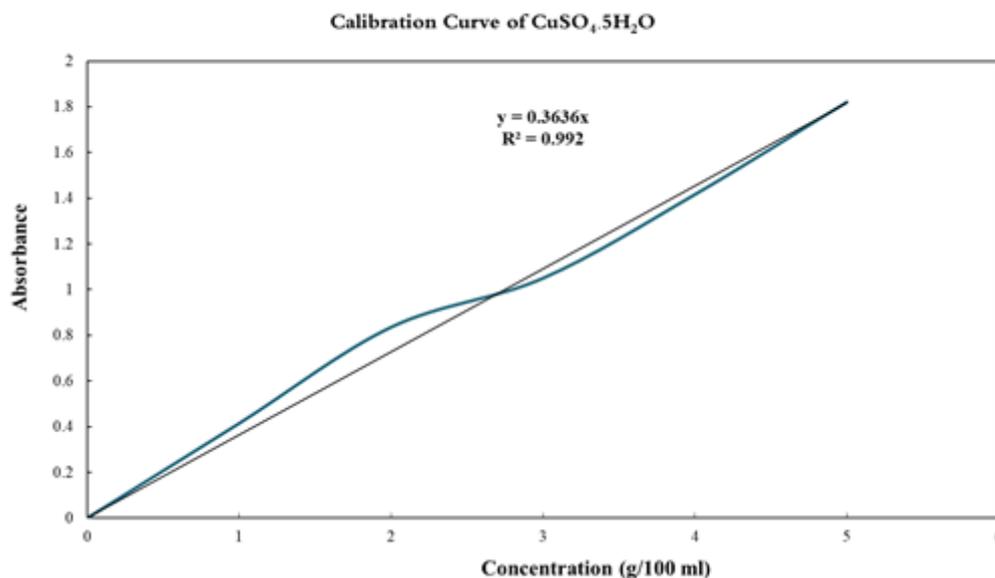
Fig. 5: Calibration curve of CuSO$_4$.5H$_2$O

Calibration curve of CoCl$_2$.6H$_2$O

Figure 6 shows the calibration curve of CoCl$_2$.6H$_2$O

Calibration curve of NiCl$_2$.6H$_2$O

Figure 7 shows the calibration curve of NiCl$_2$.6H$_2$O

Calibration curve of MB

Figure 8 shows the calibration curve of MB

Reaction kinetics

The kinetics of Cu^{2+}, Co^{2+}, Ni^{2+} and MB removal from their aqueous solutions, by CMS-g-PAAm or CMS-g-PAAm-AgNps copolymer was studied, and the percent of metal ion removal was calculated. The % removal of both metal ions and MB is expressed as the decrease in the absorbance of metal ions and MB at different time intervals rang from 0.5 – 3 h.

Reaction kinetics of the removal of metal ions and MB dye by CMS-g-PAAm-AgNPs and CMS-g-PAAm

Table 1 shows that regardless of the metal ion used, the reaction kinetics of the removal of metal ions by CMS-g-PAAm-AgNPs is characterized by a fast rate at the first 30 minutes followed by a slower rate till the end of 3 h at the reaction conditions used. This reveals the powerful effect of CMS-g-PAAm-AgNPs to absorb the metal ions as a result of the effect of chemical structure of the copolymer which contains both OH and COOH groups in its structure with their ability to absorb and interact with the metal ion and MB.

In addition, degradation of MB dye could take place due to the catalytic activity of AgNPs [19] structure in CMS-g-PAAm-AgNPs composite.

PAAm-AgNPs and CMS-g-PAAm, 0.3g; Temperature, 70°C; time, 0.5 – 3 h; CuSO$_4$.5H$_2$O, CoCl$_2$.6H$_2$O or NiCl$_2$.6H$_2$O, 30 ml (5%); MB, 0.1%, M:L ratio, 1:500.

Percent of metal ions and MB dye removal after treatments with CMS-g-PAAm-AgNPs and CMS-g-PAAm at different time intervals

Table 2 shows the % removal of metal ions and MB by CMS-g-PAAm-AgNPs and CMS-g-PAAm at time intervals from 0.5-3 h. The % removal of metal ions and MB by CMS-g-PAAm-AgNPs and CMS-g-PAAm was calculated by determining the concentration of metal ions and MB before treatment (C0) and after treatment at time "t" (Ct) using the absorbance results in Table 1 and the equation of the calibration curves in Figures 5, 6, 7 and 8 for CuSO$_4$.5H$_2$O, CoCl$_2$.6H$_2$O, NiCl$_2$.6H$_2$O and MB respectively. Equation 1 was then applied to determine the % removal.

Table 2 shows that after the first 30 min, the % removal reached up to 81.2%, 79.88, 77.97 for Cu^{++}, Co^{++}, and Ni^{++} respectively using CMS-g-PAAm-AgNPs. Whereas for MB, % removal reached up to 99.08 using CMS-g-PAAm-AgNPs and up to 98.11 using CMS-g-PAAm. Both CMS-g-PAAm-AgNPs and CMS-g-PAAm showed very high % removal of MB. However, % removal of MB using CMS-g-PAAm-AgNPs is higher than %
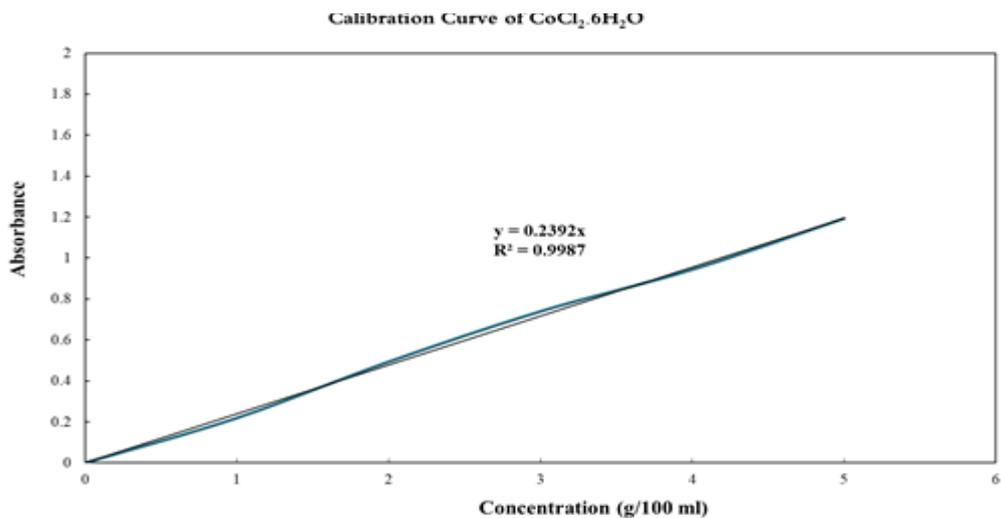
Calibration Curve of CoCl$_2$.6H$_2$O

$y = 0.2392x$
$R^2 = 0.9987$

Fig. 6: Calibration curve of CoCl$_2$.6H$_2$O

Calibration Curve of NiCl$_2$.6H$_2$O

$y = 0.2891x$
$R^2 = 0.9955$

Fig. 7: Calibration curve of NiCl$_2$.6H$_2$O

Calibration Curve of MB

$y = 1635.1x$
$R^2 = 0.9966$
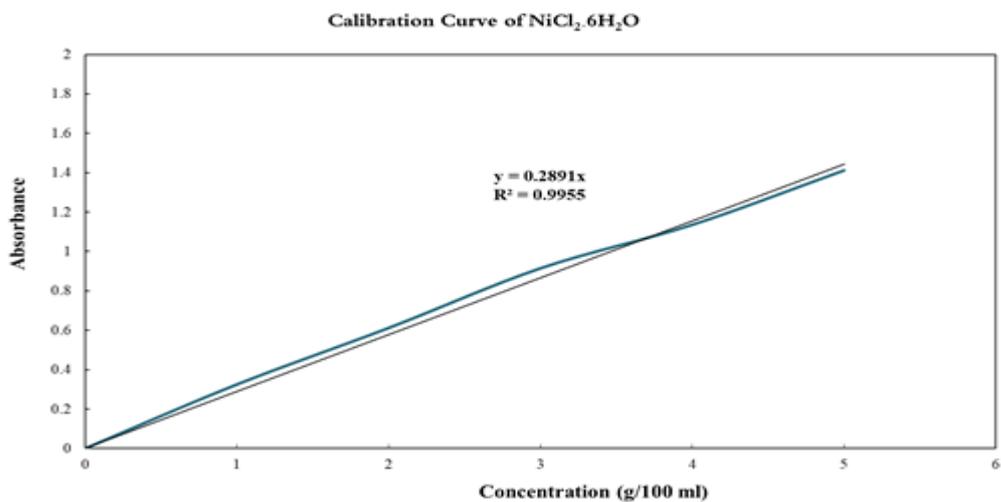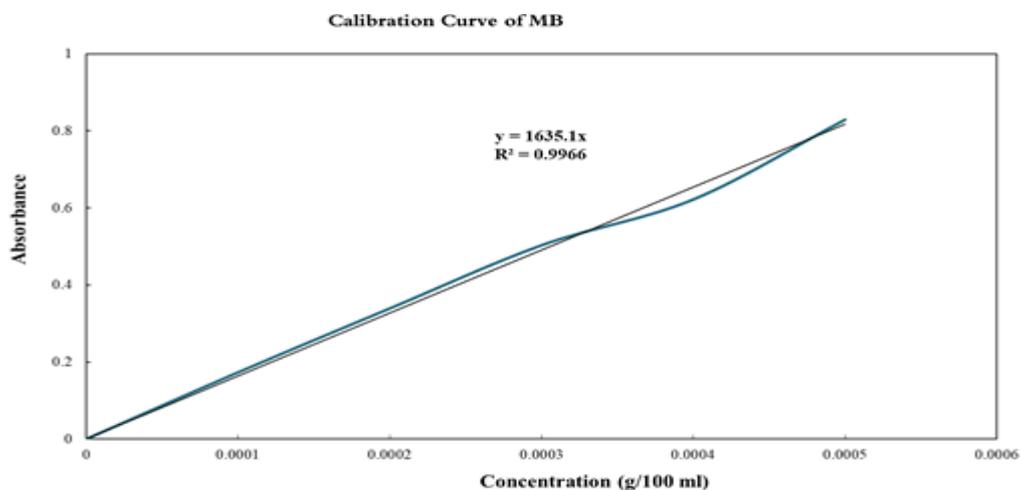
Fig. 8: Calibration curve of MB

TABLE 1: Reaction kinetics of the removal of metal ions and MB by CMS-g-PAAm-AgNPs and CMS-g-PAAm

Time (h)	Absorbance				
	Cu++/CMS-g-PAAm-AgNPs	Co++/CMS-g-PAAm-AgNPs	Ni++/CMS-g-PAAm-AgNPs	MB/CMS-g-PAAm-AgNPs	MB/CMS-g-PAAm
0	1.964	1.193	1.489	141.6	141.6
0.5	0.369	0.24	0.328	1.309	2.684
1	0.368	0.234	0.32	0.913	2.084
1.5	0.368	0.234	0.282	0.893	1.734
2	0.362	0.211	0.268	0.82	1.598
2.5	0.353	0.209	0.258	0.807	1.56
3	0.331	0.14	0.177	0.431	0.936

Time (h)	% Removal				
	Cu++/CMS-g-PAAm-AgNPs	Co++/CMS-g-PAAm-AgNPs	Ni++/CMS-g-PAAm-AgNPs	MB/CMS-g-PAAm-AgNPs	MB/CMS-g-PAAm
0.5	81.21181	79.88264878	77.97179315	99.07556	98.10451977
1	81.26273	80.38558256	78.50906649	99.35523	98.52824859
1.5	81.26273	80.38558256	81.06111484	99.36935	98.77542373
2	81.56823	82.31349539	82.00134318	99.4209	98.87146893
2.5	82.02648	82.48113998	82.67293486	99.43008	98.89830508
3	83.14664	88.26487846	88.1128274	99.69562	99.33898305

removal of MB using CMS-g-PAAm. This could be attributed to COOH of both composites. The higher % removal using CMS-g-PAAm-AgNPs is due to the AgNPs effect on the catalytic degradation of MB (as mentioned earlier). Again, after 30 min the % removal slightly increased. It is also noticed that by the end of 3h of treatment of metal ions, % removal reached up to 83.15, 88.27, 88.11% for $CuSO_4.5H_2O$, $CoCl_2.6H_2O$, $NiCl_2.6H_2O$ respectively. Percent removal of MB using CMS-g-PAAm-AgNPs reached up to 99.7% and up to 99.33% using CMS-g-PAAm. These results reflect the efficiency of the proposed composites as absorbents for metal ions and dye removal from their aqueous solutions. In other terms adding new absorbent agents for waste-water treatments.

Conclusion

It could be concluded that CMS-g-PAAm or CMS-g-PAAm-AgNps were found effective for the metal ions and MB dye removal from their aqueous solutions. It is recommend using these copolymers for utilization in waste-water treatment applications.

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