DEVELOPMENT OF A SIMPLE AMINO-MODIFIED SILICA-BASED COLORIMETRIC SENSOR FOR THE DETECTION OF COPPER (II) IONS IN AQUEOUS SAMPLES

Mosotho J. George*, Motiki F. Beleme and Limpho V. Moiloa

Department of Chemistry and Chemical Technology, National University of Lesotho, Lesotho
Email*: jm.george@nul.ls or maluti2005@gmail.com

ABSTRACT

Research projects form an important part of learning and preparing students for graduate training. While most cutting edge research requires highly sophisticated instruments, there is no such luxury in the Least Developed Countries, least of all, being accessible to undergraduate students. Consequently, undergraduate research projects require some level of improvisation and innovation to use easily available materials to carry out research, without compromising the quality of science. This paper reports the development of a simple amino-modified colorimetric sensor using silica gel modified with (3-aminopropyl)-triethoxysilane (APS) for the qualitative detection of Cu^{2+} ions in aqueous solutions in an effort to demonstrate the concept of ligand field strength and imbue interest in research in the undergraduate students. The sensor was immobilized on a glass stirring rod for simulated field applications. It responded considerably well at concentrations above 200 parts per million and neutral pH (7-8) giving response under 60 minutes of exposure with the increase in detection times as the concentration of the ions decreased. Modification of the APS with different substrates reduced its efficiency, demonstrating the necessity for primary amines. The binding of the Cu^{2+} ions seemed considerably stable for the sensor to be applied as a passive sampling device. This experiment has demonstrated that indeed, science does not only depend on sophisticated instrumentation but also simple ideas can generate interest in students while also achieving credible research results. It further demonstrates the importance of encouraging independent thinking to arouse interest as a way of improving the learning process. *[African Journal of Chemical Education—AJCE 6(2), July 2016]*

INTRODUCTION

With the persistent neglect for funding of public higher education institutions in most African countries, the offering of science-based education remains a huge challenge owing to poor or complete lack of appropriate infrastructure [1]. This is argued to have been brought about by the shift in funding policy by World Bank and the International Monetary Fund to channel funding away from higher education towards basic (primary) education [2], and its ratification and implementation by African states thus putting immense pressure on the public universities to seek alternative funding [1]. In sciences, specifically, this has been exacerbated by generally poor appreciation of science by the general public including the political authorities who hold the key to the financial resources [3, 4] Despite all these, science educators still need to sufficiently expose the students to laboratory work in order to demonstrate certain concepts as well as generate interest in sciences in the students [5, 6].

Lesotho is not an exception to this; there has been a consistent decline in funding spanning over 10 years [7]. Poor infrastructure in Lesotho affects all levels of education, from the secondary schools to the tertiary level, since most secondary schools do not have laboratories. The few that have laboratories do not have adequate facilities and consumables [8]. The importance of experiments in explaining and understanding some difficult concepts in science cannot be emphasized enough. This is especially so in chemistry where most explanations require high intuition since most phenomena studied cannot be seen, nor be heard. With limited funding, chemistry remains the hardest hit since after every chemistry experiment, the chemicals used are discarded as opposed to disciplines like physics for example, where models could be constructed from almost anything and be stored for use over multiple times. The same is true for biology, where the students could observe themselves or use plants and insect for study models.

Different scenarios such as the use of virtual laboratories and digital audio-visual pictures have been proposed for use in teaching of chemistry at both school and undergraduate levels [9]. However, it is argued, these cannot replace the impact of a real physical experiment in the laboratory [8]. As such; simple experiments that do not require the use of sophisticated instrumentation and expensive chemicals are usually employed, as long as they do not compromise the quality of science being demonstrated. Relevance of examples and materials used in a study is also very critical as it is believed to influence the interest and understanding of certain subject by the students. As a result, common phenomena and materials that are experienced or used in everyday life could also generate interest in the students. One such is the environmental degradation and waste management. Therefore drawing examples from these areas in teaching usually arouses students' interest.

Copper is one of the most abundant and widely used metals globally [10] with applications in electrical installations, construction, alloys, industrial machinery and agriculture [11]. Consequently, it often finds its way into the environment where it causes pollution. In recognition of this, the United States Environmental Protection Agency recommends the maximum acceptance level for $Cu2+$ ions at about 2×10-5 M in drinking water [12]. It is for this reason that it is necessary to search for efficient ways of not only removal, but also early detection of copper ions. There are a number of analytical methods used for quantitative determination of the $Cu2+$ ions. These include spectroscopy, namely, atomic absorption/emission spectrometry and atomic mass spectrometry [13], evanescent wave infrared absorption spectroscopy and voltammetry [14], as well as gravimetric and ion selective electrodes approaches [15].

Despite their efficiency, these techniques are relatively expensive and they commonly require highly trained personnel to operate the equipment. As such, they are rarely available in

economically challenged laboratories, especially for training of undergraduate students. This has thus sparked a considerable amount of research towards development of alternative and affordable sensors. Sensors are important for screening of suspected analytes before the somewhat expensive quantitative methods could be used even in the cases where such are not required. For example, in the cases where the suspected ions are not present or they are at very low levels that may not be detected.

This manuscript reports the preparation of a simple silica-based colorimetric sensor for copper ions in aqueous solutions. Cu^{2+} ions turn blue in the presence of a ligand with sufficiently strong ligand field to narrow the gap between the eg and t2g orbital sets. As such, it is conceptually simple to develop a simple sensor that could detect copper ions in solution using a strong ligand such as nitrogen atom. To achieve this, silica gel was modified with (3-aminopropyl)-triethoxysilane to enable the introduction of the amine groups onto silica surface which characteristically affect the ligand field of the Cu^{2+} ions leading the blue colour. Furthermore, the effect of addition of different nitrogen compounds onto the silica surface was studied in order to demonstrate the concept of ligand field strength, as well as studying the overall sensing dynamics. This is a simple experiment that was performed by two undergraduate students over a semester at National University of Lesotho, a resource-challenged university in Southern Africa. This project was undertaken as an independent study with minimal supervision by the students.

EXPERIMENTAL

Reagents and Apparatus

This experiment was performed using simple laboratory apparatus: weighing balances, stirring rods, beakers, test tubes, thermometer, hot plate, reflux apparatus.

Unless otherwise stated, general laboratory grade reagents were used as purchased. Silica gel, copper (II) nitrate, glycine, sodium chloride, sodium hydroxide, naphthalic anhydride, hexane and methanol were obtained from Associated Chemical Enterprise. Distilled water was prepared in-house using a simple water distiller. The (3-aminopropyl)-triethoxysilane was obtained from Sigma Aldrich.

Procedures

Preparation of silica and the amino-modified silica adsorbents

Preparation and modification of silica with the APS was carried out using 20 g of silica according to the procedure outlined in the PIERCE Application Note [16].A blank treated silica gel was also prepared by treating pure silica the same way the APS modification was treated.

Assembly of the probe and the sensing process

The basic sensing process was achieved by applying a thin layer of vacuum grease uniformly on the tip of a glass stirring rod (about 1 cm) followed by rolling it over silica powder (blank or modified) to attach silica particles (see Figure 1). Once this was achieved, the probe was introduced into the solution containing Cu2+ ions at the specified concentration and time accordingly and the colour change was monitored. For the initial experiment, a solution of 500 ppm Cu2+ (which was almost colourless) was used with the equilibration of 30 minutes.

Effect of varying concentration on APS modified probe

A stock solution of 5000 ppm Cu2+ solution was prepared in 250 mL volumetric flask using appropriately weighed copper (II) nitrate. Different concentrations: 500 ppm, 200 ppm and

100 ppm were prepared by serial dilution of this stock solution. 2 mL aliquots of these solutions were poured into test-tubes and used for sensing as follows: the solid silica modified with APS was coated onto a glass rod that had been smeared uniformly with vacuum grease (silicon oil) covering about 1 cm from the tip. This probe was then introduced into the 2 mL aliquots of the testing solutions and the time for development of the expected blue color was recorded.

Effect of addition of different groups on the APS modified silica

Appropriate amounts of glycine (amino acid) and naphthalic anhydride were reacted with the modified silica employing the free amino group of the APS following the procedure outlined on the APS Pierce Application Note for APS silica modification [16]. The presumed "re-modified" silica was coated on the probe and tested appropriately using the 500 ppm copper solutions.

The effect of pH on optimized amino-modified silica-based sensor

Different pH conditions were created by adding different aliquots of either HCl or NaOH to different 10 mL copper solutions at 500 ppm to achieve certain pH levels at which the efficiency of the sensor was determined following the 30-minute equilibrations of each solution.

RESULTS AND DISCUSSION

Assembly of the probe demonstration of the sensing mechanism

The assembly of the sensing probe is shown in Figure 1. Silica powder was immobilized on the solid glass rod covering about 1 cm in length using vacuum grease.
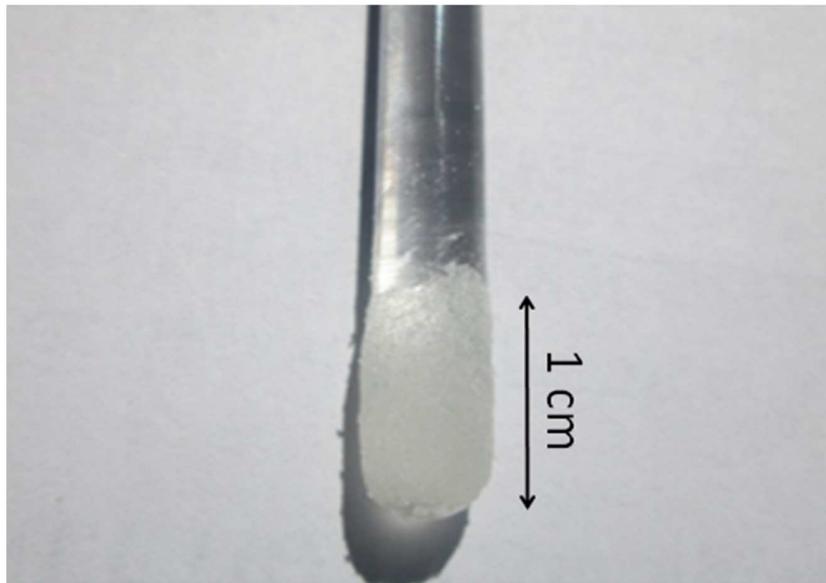
Figure 1 A photograph of the sensor: silica powder coated on the glass rod

Effect of APS silica on the probe

The APS-modified silica sensor was prepared from APS and washed silica. Figure 2 shows

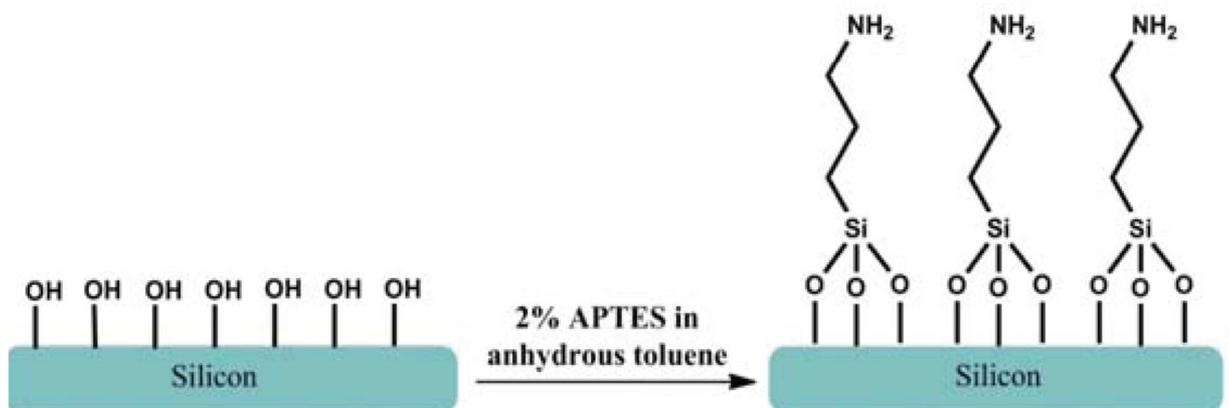the schematic presentation of the reaction of APS with silica [17].

Figure 2 Schematic of presentation of APS modification of silica

The schematic diagram in Figure 2 shows how APS modified silica is formed yielding a

primary amine which complexes $Cu2+$ ions leading to a blue color as seen in Figure 3.

Figure 3 A photograph of APS-modified silica sensor after 30-minute exposure to the 500 ppm Cu2+ solution

Blue color only developed on the APS silica and not on the blank silica probe used as a control. This was a positive sign that the silica gel was modified with the APS as anticipated. Thereafter, the concentration effect study was conducted to identify the lowest concentration that this probe could detect in a 30-minute period.

Effect of varying Cu2+ ions concentrations on APS modified silica sensor

The effect of varying concentration was studied based on the time it takes the probe to turn blue when immersed in Cu2+ solutions of different concentrations. When the sensor was suspended in 4000 ppm, 3000 ppm, 1000 ppm and 500 ppm Cu2+ solution, blue colour developed immediately upon contact with the Cu2+ solution. However, at 200 ppm it took four hours for blue color to develop while at 100 ppm it took four days for blue color to develop (see Figure 4).
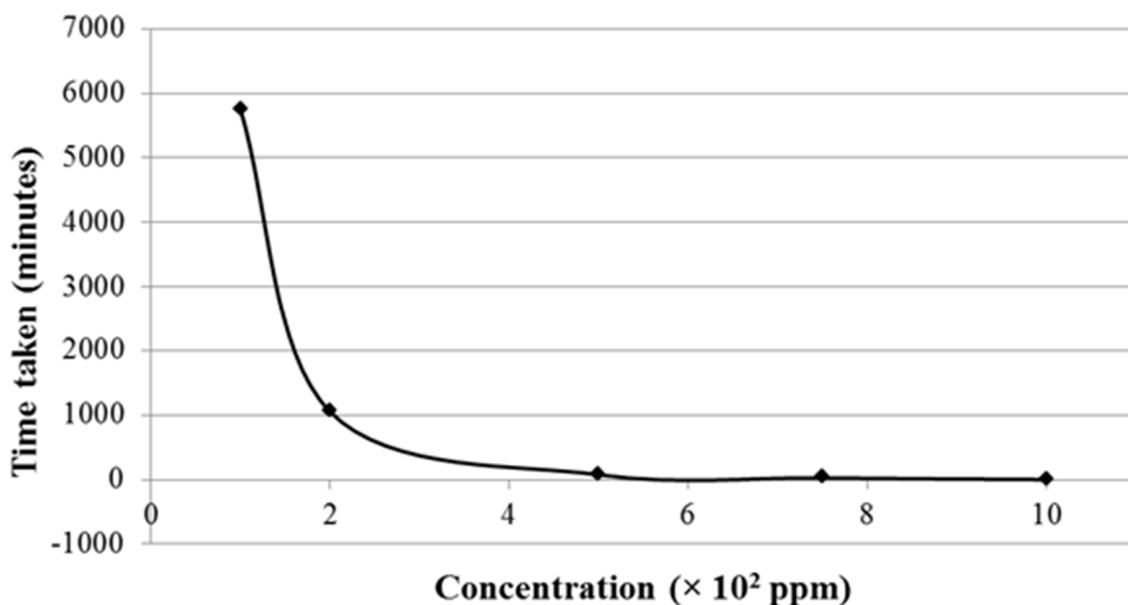
Figure 4 A plot of concentration against time taken for the probe to develop a blue color

From Figure 4, it seems that the rate of adsorption is first order in nature, where the rate depends on the concentration of Cu2+ ions in water, thus the color appearance. At low Cu2+ concentration, few nitrogen atoms interact with these ions forming few metal-ligand complexes whose colour is unobservable by the naked eye. Therefore, since at 200 ppm, there was little blue color on the surface of the silica sensor; furthermore this only developed after almost 4 hours. These results suggest that mass transfer is important in this experiment: at low concentration the probability of the ions reaching the probe is much less than at higher concentration.

Effect of addition of different groups on the APS modified silica

The significance of adding these groups was two-fold: 1) to increase the efficiency of the APS-modified silica sensor through provision of a multi-dentate chelation of the Cu2+ ions; and 2) to study the effect of different groups on the sensing properties by varying the ligand field

10

strength. It was believed groups like amino-acids, such as glycine, would increase the binding strength of copper ions due to multiple binding sites, hence probably lead to increased colour intensity on the probe.

Figure 5 shows the picture of glycine modification and APS modified silica sensor in 500 ppm copper (II) solution

Figure 5 A photograph of glycine-modified APS-silica probe suspended in 500 ppm copper solution

As can be seen, the probe did not turn blue as was expected instead the solution turned blue. The blue colour was seen to concentrate at the bottom of the test tube rather than dispersed evenly throughout the solution. This is possibly due to the aggregates of the Cu2+ – glycine complexes into possibly some nano/micro particles that settled down due to their resulting density. These aggregates compete with the probe hence reduce the activity of the probe as can be seen.

The behavior leads to a suspicion that perhaps glycine did not react with the APS-modified silica, but rather only adsorbed onto the surface, hence it peeled off when subjected to Cu2+ ions. The chelation of the ions by the freely suspended glycine reduces the interaction of the ions with

11

APS hence no detection or sensing on the probe. Suffice to say, the left APS-modified silica sensor did not turn blue because it might be all copper ions have already complexed with the suspected desorbed glycine.

To assess the interaction of different NH groups propylamine (primary amine) and acetamide (a secondary amine – amide), were deployed. When propylamine was added to a solution of 500 ppm Cu2+, tiny blue microdroplets were seen over time developing in the solution and slowly settling at the bottom of the test tube yielding a similar scenario to that depicted in Figure 5. In the case of acetamide, the blue color took a longer time (45 min – 1 hr) to appear. This confirms the idea that the primary amines are more sensitive than the secondary amines. It also points towards the possibility competition between glycine condensation and the reaction between glycine and the primary amines on the APS-modified silica. This would make sense since the APS is immobilized onto silica while the glycine molecules are freely suspended in solution, hence increasing their chances of collisions, leading to a higher reaction rate for this process.

The observation of the glycine modified probe, therefore, suggests that the glycine-modified APS-silica would not be suitable to be used as a field solid-based sensor but can be used as a "wet" laboratory sensor.

When the APS-modified silica was modified further with naphthalic anhydride generating an imide (a tertiary amine) instead of a primary amine, the sensor failed to yield any positive results towards the Cu2+ ions; thus confirming the success of the modification, while also confirming the importance of the free amines.

Effect of pH on optimized APS-modified silica

        The pH of the aqueous medium is very important as it influences the uptake of the adsorbate due to the electronic distributions. The chemical characteristics of both the adsorbate and adsorbent vary with pH since pH of the solution affects the degree of ionization and speciation of various pollutants which subsequently leads to the change in the reaction kinetics and the overall dynamics of the adsorption process. The effect of pH is demonstrated in Figure 6 with the visual scores of the intensities of the colors since there were no instrumental techniques that could be used for this.
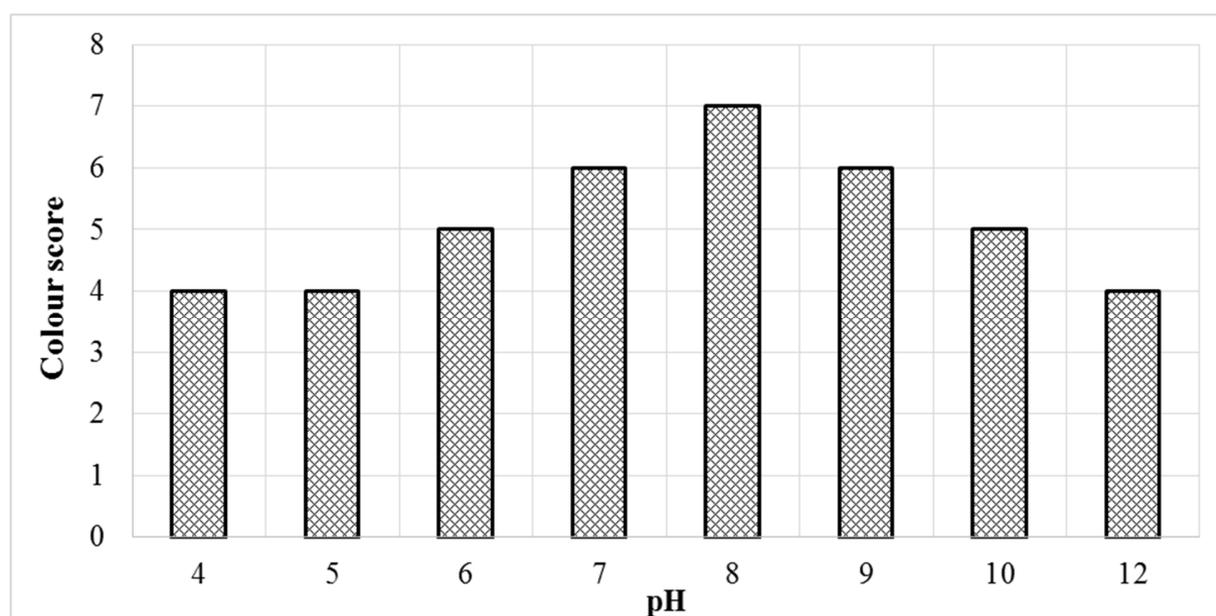

Figure 6 The effect of pH of the test solution on the effectiveness of the sensor (score /10)

        As can be seen in Figure 6, efficiency peaked at pH 8 and dropped thereafter. This could be explained in terms of poorer electron density at the lower pH values and the possible formation of hydroxyl complexes at pH values higher than 8, affecting the affinity of the sensor. Most hydroxides of the heavy metals are insoluble. As such these would render the metal ions less available for sensing.

CONCLUSIONS

This study has demonstrated that simple hand held sensors can be prepared cheaply by employing simple chemistry. The type of interactions between the analyte and the sensor are key in deciding how the sensor should work. This work has further demonstrated in a practical way two issues: development of a simple screening sensor and the ligand field theory. It was intriguing that free amino acids such as glycine could not react with the APS modified silica. This places a limitation on the groups that can be added onto the surface while retaining the free amino group responsible for the sensing. The fact that the probe withstood exposure to water demonstrated the known chemistry that amines show higher ligand field and affinity towards Cu2+ ions than the water molecules, hence the sensor can be used easily for field operations as a potential passive sampler.

Besides the strength of the interactions, the other key to success of this sensor is the loading of the APS, as well as the strength of the silica coating onto the glass rod using the silicone oil. These are some of the limitations realized in this study which will be the focus of the follow-up study. To take this into post graduate research, issues such as the determination of amount of nitrogen in the APS-sensor, chemically immobilizing APS on the glass-rod, as well as quantitative determination of the amount of Cu2+ ions adsorbed by the sensor are some of the features to be considered further.

Overall, the main objective of demonstrating simple molecular interactions leading to detection of a certain analyte such as copper has been demonstrated. This in deed demonstrates that even simple approaches could still be used to perform basic research that could entice students into pursuing graduate studies. The students who participated in this have indicated the desire to pursue the same project in the graduate studies. This experiment has helped to improve the

students' enthusiasm about the subject while strengthening the understanding of the ligand field

theory.

REFERENCES

1. S. M. Mutula, Financing public universities in eastern and southern Africa: implications for information services. The Bottom Line: Managing Library Finances. 2001, 14(3), 116-131.
2. S. Parker, Lessons from a ten-year funder collaborative: A case study of the partnership for higher education in Africa. New York: Clear Thinking Communications. 2010.
3. A. Irwin and B. Wynne, Misunderstanding Science? The Public Reconstruction of Science and Technology. Cambridge University Press. 1996.
4. A. Pouris and A. Pouris, The state of science and technology in Africa (2000–2004): A scientometric assessment, Scientometrics. 2009, 79(2), 297–309.
5. W.S. Harwood and M.M. McMahon, Effects of integrated video media on student achievement and attitudes in high school chemistry, J. Res. Sci. Teach. 1997, 34(6), 617–631.
6. M. Prince and R. Felder, The many faces inductive teaching and learning. J. Coll. Sci. Teach., 2007, 36(5), 14-20.
7. M.M. Sejanamane, Creating champions, The National University of Lesotho Annual Stakeholders Forum, Maseru, Lesotho. 2014.
8. M.J. George and M. Kolobe, Exploration of the potential of using a Virtual Laboratory for chemistry teaching at secondary school level in Lesotho. S. A. J. Chem. 2014, 67, 113-117.
9. A. Velázquez-Marcano, V. M. Williamson, G. Ashkenazi, R. Tasker and K. C. Williamson, J. Sci. Edu. Tech. 2004, 13(3), 315-323.
10. Y. Yang, F., Huo, C. Yin, Y. Chu,, J. Chao, Y. Zhang and D. Liu, Combined spectral experiment and theoretical calculation to study the chemosensors of copper and their applications in anion bioimaging. Sensors and Actuators B: Chemical, 2013, 177, 1189-1197.
11. Y. K. Jang, U. C. Nam, H. L. Kwon, I. H. Hwang, and C. Kim, A selective colorimetric and fluorescent chemisensor based on naphthol for detection of Al3+ and Cu2+. Dyes and Pigments, 2011, 99, 6-13.
12. Q. Lin, P. Chen, J. Liu, Y. Fu, Y. Zhang and T. Wei, Colorimetric chemosensor and test kit for detection copper (II) cations in aqueous solution with specific selectivity and high sensitivity. Dyes and Pigments, 2013, 98, 100-105.
13. J. Wang, Y. Xie, Z. Wang and Q. Song, A highly sensitive and selective naked-eye probe for detecting copper ion based on 2,3-modified Bodipy derivatives. Sensors and Actuators B: Chemical, 2014, 194, 149-155.
14. L. Feng, L. Zhang, L. Wen, S. Shen and Y. Guan, Colorimetric determination of copper (II) ions by filtration on sol-gel membrane doped with diphenylcarbazide. Talanta, 2011, 176, 913-917.
15. V.K. Gupta, A.K. Singh, M.R. Ganjali, P. Norouzi, F. Faridbod and N. Mergu, Comparative study of colorimrtric sensors based on newly synthesized schiff bases. Sensors and Actuators B: Chemical, 2013,182, 642-651.
16. Pierce Technical Note 8037, 3-Aminopropyltriethoxysilane, Illinois, USA.
17. R. G. Acres, A. V. Ellis, J. Alvino, C. E. Lenahan, D.A. Khodakov, G.F. Metha and G.G. Andersson, Molecular Structure of 3-Aminopropyltriethoxysilane Layers Formed on Silanol-Terminated Silicon Surfaces, J. Phys. Chem. C, 2012, 116, 6289-6297.