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Synthesis and Characterization of Polyaniline/Chitin (Squid Pens) for the Removal of Chromium (VI) from Aqueous Solution

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The rapid growth of the industrial sector has contributed to the increasing amount of heavy metal waste in environmental water bodies. It has become a critical situation in many developing countries. Among the heavy metals, chromium (Cr) (VI) has been studied extensively due to its toxic nature in aqueous solution. Recently, bio-conducting polymers have been reported to be successful in removing heavy metals from aqueous solutions. In this study, chitin was extracted from squid pens and integrated with polyaniline (PANI) via a chemical oxidative method. The integration of chitin with PANI was confirmed by Fourier Transform Infrared (FTIR) spectroscopy, which indicated that the essential peaks of both chitin and PANI were present in the PANI/chitin composites. The removal of Cr (VI) was evaluated by Atomic Absorption Spectroscopy (AAS). Several removal optimizations were made by evaluating the effects of pH, contact time, and mass of adsorbent. The results revealed that PANI/chitin removed the highest percentage of Cr (VI) at pH 3, with 12 minutes of contact time and 20 mg of the adsorbent in a solution with an initial concentration of 10 ppm Cr (VI) at 298.15 K.

Key words: Heavy metal; polyaniline; squid pens; removal; chitosan; chromium

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Industries such as electroplating, automotive, mining and fertilizer manufacturing are the major contributors for the environmental heavy metal contamination. Heavy metals are required for various biochemical processes, but they can be life-threatening due to their toxicity, persistence, and potential to bioaccumulate if they are present at levels beyond the permissible limits [1]. Among the heavy metals, chromium shows a high tendency to bioaccumulate in the environment. It originates from anthropogenic activities such as glazing, chromium plating, pigments, metal finishing, and leather tanning [2,3]. Chromium exists in the environment in different forms such as trivalent Cr (III) and hexavalent Cr (VI). Unfortunately, this heavy metal has a negative effect on both humans and the environment. Cr (VI) is highly toxic, carcinogenic, and mutagenic [4], and it can cause diseases such as lung cancer, skin rashes, stomach upset and ulcers, respiratory problems, reduced immune systems, change of genetic component, kidney and liver breakdown [2,5].

Owing to the low cost of disposal and no expertise available in handling the waste, manufacturers have been discarding waste containing trace levels of heavy metals such as chromium into the environmental water bodies such as rivers, lakes, and drains [6]. This leads to an increase in human exposure to chromium. The removal of chromium is one way to resolve this problem. However, chromium removal involves high operating and maintenance costs, and the available technologies are expensive[1]. To ensure that the water supply is safe, the removal of chromium is crucial.

The quality of water must be maintained to make sure that it is safe for use in our daily life. Several methods, including oxidation/precipitation, ion exchange, adsorption, nanofiltration, reverse osmosis, bioremediation, solvent extraction, and coagulation/co-precipitation, have been proposed to eliminate Cr (VI) [6, 7, 8]. Among these methods,

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adsorption is one of the best methods available as it is low cost, easy to operate, and uses fewer chemicals [3, 4, 7]. Adsorption is a favourable technology for the removal of Cr (VI) as it shows high performance and sorption capacity, lower cost, quick and easy regeneration activity [2,7].

Bio-conducting polymers have been shown to have a significant impact on the removal of heavy metals such as lead (Pb), cadmium (Cd), and chromium. Due to their excellent adsorption efficiency, low cost, wide availability, and the inclusion of several functional groups, the use of bio-conductive polymer composite materials as adsorbents has recently received widespread attention [9]. One of the bio-conducting polymers that can be used for the adsorption of Cr (VI) is polyaniline/chitin (PANI/chitin). According to Sahnoun and Boutahala (2018), PANI is one of the most attractive polymers due to its easy preparation, low-cost monomers, high electrical conductivity, and environmental stability [10]. PANI is widely used in plastics, batteries, energy storage devices, sensors, light-emitting diodes, corrosion inhibition, anti-static food packaging materials, and more recently it has been used to adsorb/remove organic colors and pollutants [11].

Chitin is a bio-renewable, eco-friendly, biocompatible, biodegradable, and biofunctional material. It is suitable for essential applications such as chelating agents, water treatment additives, drug carriers, biodegradable pressure-sensitive adhesive tape, clotting agents, and membrane technology [12]. Chitin is the second most abundant organic polysaccharide that can be obtained from crustacean shells [1]. Chitin that can be found in squid pens is an example of a biopolymer material. Squid pens are by-products that are not used and thus becomes waste [13]. It is estimated that at least 10^{11} t of chitin are produced and degraded/discarded, while only less than 150 000 t of chitin are utilized for commercial use [12,14]. The increasing waste from the industrial processing of seafood has become a problem [15].

In the present study, chitin biopolymer was for the first time extracted from waste squid pens and co-synthesized with PANI via the chemical oxidative method. The percentage of Cr (VI) removed from aqueous solution using PANI/chitin was evaluated by Atomic Absorption Spectroscopy. We also report here some important optimizations that were made by evaluating the effects of pH, contact time, and amount of adsorbent on the removal of Cr (VI).

EXPERIMENTAL

Materials

Squid pens from *Loligo Chinensis* (squid) were collected from the local market in Tanjong Karang. Reagents such as sodium hydroxide (NaOH), ammonium persulfate (APS), aniline, 37% hydrochloric acid (HCl), potassium dichromate were purchased from R&M Chemical Sdn. Bhd in Shah Alam. Deionized water was used throughout the analysis.

Extraction of chitin from squid pens

Squid pens were cut into pieces and dried at 50 °C for 8 hours using an oven. Dried squid pens were ground into particles using a laboratory Panasonic blender and sieved with a 250 μm sieve. Then, 5 g of squid pen powder was mixed with 4 wt.% NaOH at a solid/solvent ratio of 1:10 (w/v) at 80°C for 10 hours. The product obtained was filtered using suction filtration and was washed with deionized water. The product was then dried in an oven at 60 °C for 12 hours [13].

Synthesis of PANI

Pristine PANI was synthesized via a chemical oxidative method. Typically, 20.83 ml of 12 M HCl was diluted in a 250 ml volumetric flask with deionized water. Then, 1.30 ml of aniline was added to 100 ml of 1 M HCl. The solution was then stirred for 1 hour. Meanwhile, in a 50 ml conical flask, about 3.42 g of APS was added to 30 ml of 1 M HCl in the monomer: oxidant ratio of 1:1. 2.5 ml of this APS solution was added to the HCl-aniline solution every 5 minutes for 1 hour. The temperature was controlled at between 0-5 °C. The solution was subsequently stirred for 24 hours, at the same temperature [16]. Next, the precipitates were filtered using suction filtration to obtain the PANI, which was then washed with 100 ml of deionized water. Finally, the PANI was dried and kept in a desiccator before use.

Synthesis of PANI/chitin

The synthesis of PANI/chitin was carried out via a chemical oxidative method in the presence of a chitin filler. Typically, 1.30 g of chitin was added to 100 ml of 1 M HCl. The mixture was stirred for 1 hour. Then, 1.30 ml of aniline was added to the mixture and it was stirred for 1 hour. Meanwhile, in a 50 ml conical flask, 3.42 g of APS was added to 30 ml of 1 M HCI. This APS solution was added to the chitin/aniline suspension for every 5 minutes for 1 hour. The solution was then stirred for 24 hours. Next, the PANI/chitin was filtered using suction filtration and then washed with 100 ml deionized water. Lastly, the PANI/chitin was dried in an oven at 60 °C for 6 hours [9].

Characterization technique

An Attenuated Total Reflectance-Fourier Transform Infrared (ATR-FTIR) spectrometer model Perkin-Elmer RX1 was used for the analysis. The infrared spectra (IR) obtained was used to analyze the changes in structure and the presence of PANI, chitin, and PANI/chitin surface functional groups between 4000-650 cm^{-1}. The samples were ground to a powder with a mortar and pestle before analysis.

Preparation of Cr (VI) stock solutions

About 0.05 g of potassium dichromate, ($K_2Cr_2O_7$) powder was diluted with deionized water in a 500 ml volumetric flask as a stock solution with 100 ppm. After that, about 5 ml of this 100 ppm stock solution was diluted with deionized water in a 50 ml volumetric flask to obtain a 10 ppm concentration of $K_2Cr_2O_7$.

Removal and determination of Cr (VI)

10 mg of the synthesized PANI/chitin was weighed and placed in a tightly sealed glass vial with 10 ml of 10 ppm $K_2Cr_2O_7$ stock solution. The solution was then placed on a water bath shaker at 150 rpm for 6 minutes at room temperature. The supernatant was subsequently filtered and transferred to a clean glass vial. The concentration of the obtained solution was measured by Atomic Absorption Spectroscopy (AAS).

The percentage of removal, %R was calculated using equation 1:

$$\%R = [(Co - Ce) / Co] \times 100 \quad (1)$$

where Co and Ce are the initial and final concentrations of metal ions, respectively (ppm).

Effect of pH

The effect of pH was tested at a range of pH 2 to pH 5 only, as Cr (VI) is present in its most stable ionic form under acidic conditions [9]. pH in the basic region was not tested as Cr (VI) tends to precipitate at high pH levels, which might provide a misleading result. 0.1 M HCl was used to adjust the pH range of the aqueous solutions.

Effect of contact time

The effect of contact time between 2-16 minutes was investigated in this study. 10 mg of PANI/chitin, at pH 3, was transferred to a glass vial with 10 ppm of $K_2Cr_2O_7$. The percentage of Cr removal was estimated based on equation 1.

Effect of mass adsorbent

Different amounts of PANI/chitin adsorbent were used, ranging from 10 - 40 mg, in this study. The concentration of $K_2Cr_2O_7$ (10 ppm) at room temperature and pH 3 was maintained. The solution was shaken for 12 minutes before analysis.

RESULTS AND DISCUSSION

The FTIR spectra of PANI, chitin, and PANI/chitin are shown in Figure 1 and summarized in Table 1. The chitin spectrum shows the presence of O-H and C-H extended vibration bands at 3285 cm^{-1} and 2884 cm^{-1}. The stretching vibrations of amide I and amide II are also present at 1641 cm^{-1} and 1557 cm^{-1}.The PANI spectrum has its main bands at 1558 cm^{-1} and 1479 cm^{-1} indicating a C=C stretching vibration that belongs to the quinoid and benzenoid rings, respectively [17-19]. In addition, the peak at 1301 cm^{-1} indicates C-N stretching [15-16]. Meanwhile, the bands in the range of 3000-3600 cm^{-1} correspond to secondary amine stretching (N-H) vibrations [18].

In comparison, the PANI/chitin composite exhibits a peak at 3300 cm^{-1} that was assigned to the stretching vibration of O-H. The peaks at 1615 and 1510 cm^{-1} represent the stretching vibration of amide groups I and II of chitin respectively. Other peaks at 1510, 1479, and 1300 cm^{-1} correspond to the stretching vibration frequency of C=C in the quinoid ring, C=C in the benzenoid ring, and C-N, respectively. In conclusion, the presence of all these bands confirm that PANI has been successfully integrated with chitin [20]. The proposed structure of PANI/chitin is shown in Figure 2.

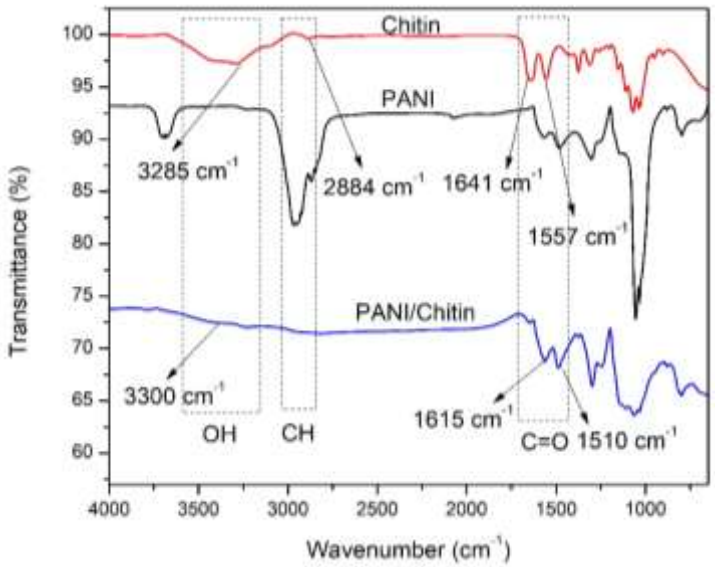

Figure 1. FTIR spectra of chitin, PANI, and PANI/chitin

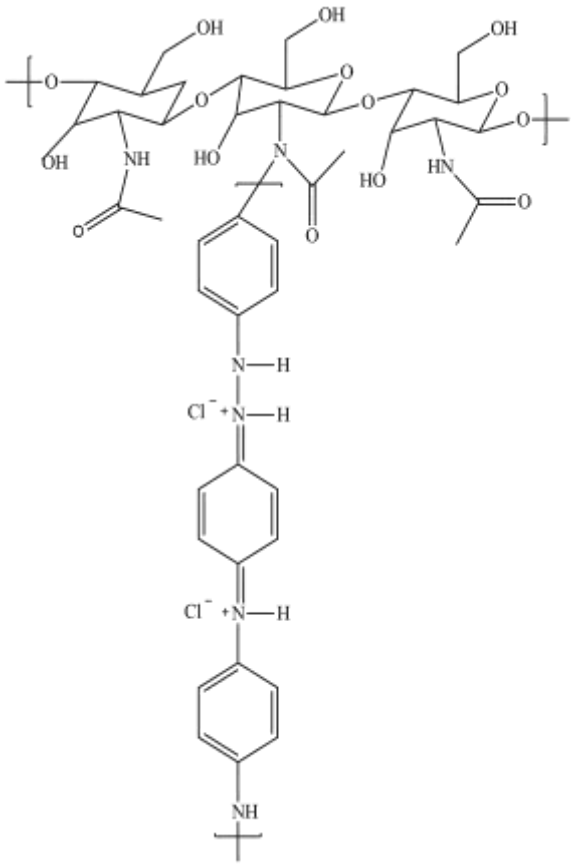

Figure 2. Structure of PANI/chitin

Table 1. FTIR characterization of the sample

Samples	Wavenumber (cm^{-1})	Assignment
PANI	1558	C=C of quinoid ring (stretching)
	1479	C=C of benzenoid ring (stretching)
	1301	C-N (stretching)
	3681	Amine (stretching)
Chitin	3285	O-H (stretching)
	2884	C-H (stretching)
	1641, 1557	Amide I, Amide II (stretching)
PANI/chitin	3300	O-H (stretching)
	1615, 1510	Amide I, Amide II (stretching)
	1510	C=C of quinoid ring (stretching)
	1479	C=C of benzenoid ring (stretching)
	1300	C-N (stretching)

Effect of pH

In this experiment, the effect of pH was studied because pH has an important role in controlling the percentage of Cr removal. The removal quality of PANI/chitin was greatly dependent on the pH value, as shown in Figure 3. The highest percentage of removal (64.78%) was obtained at pH 3. Singh and Nagendran (2014) also previously reported that pH 3 was the optimum pH for the removal of chromium using chitin and chitosan, although the contact time was longer [1].

Chromium ions are bound by electrostatic interactions with the negatively charged surface of the adsorbent [21]. In this study, the removal percentage increased from pH 2 to pH 3, but it then declined as the pH increased to 5. There is a significant decrease in sorption as chromium starts to precipitate due to the alkaline nature of the adsorbent surface [1]. This shows that the adsorption of Cr (VI) is more favorable at a lower pH. Therefore, throughout these experiments, the initial pH of the Cr (VI) ion solutions was maintained at pH 3.

Effect of contact time

The effect of contact times between 2 – 16 minutes was studied to determine the optimum time for the removal of Cr (VI). A rise in the percentage of removal for Cr (VI) was shown as soon as the experiment began (Figure 4). The increase was probably due to the numerous adsorption sites that are available on the adsorbent surface. However, after 12 minutes, there was a decrease. This shows that the reaction had achieved saturation, and the Cr (VI) ions were already completely adsorbed onto the available sites of PANI/chitin [21]. Therefore, 12 minutes was found to be the optimum contact time for the removal of Cr (VI) ions.

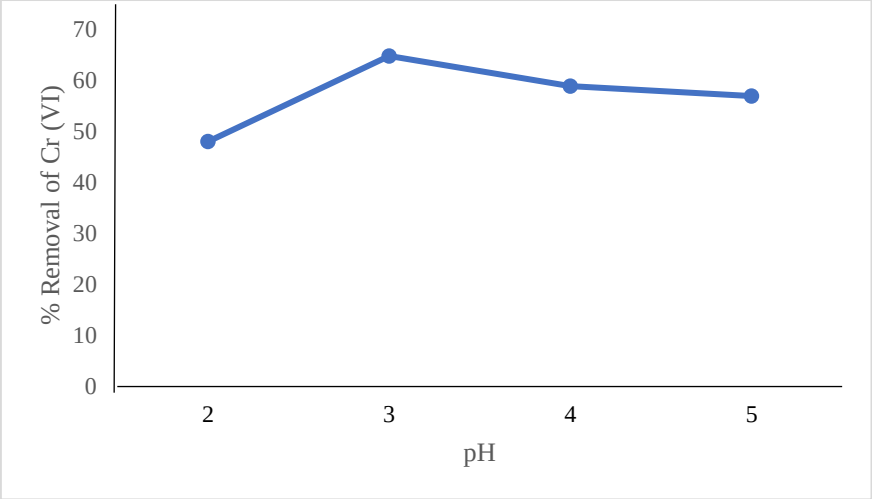

Figure 3. Effect of pH (condition: mass adsorbent 10 mg, initial concentration: 10 ppm, temperature: 298.15 K)

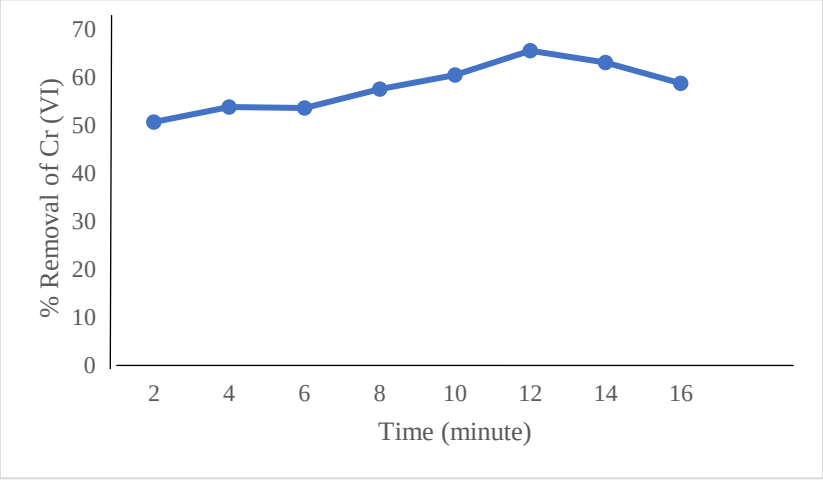

Figure 4. Effect of contact time (condition: pH 3, mass of adsorbent 10 mg, initial concentration: 10 ppm, temperature 298.15 K)

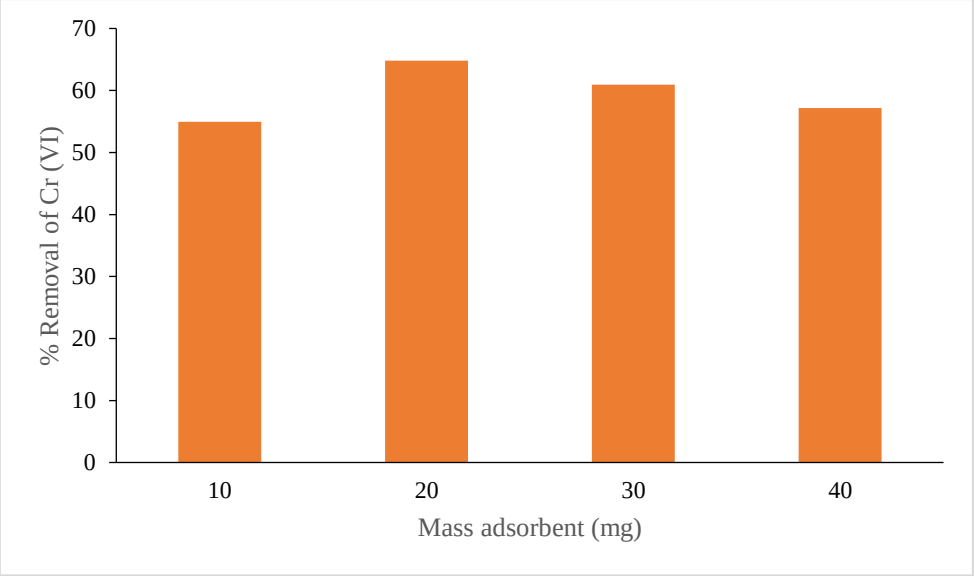

Figure 5. Effect of mass adsorbent (condition: pH 3, contact time 12 minutes, initial concentration 10 ppm, temperature 298.15 K)

Effect of mass adsorbent

Different amounts of PANI/chitin adsorbent (10 to 40 mg) were used to determine the optimum dosage to remove Cr (VI) while the pH and contact time were fixed. Figure 5 shows that an increasing amount of adsorbent also led to an increasing percentage of Cr (VI) removal. However, the percentage of removal decreased when more than 20 mg of PANI/chitin was used. The increased amount of adsorbent may cause aggregation, and consequently, the available adsorption sites would decrease as well [21]. Therefore, 20 mg of PANI/chitin was selected as the optimum mass adsorbent for 10 ppm of Cr (VI).

CONCLUSION

In conclusion, chitin was successfully extracted from squid pens and co-synthesized with PANI to remove Cr (VI) ions from aqueous solution. FTIR spectroscopy indicated the effective integration of squid pen chitin with PANI. The PANI/chitin revealed that 10 ppm of Cr (VI) could be effectively removed under the following conditions: pH 3, a contact time of 12 minutes and with 20 mg of the mass adsorbent. This experiment was the first attempt to test the removal capability of squid pen chitin with PANI. For further work, we suggest the investigation of other optimizations such as the effects of temperature, and initial Cr (VI) concentration as well as a study of the kinetic mechanisms that take place between PANI/chitin and Cr (VI) ions.

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REFERENCES

1. Singh, P. and Nagendran, R. (2014) A comparative study of sorption of Chromium (III) onto chitin and chitosan, *Applied Water Science*, **6**, 199–204.

2. Karthik, R. and Meenakshi, S. (2014) Facile synthesis of cross linked-chitosan-grafted-polyaniline composite and its Cr (VI) uptake studies, *International Journal of Biological Macromolecules*, **67**, 210–219.

3. Vakili, M., Deng, S., Cagnetta, G., Wang, W., Meng, P., Liu, D. & Yu, G. (2019) Regeneration of chitosan-based adsorbents used in heavy metal adsorption: A review. *Separation and Purification Technology*, **224**, 373–387

4. Yavuz, A. G., Dincturk-Atalay, E., Uygun, A., Gode, F. and Aslan, E. (2011) A comparison study of adsorption of Cr (VI) from aqueous solutions onto alkyl-substituted polyaniline/chitosan composites, *Desalination*, **279**, 325–331.

5. Sun, H., Brocato, J. and Costa, M. (2015) Oral Chromium Exposure and Toxicity Compliance with Ethics Guidelines Human and Animal Rights and Informed Consent HHS Public Access, *Curr. Environ. Health Rep.*, **2**, 295–303.

6. Zhang, L., Zeng, Y. and Cheng, Z. (2016) Removal of heavy metal ions using chitosan and

modified chitosan: A review, *Journal of Molecular Liquids*, **214**, 175–191.

7. Golbaz, S., Jafari, A. J., Rafiee, M. and Kalantary, R. R. (2014) Separate and simultaneous removal of phenol, Chromium, and cyanide from aqueous solution by coagulation/precipitation: Mechanisms and theory, *Chemical Engineering Journal*, **253**, 251–257.

8. Burakov, A. E., Galunin, E. V., Burakova, I. V., Kucherova, A. E., Agarwal, S., Tkachev, A. G. and Gupta, V. K. (2018) Adsorption of heavy metals on conventional and nanostructured materials for wastewater treatment purposes: A review, *Ecotoxicology and Environmental Safety*, **148**, 702–712.

9. Karthik, R. and Meenakshi, S. (2016) Biosorption of Pb(II) and Cd(II) ions from aqueous solution using polyaniline/chitin composite, *Separation Science and Technology (Philadelphia)*, **51**, 733–742.

10. Sahnoun, S. and Boutahala, M. (2018) International Journal of Biological Macromolecules Adsorption removal of tartrazine by chitosan / polyaniline composite: Kinetics and equilibrium studies, *International Journal of Biological Macromolecules*, **114**, 1345–1353.

11. Sambasevam, K. P., Mohamad, S. and Phang, S. W. (2017) Chemical Sensor For Hydrazine Detection Using Polyaniline Thin Film, *Malaysian Journal of Analytical Science*, **21**, 762–769.

12. Zargar, V., Asghari, M. and Dashti, A. (2015) A Review on Chitin and Chitosan Polymers: Structure, Chemistry, Solubility, Derivatives, and Applications, *ChemBioEng Reviews*, **2,** 204–226.

13. Huang, J., Zhao, D., Hu, S., Mao, J., Mei, L. (2012) Biochemical activities of low molecular weight chitosans derived from squid pens, *Carbohydrate Polymers*, **87**, 2231–2236.

14. Hamed, I., Özogul, F. and Regenstein, J. M. (2016) Industrial applications of crustacean by-products (chitin, chitosan, and chitooligosaccharides): A review, *Trends in Food Science and Technology*, **48**, 40–50.

15. Eddine, B., Sila, A., Haddar, A., Bougatef, A. and Ali, M. (2017) β-Chitin and chitosan from squid gladius: Biological activities of chitosan and its application as clarifying agent for apple juice, *International Journal of Biological Macromolecules*, **104**, 953–962.

16. Mohd Norsham, I. N., Baharin, S. N. A., Raoov, M., Shahabuddin, S., Jakmunee, J. & Sambasevam, K. P. (2020) Optimization of waste quail eggshells as biocomposites for polyaniline in ammonia gas detection, *Polymer Engineering and Science*, **60**, 1–13.

17. Mazlan, N. A., Sapari, J. M. and Sambasevam, K. P. (2020) Synthesis and Fabrication of Polyaniline/eggshell Composite in Ammonia Detection, *Journal of Metals, Materials and Minerals*, **30,** 50**–**57.

18. Mustapa, R., Abu Mansor, Z. I. and Sambasevam, K. P. (2018) Fabrication of Polyaniline Based Chemical Sensor for Ammonia Gas Detection, *Journal of Physical Science*, **29,** 9–16.

19. Albar, M. M., Jamion, N. A., Baharin, S. N., Raoov, M. and Sambasevam, K. P. (2020) Preparation of Novel Commercial Polyaniline Composites for Ammonia Detection, *Solid State Phenomena*, **301**, 124**–**131.

20. Karthik, R. and Meenakshi, S. (2015) Removal of Pb (II) and Cd (II) ions from aqueous solution using polyaniline grafted chitosan, *Chemical Engineering Journal*, **263**, 168–177.

21. Padmavathy, K. S., Madhu, G. and Haseena, P. V. (2016) A study on Effects of pH, Adsorbent Dosage, Time, Initial Concentration and Adsorption Isotherm Study for the Removal of Hexavalent Chromium (Cr (VI)) from Wastewater by Magnetite Nanoparticles. *Procedia Technology*, **24**, 585–594.