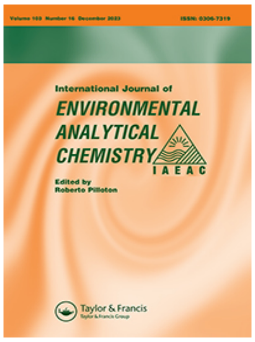

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Polyaniline-coated charcoal ash: a novel high-capacity adsorbent for removal of thiocyanate ions from aqueous solutions

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ABSTRACT

Removal of thiocyanate (SCN−), which is widely used in many industrial processes is of concern due to this toxicity. In this work, the potential of polyaniline-coated charcoal ash (PANI-CCA) as a low-cost and efficient adsorbent was evaluated in order to remove thiocyanate ions from aqueous solution. Morphologies and chemical composition of the PANI-CCAhave been examined by using scanning electron microscopy and X-ray fluorescence spectrometry (XRD). Batch experiments were performed to examine the effects of operating conditions such as pH (6.0–10.0), ash dosage (0–0.30 g/50 ml), initial dye concentration (50–1500 mg/L), agitation period (2.5 min-24 hr) and temperature (25–60 C). The efficiency of adsorption process was evaluated by applying Langmuir, Freundlich, Temkin and Halsey isotherm models. Among the performed isotherm models, Freundlich isotherm provided the best correlation for SCN ions onto PANI-CCAand the Freundlich constant related to the sorption capacity was calculated as 7.69 mg/g at an initial pH of 8.7 for the 50–1500 mg/L SCN- at 25° C.Thermodynamic parameters were calculated as ΔG = 1.95–1.57 kJ/mol, ΔH = −4.66 kJ/mol, and ΔS = −0.0094 kJ/mol K at T = 288–333 K. The experimental data fitted well to the pseudo second-order kinetic model (r^2 = 0.999) and the kinetic model constants were calculated as k_2 = 0.1858–0.0185 g/mg min, h = 24.48–113.09 mg/g min and $q_{e,cal}$ = 12.16–78.19 mg/g at 50–500 mg/L of SCN^- concentration. The negative values of isosteric enthalpy change, free energy change, and entropy change indicated an exothermic, spontaneous characteristics and decreasing disorder of the process, respectively.The overall results of the study demonstrated the good efficiency of PANI-CCA in adsorption of thiocyanate at compared to other adsorbents.

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1. Introduction

Thiocyanate (SCN^-) forms as a result of the interaction of free cyanide (CN^-, HCN) with sulphur and is a toxic pollutant existing in industry effluents such as the mining industry, the coal coking, quinine factories, base metal mills, gold mines, hydrometallurgy, flotation, printing and dyeing textiles, acrylic fibre production, photofinishing and electroplating industry [1]. Thiocyanatepresent in somecoalcokingandcoalconversioneffluents in theconcentrationrange of 17–1500 mg/L. On theotherhand, in chemicalmanufacturing-plantseffluents 11 to 50 mg CN^-/L of thiocyanateconcentrationshavebeendetected [2]. Despite its relatively low toxicity when compared with HCN, thiocyanate is also potentially toxic due to its resistance to hydrolysis and non-volatility [3]. Moreover, when wastewater containing thiocyanate is chlorinated, highly toxic cyanogen chloride (CNCl) is formed. Therefore, it is obligatory to remove SCNs from wastewaters before discharge to the environment [4–6].

Several researchers dealt with the removal of thiocyanate using physic-chemical methods such as ZnO_2 activated carbon, active carbon felt, Fe(III)/Cr(III) hydroxide, surfactant modified coir pith, anion-exchange resin, ferrihydrite, activated carbon, zeolite, diatomite, sepiolite, hydrotalcite, steel-making residues and synthetic hydrotalcite sol [3,7–13]. There are also several attempts for biological processes for removal of the compound from wastewater [14]. However, biological processes have a lot of disadvantages such as requirement of long retention times, large area and high sensivity towards processes factors such as pH, temperature and solid contents [11]. Undoubtedly, adsorption is a well-established and powerful method which is widely used to remove numerous pollutants from wastewater streams. The simplicity of the operation and high efficiency are regarded to be the outstanding advantages of the process.Beside these benefits, operational costs can be minimised by utilisation of low cost natural materials, waste and composites.

Efficiencies of various natural materials such as zeolite, sepioliteand starch have already been tested for the treatment of different pollutants [15–17]. Besidesthese natural sorbents which have the common properties of being locally available and cheap, waste-derived adsorbents constitute a more specific group as they provide an effective, economical and eco-friendly option: *'waste mitigation by waste'* [18]. Benefits of resource generation and pollution abatement have been provided simultaneously by utilisation of waste-derived sorbents [19].

There are several studies performed to investigate the usability of different industrial and agricultural wastes as an adsorbent. In these studies, the industrial materials (such as PET and waste tires, waste polyurethaneand agricultural wastes (such as cassava peel, rice husk) have been used to obtain efficient activated carbon species [20–23]. There are some pretreatment procedures applied to obtain waste-derived adsorbents. These procedures exhibit significant diversity considering both the nature of the raw material and the properties of the targeted pollutants. In some cases a simple chemical activation (such as acid modification) is sufficient [24] whereas in some cases different chemical processes (such as doping, coating) may be enough to enhance the adsorption capacities.

Another option is composite materials which present a combination of two or more materials' advantages (e.g. natural/waste-derived materials and polymeric materials) to obtain high removal efficiencies at a lower cost and so on to increase the adsorption efficiency [25–27]. Recently, researchers have deal with Polyaniline (PANI) composite due to their high electrochemical properties, easy protonation reversibility, excellent environmental stability, ease of doping, relatively easy synthesis technique, good dispersion and abundant of amino groups [28–30]. PANI is a polyaromatic amine with conductive properties because of the presence of the conjugated π electron system in its structure. PANI has three form; I) namely fully oxidised pernigraniline, II) half-oxidised emeraldine base (EB) (the most stable form of PANI) and III) fully reduced leucoemeraldine base (LB) [29]. The oxidation is carried out using ammonium peroxodisulfate or potassium dichromate in HCl or H_2SO_4 medium. The anions of the medium, i.e. Cl^-or $SO_4^{-2}$are incorporated in the matrix.These anions can be replaced by another suitable anion uponequilibration [31]. In literature, PANI composites made up of different materials such asnanocellulose, ceria nanoparticles, Fe_3O_4, chitin, montmorillonite, silica gel, sawdust,natural sand and clay, manganese dioxideand beidellitehave synthesised [32–42]. These composites provided more effective removal efficiencies than single material use on the wastewater treatment applications.

In this study, it was aimed to investigate the efficiency of PANI-CCAfor adsorption of thiocyanate from aqueous solutions. Results of the preliminary tests performed with raw charcoal ash have introduced the necessity of a modification process to improve the adsorption capacity of the charcoal ash versus the thiocyanate. With this aim, raw charcoal ash was coated with PANI which can interact with many pollutant species due to thelarge amount of amine and imine nitrogen content. Characterisations of raw and used adsorbents have been made with X-ray Fluorescence (XRF), scanning electron microscopy(SEM) and Brunauer, Emmett and Teller(BET) surface analysis measurements. As well as conventional isotherms, kinetic and isotherm studies have been performed in order to examine the efficiency of the synthesised adsorbent. The novelty of this study is that PANI-CCA composite synthesised for the first timehas the best adsorption efficiency among the other adsorbents used up to now for the removal of SCN^-.The used adsorbent is also economic and ecofriendly as it is waste-derived material.

2. Materials and methods

2.1. Materials

Ammonium persulphate (APS), hydrochloric acid, aniline monomer, sulphuric acid, and sodium hydroxide were supplied from a Merck. Potassium thiocyanate was received from Sigma-Aldrich. All the used chemicals supplied by Merck were of an analytical grade and used without further purification. All the chemicals used in this study have high purity $\geq 99.0\%$.

2.2. Preparation and characterisation ofPANI-CCA

Polymerisation reactions of PANI and PANI-CCAcomposite have been presented in Figure 1. PANI is a polyaromatic amine that can be easily synthesised chemically from bronsted acidic aqueous solutions as shown in Figure 1(a). The PANI-CCAsynthesis mechanism include simultaneous movements of both the PANI synthesis and the activation of the charcoal ash and also activated charcoal ash bind to the NH groups on the PANI

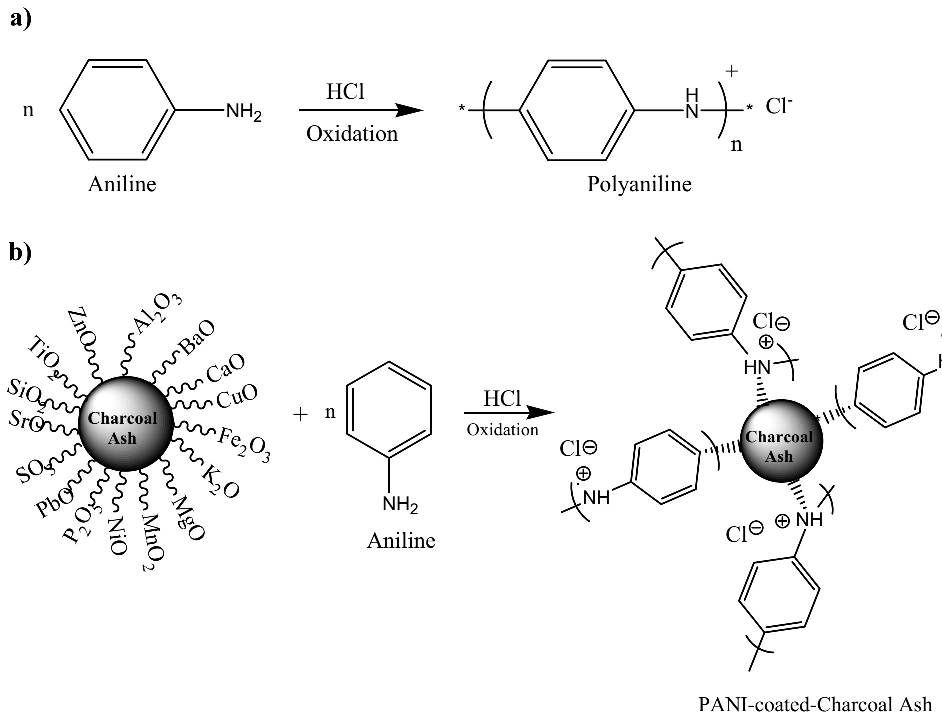


Figure 1. The overall polymerisation reaction of a) PANI and b) PANI-CCA composite.

(Figure 1(b)). The preparation procedure of PANI-CCAbasically involved six steps: (i) 1 g of charcoal ash was added to 100 ml HCl (1 M) solution and the solution was mixed at a stirring rate of 500 rpm (ii) 2.2820 g ammonium persulphate (APS, 0.1 M) was added into the HCl solution at room temperature (iii) 0.931 ml of aniline monomer (0.1 M) (wt. 24% of the charcoal ash content) was injected slowly (iv) the polymerisation was carried out at room temperature for 2 h (v) in order to remove the unreacted monomers and oxidants, the dark blue final product was washed thoroughly with 500 ml of deionised water (vi) the product was dried at 60°C for 24 h. Thus, the molar ratio of APS and aniline was adjusted as 1.0.

The morphologies of raw charcoal ash, PANI-CCAbefore and after adsorption tests were obtained from Scanning Electron Microscope-Energy Dispersive X-Ray (SEM, Philips XL30S-FEG). The BET surface area was measured from the N_2 adsorption/desorption isotherms with a Micromeritics ASAP 2010 analyser (US).

Besides, the chemical composition of charcoal ash was determined witha Philips PW-2404 wavelength dispersive XRF spectrometer. In the composition of the charcoal ash determined with semi-quantitative elemental analysis, CaO and SO_3 compounds are found inthe highest ratios of 46.48% and 46.22%,respectively. On the other hand, the component ratios of SiO_2, MgO, P_2O_5, MnO_2, Al_2O_3, Fe_2O_3, K_2O, TiO_2, BaO, SrO, ZnO, NiO and PbO are less than 2%. According to these results, the charcoal ash contains metal oxide, non-metal oxide and semi-metal oxides.It is known that metal oxides such as TiO_2, ZnO and MnO_2 act as super catalysts in wastewater treatment and increase adsorption capacity. However, it is possible that the more effective compounds in the adsorption mechanisms of the ash are CaO and SO_3.

2.3. Experimental procedure and instrumentation

In the study, batch tests were performed in order to investigate the efficiency of PANI-CCA in the removal of thiocyanate. With this aim, a NUVE ST-402 model batch reactor was used. Different concentrations of thiocyanate solutions were prepared from stock solution. A sample volume of 50 mL was preferred throughoutthe experiments. pH adjustments were performed by using HANNA Instrument 211 model pH-metre adding required amounts of 0.1 N H_2SO_4 and 0.1 N NaOH.

Predetermined adsorbent dosages were added into the 50 mL of thiocyanate solutions and the samples were shaken. At the end of the required contact time, PANI-CCAwas separated from the sample by filtration. The remaining SCN concentrations were analysed using standards methods [43]. Ferric and thiocyanate ions form an intense red colour suitable for colorimetric determination at 460 nm of wavelength by UV-Vis spectrophotometer (Hach Lange DR6000). This experimental procedure was applied in order to investigate the impacts of pH, adsorbent dosage, agitation period and temperature.

3. Results and discussion

In this study, the effects on the SCN^-removal of experimental factors such as pH, adsorbent dosage, agitation time, temperature and thiocyanate concentrations were particularly investigated with particle adsorption tests using waste derived adsorbent (PANI-CCA).

3.1. The characterisation of charcoal ash, PANI-CCA and used PANI-CCA composites

Surface morphologies of the charcoal ash, PANI-CCA and used PANI-CCA composites were determined by a SEM. The SEM image of the charcoal ash was composed of the agglomerated fine powder-like particles at the micron scale and its surface includes a heterogeneous morphology (Figure 2(a)). The shiny points in Figure 2(b) represent the coated surface of the charcoal ash by PANI and the surface polymerisation onto the

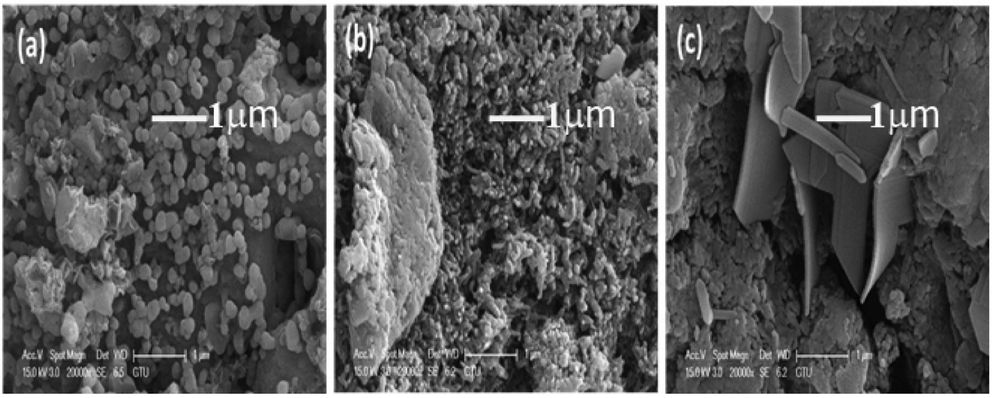


Figure 2. SEM image of (a) charcoal ash (b) PANI-CCA and (c) used PANI-CCA.

charcoal ash is quite noticeable. Besides,the micro porous structure provides a good platform for thiocyanate removal. This fibre-like micro porous structure probably formed during the contact of charcoal ash with acid (HCl). On the other hand, an image of used PANI-CCA(Figure 2(c)) demonstrated layered and flaky structure due to accumulation between adsorbent microstructures of the SCN^{-}.

The single point surface area, BET specific surface area, Langmuir surface area and adsorption average pore width were calculated as 1.453 m^2/g, 1.558 m^2/g, 2.201 m^2/g, 19.406 nm for raw charcoal ash and 28.146 m^2/g, 29.640 m^2/g, 41.238 m^2/g, 21.363 nm for PANI-CCA, respectively. According to IUPAC (The International Union of Pure and Applied Chemistry), the pore sizes of the adsorbents were classified in 4 different ways according to the mean pore radius (r): i) Macro-pores ($r > 25$ nm), ii) Meso-pores ($1 < r < 25$ nm), iii) Micro-pores ($0.4 < r < 1$ nm), and iv) Submicron-pores ($r < 0.4$ nm). The PANI-CCAhas a meso-pore structure and therefore the SCN can be adsorbed to more internal regions of the adsorbent surface. This prediction is compatible with the SEM image showing that the used PANI coated ash filled the micro-cavities. As is well known, the increased surface area of adsorbent enhances removal capacity, the results showed that the coating surface polymerisation of PANI increased the surface areas. However, the surface areas of PANI-CCA (28–41 m^2/g) are significantly lower from that of activated carbon (600–1000 m^2/g). In this study, the smaller surface areas and higher removal efficiencies by PANI-CCA showed that the SCN^{-} removal mechanism with PANI-CCAis dependent on the ion exchange process. This result is also consistent with the SCN^{-} removal mechanism for polyaniline/composite materials of reported in the literature [44,45].

3.2. Effect of pH and adsorbent dosage on SCN^{-} adsorption

The pH of wastewater effect not only the active sites on the adsorbent surface (the adsorption capacity) but also the charge of pollutants [10,46]. Due to this importance of the pH, the optimum pH value having maximum removal efficiency is examined in this study. The different amounts of the adsorbent (in the range 0.01–0.3 g) were added into thiocyanate solutions with different pH values (in the range 6–10). Since thiocyanate protonatesto species such as HSCN at acidic mediums ($pH < 6$), this study wasnot conducted under strongly acidic conditions.During experiments the initial SCN^{-} concentration (100 mg/L), agitation period (20 hours) and temperature (25°C) were kept constant.

As seen in Figure 3, the removal of SCN^{-} by the PANI-CCAhas shown no significant differences in the pH range of 6–10.This phenomenon can be explained by the electrostatic interaction of SCN^{-} with cations on adsorbent (Figure 4). Under these conditions, PANI-CCAis suitable for the adsorption of anions [7,44,45,47].SCN^{-} anions can perform electrostatic interaction with NH^{+} cations on PANI-CCA, and resulting in the removal of SCN^{-}anions.An Adsorbent dosage of 0.2 g/50 mL was found to be optimum with an adsorption efficiency higher than 90% for all of the tested pH values. Considering these results, the later experimental studies were carried out at the original pH value of the solution($pH = 8.7$).

3.3. Effect of initial thiocyanate concentration on SCN adsorption

The adsorption capacities and the removal efficienciesatthe different initial thiocyanate concentrations ($C_0 = 50$, 100, 300 and 500 mg/L) and the different times

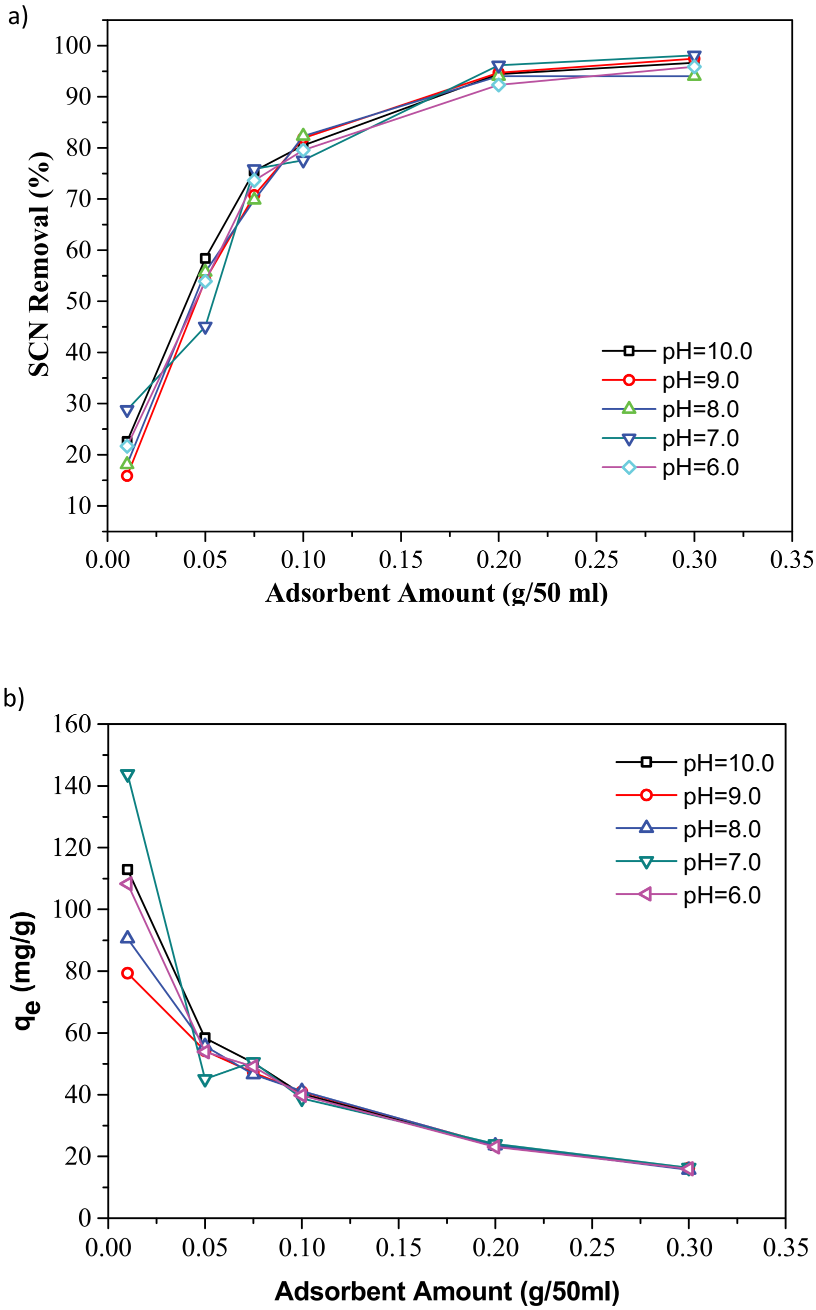


Figure 3. The effect of pH for different adsorbent dosages a) on the removal of SCN and b) on the adsorption capacity(C_0 = 100 mg/L SCN, V = 50 ml, T = 25°C, t = 24 hr, and w = 300 rpm).

(0–240 min) were tested in this section (Figure 5).These experiments were carried out by keeping the temperature (25°C), the adsorbent dosage (0.2 g/50 mL or 4 g/L) and pH (8.7) constant.The PANI-CCA removed more SCN ions in the first 10 min of contact

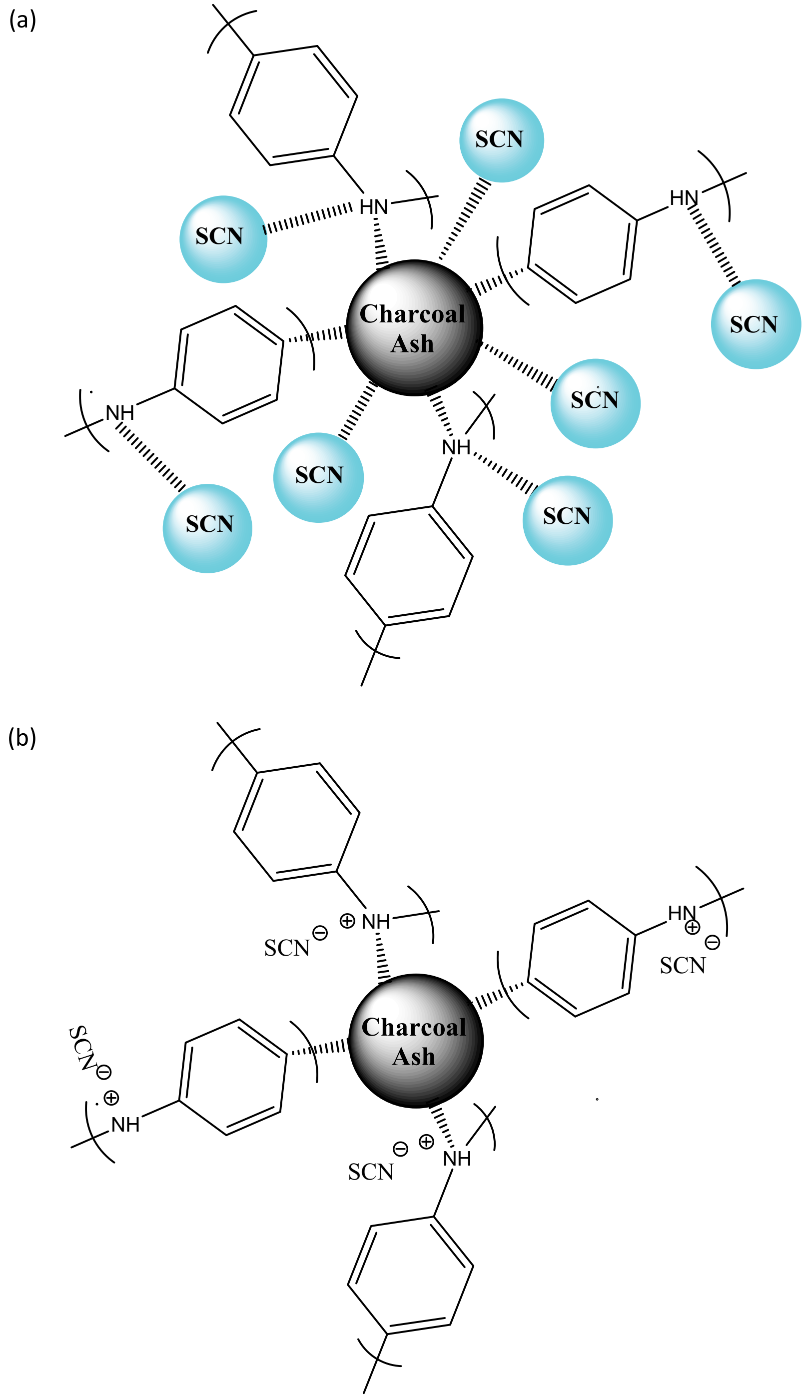


Figure 4. Proposed pathway of SCN removal by PANI-CCA composite: a) with the electrostatic interaction, b) with the ion exchanged mechanism.

time due to the active sites and functional groups, and the equilibrium was established between 20–30 min for all different SCN concentrations (Figure 5(a)). The adsorption capacity at the equilibrium state increased from 11.95 mg/g to

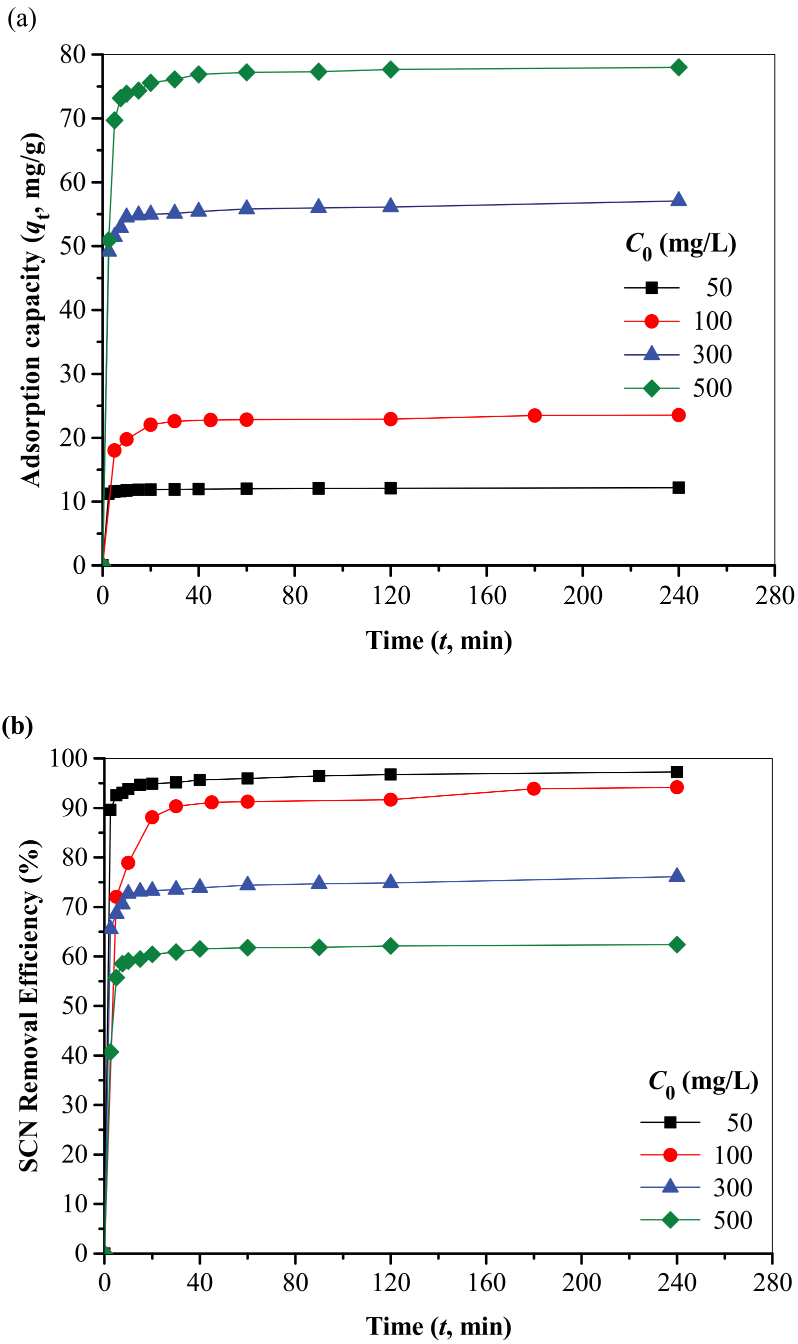


Figure 5. The effect of time for different initial SCN concentrations on a) the adsorption capacity and b) the removal efficiency of SCN ($pH = 8.7$, $m = 0.2$ g/50 ml, $V = 50$ ml, $T = 25$°C, $t = 24$ hr, and $w = 300$ rpm).

77.41 mg/g for the increased initial adsorbent concentration of 50 mg/L and 500 mg/L (Figure 5(a)), respectively. The higher SCNconcentrations have provided a higher driving force to overcome all mass transfer resistances, resulting in the high adsorption of SCN ions.

The adsorption kinetics of SCN is significant as it provides valuable insights into the reaction pathways and the mechanism of the reactions. The adsorption results have been analysed using the pseudo-first order and pseudo-second order kinetic models. The adsorption kinetics of pseudo first order and pseudo second order for SCN ions onto the PANI-CCAis shown in Figure 6.

The Lagergren rate equation was the first rate equation for the sorption of liquid/solid system based on solid capacity [48]. The first rate equation is one of the most widely used sorption rate equations for the sorption of a solute from a liquid solution. It may be represented as follows:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \tag{1}$$

Integrating Equation 1 for the boundary conditions t = 0 to t = t and q_t = 0 to $q_t = q_t$, gives:

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1}{2.303}t \tag{2}$$

which is the integrated rate law for a pseudo-first order reaction, where q_e is the amount of SCN adsorbed at equilibrium (mg/g); q_t is amount of SCN adsorbed at time t (mg/g); k_1 is the equilibrium rate constant of pseudo-first sorption (L/min).The adsorption kinetics can be described by a pseudo-second order model and the differential equation is as follows [49]:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \tag{3}$$

Integrating Equation (3) for the boundary conditions t = 0 to $t = t$ and q_t = 0 to $q_t = q_t$, gives:

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + k_2t \tag{4}$$

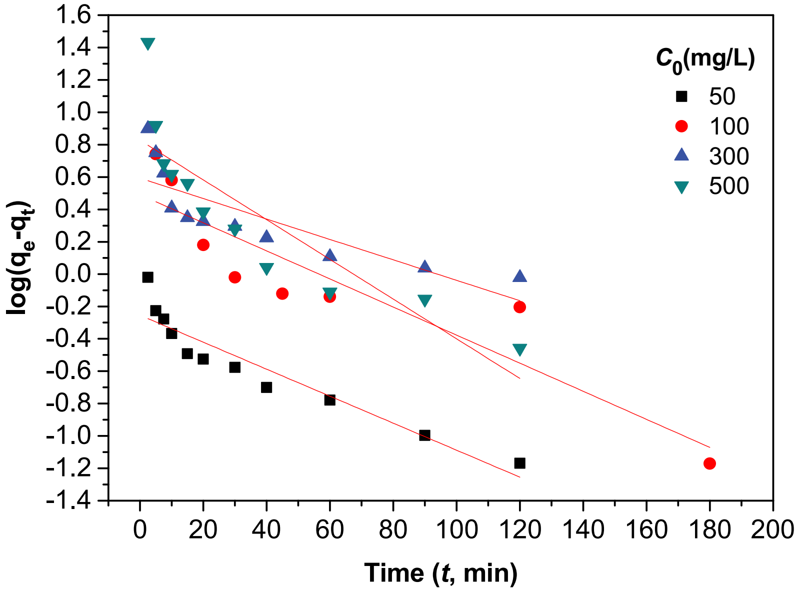
which is the integrated rate law for a pseudo-second order reaction. $q_e$is the amount of SCN ion adsorbed at equilibrium (mg/g) and $k_2$is the equilibrium rate constant of pseudo-second order adsorption (g/mg min). Equation (4) can be rearranged to obtain a linear form:

$$\frac{t}{q_t} = \frac{1}{k_2q_e^2} + \frac{1}{q_e}t \tag{5}$$

where $h = k_2q_e^2$ is the initial adsorption rate (mg/g min). The kinetic parameters (k_2, q_e and h) can be determined experimentally from the slope and intercept of a plot of (t/q_t)against t. Figure 6 shows a plot of the linearised form of the pseudo-second order model in Equation (5) for the sorption of SCN ions onto the PANI-CCAat various initial SCN concentrations.

The derived kinetic parameters of the pseudo first and pseudo second order model was estimated by a nonlinear regression method and tabulated in Table 1. As observed, the experimental kinetic data is better fitted by the pseudo second order model (r^2 = 0.999 for

(a)



(b)

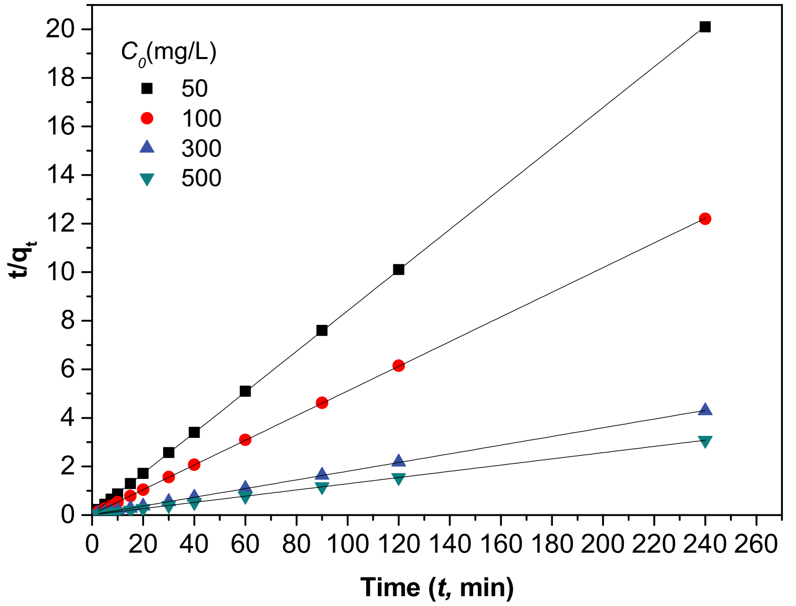


Figure 6. The adsorption kinetic models of (a) pseudo first order and (b) pseudo second order applied inadsorption of SCN ions onto PANI-CCA($pH = 8.7$, $m = 0.2$ g/50 ml, $V = 50$ ml, $T = 25$°C, $t = 24$ hr, and $w = 300$ rpm).

Table 1. Kinetic parameters for the adsorption of SCN ion at various SCN concentrations ($pH = 8.7$, $m = 0.2$ g/50 ml, $V = 50$ ml, $T = 25°C$, $t = 24$ hr, and $w = 300$ rpm).

	Pseudo-first-order model				Pseudo-second-order model				
C_0	k_1	$q_{e,exp}$	$q_{e,cal}$	r^2	k_2	h	$q_{e,exp}$	$q_{e,cal}$	r^2
(mg/L)	(L/min)	(mg/g)	(mg/g)	(-)	(g/mg min)	(mg/g min)	(mg/g)	(mg/g)	(-)
50	0.0192	11.95	0.56	0.883	0.1858	27.48	11.95	12.16	0.999
100	0.0201	23.31	3.11	0.807	0.0273	15.24	23.31	23.61	0.999
300	0.0145	55.90	3.92	0.662	0.0227	73.79	55.90	57.01	0.999
500	0.0283	77.92	6.72	0.737	0.0185	113.09	77.92	78.19	0.999

all SCN concentrations). Also, the calculated value ($q_{e,cal}$) that was derived from the pseudo second order equation is quite similar to those obtained experimentally, which indicates that the pseudo second order model is more suitable for the observed kinetics than the pseudo first order model. The pseudo first and pseudo second order models were used to fit the experimental data of SCN adsorption by using nonlinear regression method. To evaluate the goodness of fitting and the suitability of the model, the coefficient of determination (r^2) and normalised standard deviation (Δq, %) were used in the kinetic model study. A higher value of r^2 and lower value of Δq denoted better model fitting. The standard deviation Δq (%) was calculated as follows:

$$\Delta q(\%) = \sqrt{\frac{\left[(q_{e,\exp} - q_{e,cal})/q_{e,\exp}\right]^2}{n-1}} x100 \tag{6}$$

In this case, the normalised standard deviation of 50, 100, 300, and 500 mg/L for initial SCN concentrations are calculated as 0.530, 0.487, 0.599, and 0.105% for the pseudo second order model and 28.74, 32.75, 28.04, and 27.55% for the pseudo first order model, respectively. The resulted Δq (%) values are relatively lower for the pseudo second order than the pseudo first order model.

The correlation coefficients for the pseudo-second order rate law are greater than 0.99 for all systems with contact times of 240 min. As clearly seen from Table 3, in the pseudo-second-order reaction kinetic, the calculated values of q_e are closer to the experimental values for all of the tested concentrations. Furthermore r^2 values obtained for the pseudo-second-order reaction kinetic are significantly higher. In addition, the equilibrium sorption capacity for pseudo-second-order model are slightly more reasonable than those of the pseudo-first-order model when comparing predicted results with experimental data because all of the equilibrium sorption capacities, q_e, are lower than the experimental results. Since most of the pseudo-first-order model calculated q_e values deviate by >80% from the experimental values it suggests that the sorption of SCN ions onto the PANI-CCA follows the pseudo-second-order model. The pseudo-second-order rate constant, k_2, show a decrease from 0.1858 to 0.0185 g/mg per min with SCN concentration from 50 to 500 mg/L. The initial sorption rate, h, decreases from 27.48 to 15.24 mg/g min with an initial SCN concentration from 50 to 100 mg/L and then increased from 15.24 to 113.09 mg/g per min with an initial SCN concentration from 100 to 500 mg/L. When increasing the initial SCN concentration from 50 to 500 mg/L, the experimental specific sorption at equilibrium, q_e, increased from 11.95 to 77.92 mg/g. From the correlation between C_0 and $q_{e,cal}$ the following equation was obtained: $q_{e,cal} = 7.997 + 0.1463 \times C_0$

($r^2 = 0.975$). That's why, this suggests that this sorption system is not a first order reaction and that the pseudo-second order model, based on the assumption that the rate-limiting step may be chemical sorption or chemisorption involving valency forces through sharing or exchange of electrons between sorbent and sorbate, provides the best correlation of the data. These results indicate the proposed mechanism for the removal of thiocyanate by PANI-CCAseems to be driven by an ion exchange process as compatible with the BET surface analysis results. These results are also equal to literature [30,50].

3.4. Isotherm studies of SCN adsorption

The analysis of the adsorption isotherm data is an important step in finding a suitable model to be used for adsorption system design.Adsorption isotherm studies were carried out on four isotherm models which are the Langmuir, Freundlich, Tempkin and Halsey. The applicability of the isotherm models to the adsorption study was determined by judging r^2 values. Besides,the pseudo-first and second-order kinetic models were applied to experimental data. Isotherm calculations have been performed by using data in a wide concentration range (200–1500 mg/L) as thiocyanate concentrations change in this range in real wastewaters [9]. In this way, we have aimed to obtain realistic knowledge about the adsorption characteristics of the developed adsorbent for thiocyanate. During isotherm calculations, equilibrium adsorption capacities, q_e(mg/g) were determined by the following formula:

$$q_e = \frac{(C_0 - C_e)V}{m} \tag{7}$$

In the Equation (7), C_0 and C_e (mg/L) denote the initial and equilibrium concentrations of thiocyanate in solution, V (L) show the sample volume, and m (g) is the amount of the adsorbent.

The Langmuir isotherm model assumes that adsorption takes place on a monolayer and there are homogeneous adsorption sites on the surface [51]. Equations for the applied isotherm models have been presented in Table 2. The Langmuir isotherm can be expressed by Equation (8) where V_m (mg/g) and k are the monolayer adsorption capacity and empirical equilibrium constant, respectively. Adsorption on heterogeneous surfaces can be explained by a Freundlich isotherm. In Equation (9) the terms K_f and $\frac{1}{n}$ denote the adsorption capacity of the adsorbent and adsorption intensity, respectively. As recognised, the magnitude of $\frac{1}{n}$ value gives information about the favourability of the adsorption. Favourable adsorption conditions can be represented by $\frac{1}{n}$ values between 0 and 1. In this study, Temkin isotherm was used to obtain knowledge regarding adsorbate-adsorbate interactions. The linear form of this isotherm may be represented by Equation

Table 2. Applied isotherm equations.

Isotherm	Equation	Isotherm parameters	Plot	
Langmuir	$q_e = C_e V_m k/1 + kC_e$	k and V_m	$\frac{C_e}{q_e}$ versus C_e	(Equation 8)
Freundlich	$q_e = K_f C_e^{1/n}$	K_f and $\frac{1}{n}$	$\log q_e$ versus $\log C_e$	(Equation 9)
Temkin	$q_e = B\ln A + B\ln C_e$	A and B	q_e versus $\ln C_e$	(Equation 10)
Halsey	$q_e = K_H^{1/n}/C_e^{1/n}$	K_H and n_H	$\log q_e$ versus $\log C_e$	(Equation 11)

(10). In the equation A denotes the Temkin parameter related to the equilibrium binding energy and B is the Temkin constant related to adsorption heat [52].The Halsey isotherm is another two-parameter adsorption isotherm which is used to explain multilayer adsorption and demonstrate the heteroporous nature of the adsorbent. The Hasley isotherm equation can be expressed by Equation (11) where K_H and n_H are the Halsey isotherm constant and exponent, respectively [53].

In this study the isotherm parameters were determined from the intercept and slope of the concerned plots. The Plots of the applied isotherm models have been presented in Figure 7.

Calculated isotherm parameters and r^2 values of the applied isotherms have been summarised in Table 3. As seen from the results of the isotherm studies, the equilibrium data can be best explained by Freundlich and Halsey isotherms which provide higher r^2 values. These results confirm heterogeneous adsorption surface and multilayer adsorption phenomenon. The adsorption process is regarded to be favourable considering calculated adsorption intensity between 0 and 1 (0.43). Furthermore,the adsorption efficiency of the developed adsorbent is found to be superior with V_m value of 178.57 mg/g.

3.5. Results of thermodynamic studies

Feasibility of the adsorption process has also been evaluated considering thermodynamic parameters such as free energy change (ΔG), isosteric enthalpy change (ΔH) and entropy change (ΔS). The Following equations were used to determine the thermodynamic parameters:

$$K_c = \frac{C_{ads}}{C_e} \tag{12}$$

$$\Delta G = -RT\ln K_c \tag{13}$$

$$\Delta G = \Delta H - T\Delta S \tag{14}$$

$$\ln K_c = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \tag{15}$$

In the equations C_{ads} and C_e are the equilibrium adsorption capacity of PANI-CCA(mg/g) and equilibrium concentration of thiocyanate (mg/L). The Equilibrium constant has been denoted by K_c. Finally R and T show a universal gas constant (J/mol K) and absolute temperature (K). Isosteric enthalpy change and entropy change values were calculated from the Van't Hoff plot of $\ln K_c$ versus $1/T$ (Figure 8).

Calculated thermodynamic parameters have been summarised in Table 4. Considering the negative values of ΔG and ΔH parameters, it can be concluded that the adsorption process is spontaneous and exothermic. Furthermore, the negative value of ΔS is a marker of the regularity of solute molecules during the process. This means that there are no more free ions causing chaos in the aqueous media [54].

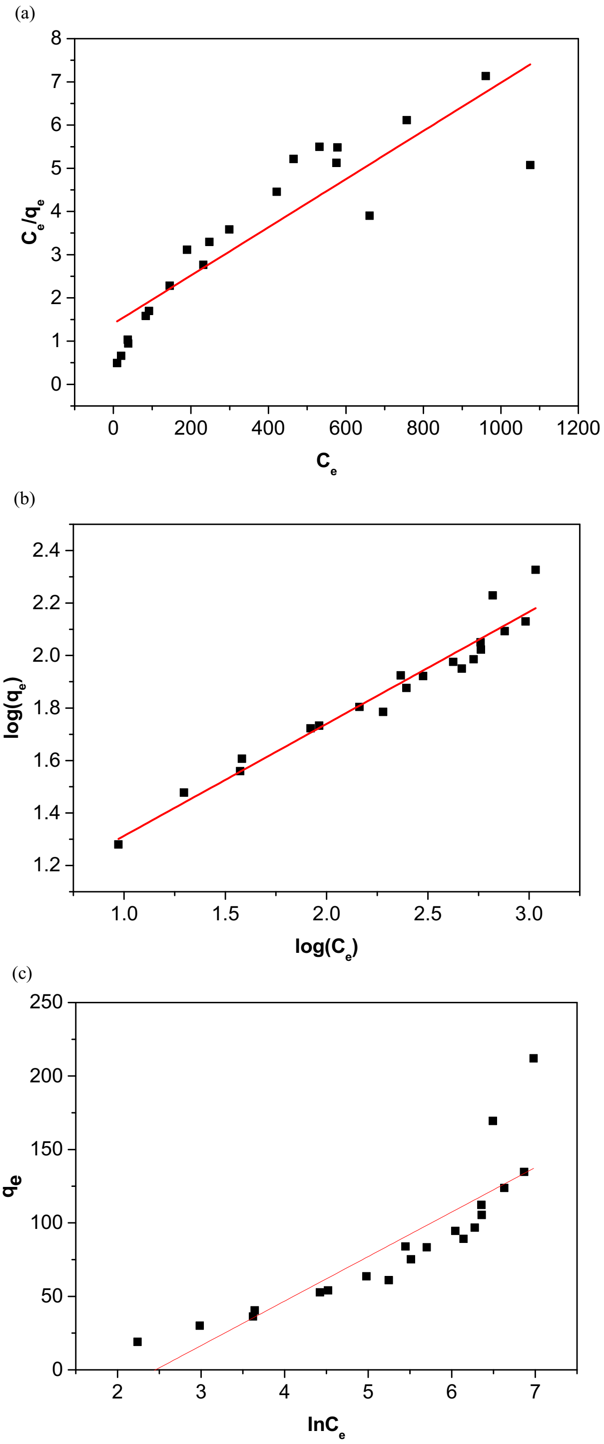


Figure 7. Plots of the applied (a) Langmuir (b) Freundlich and Halsey (c) Temkin isotherm models(C_0 = 200–1500 mg/L, pH = 8.7, m = 0.2–0.5 g/50 ml, V = 50 ml, T = 25°C, t = 24 hr, and w = 300 rpm).

Table 3. Isotherm parameters determined for adsorption of thiocyanate by using PANI-CCA ($C_0 = 200–1500$ mg/L, $pH = 8.7$, $m = 0.2–0.5$ g/50 ml, $V = 50$ ml, $T = 25$°C, $t = 24$ hr, and $w = 300$ rpm).

Langmuir isotherm constants			Freundlich isotherm constants			Temkin isotherm constants			Halsey constants		
V_m	k	r^2	K_f	$1/n$	r^2	A	B	r^2	K_H	n_H	r^2
178.57	0.004	0.80	7.69	0.43	0.95	0.086	30.3	0.74	0.125	−2.343	0.95

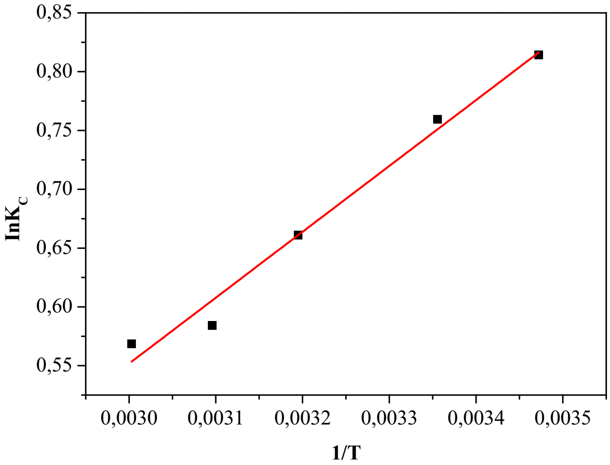


Figure 8. Van't Hoff plot for the adsorption of thiocyanate by PANI-CCA(C_0 = 300 mg/L, pH = 8.7, V = 50 ml, t = 24 hr, and w = 300 rpm).

Table 4. Thermodynamic parameters (C_0 = 300 mg/L, pH = 8.7, V = 50 ml, t = 24 hr, and w = 300 rpm).

Temperature (K)	ΔG(kJ/mol)	ΔH^a (kJ/mol)	ΔS^a(J/mol K)
288	−1.95	−4.66	−9.39
298	−1.88		
313	−1.72		
323	−1.57		
333	−1.57		

Theoverallresults of this study clearly confirm the appropriateness of the developed adsorbent, PANI-CCAin thiocyanate removal. In addition to experimental and theoretical studies which are performed to examine the efficiency of this adsorbent, we have also investigated the adsorption capacities of the other adsorbents in order to obtain comparable results. Acquired knowledge has been summarised in Table 5. As seen in Table 5, the adsorption capacities of PANI-CCAash yielded a significantly higher adsorption capacity when compared with the other studies. The adsorption capacity of raw charcoal ash has increased from 12.75 to 178 mg/g after the PANI coating process. Therefore, anion-exchange resin has a lower adsorption capacity compared to thisworking temperature (25°C), although the higher adsorption capacity has been achieved in the thiocyanate adsorption studies with anion-exchange resin (50°C) [11].Considering studies in literature, the adsorption capacity of thiocyanate increased with an increase in temperature.The adsorption capacity results obtained in this study are higher than the adsorption capacity obtained by the removal of thiocyanates by anion exchange resinbetween 20–30°C [11].This significant improvement

Table 5. Adsorption capacity results for thiocyanate removal with different adsorbents in literature and this study.

Adsorbent type	*T* (°C)	q_e(mg/g)	K_f(mg/g)	References
Anion-exchange resin	20	141.04	5.36	[5]
Synthetic hydrotalcite sol	20	98.30	-	[3]
PANI-coated charcoal ash	**25**	**178.57**	**7.69**	**This study**
Ferrihydrite	25	166.7	-	[10]
AgCl nanoparticles-loaded hydrotalcite	25	108.60	-	[39]
Hydrotalcite	25	100.00	-	[11]
Commercial activatedcarbon	25	12.90	-	[11]
Raw charcoal ash	**25**	**12.75**		**This study**
Zeolite	25	11.40	-	[11]
Steel-making slag	25	6.70	-	[11]
Diatomaceous earth	25	1.50	-	[11]
Anion-exchange resin	30	157.48	6.12	[5]
Calcined hydrotalcite	30	96.70	-	[1]
Surfactant-modified coir pith	32	8.60	1.81	[9]
Fe(III)/Cr(III) hyroxide	32	3.28	0.034	[8]
$ZnCl_2$ activated coir pith carbon	35	16.20	6.39	[6]
Anion-exchange resin	40	174.22	12.27	[5]
Anion-exchangeresin	50	191.20	15.92	[5]

indicates the attraction of PANI towards thiocyanate and considering the studies noted in literature so far, PANI-CCAshows that it is a highly effective adsorbent for thiocyanate.

4. Conclusions

The treatment of thiocyanate from wastewater is obligatory as it is a potentially toxic compound causing various harmful impacts in the discharged media. In this study, an abundant waste material (charcoal ash) was used in thiocyanate removal. An adsorption capacity of raw charcoal ash has been improved significantly by the utilisation of the PANI coating process. This improvement can be explained by an enhancement of surface area which is proved by the results of the BET analysis. The BET-specific surface area of the adsorbent has been increased from 1.5581 m^2/g to 29.6403 m^2/g by a coating process. Surface morphologies of raw charcoal ash, PANI-CCAbefore and after adsorption tests were also investigated visually by SEM analysis. The efficiency of the developed adsorbent was evaluated by conventional two parameter isotherm models. The Freundlich and Halsey isotherm models provided higher r^2values of 0.95 and 0.94, respectively confirming heterogeneous and a multilayer adsorption phenomenon. It has been identified that PANI-CCAused as adsorbent in this study have the best adsorption efficiency among the other adsorbents used up to now for the removal of SCN- in literature. Kinetic data was best fitted by pseudo-second-order reaction kinetic considering closer experimental and calculated adsorption capacities and higherr^2values. The Results of kinetic studies indicate that involved removal mechanism seems to be driven by an ion exchange process which is in good accordance regarding PANI adsorbents within literature. The removal of thiocyanate by PANI-CCA is supposed to be a spontaneous and exothermic process considering negative values of ΔG and ΔH parameters. Experimental and theoretical results of this study demonstrate that PANI-CCAis promising for the removal of thiocyanate from aqueous solutions.The results of this work showed that polyaniline has a high potential as an adsorbent and the high cost of it can be decreased by making composite with a natural material. However, the studies on obtaining the cheaper aniline monomer and the regeneration of the adsorbents with higher efficiency are necessary in the future.

Disclosure statement

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