

REVIEW ON COMPARATIVE STUDY FOR REMOVAL OF ORGANIC POLLUTANTS USING DIFFERENT FORMS OF GRAPHENE OXIDE

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Abstract- Textile wastewater due to the presence of dyes effluents has become a severe environmental problem worldwide and has reached on alarming stage. Therefore, from past few decades, different practices have been used by researchers and scientist to eliminate these effluents. Among them, adsorption is one most effective method due to its low cost, ease availability and handling. Recently, graphene oxide and its composites are gaining a lot of attention for removing not only dye effluents but other contaminants also. The present review reveals the importance of graphene oxide and their composites to eliminate dyes affluents from waterbodies along with classification of dyes and different adsorption techniques.

Keywords: Dye effluents, Adsorption, Graphene oxides, Textile wastewater.

1. INTRODUCTION

In 21st century, the major problem faced by the world is water pollution which is due to the rapidly growing industrialization, urbanization results in creating huge stress on use of water. The major contributor of water pollution is wastewater effluents such as dyes, heavy metals, pesticides, drugs etc. Among air, soil, noise and water pollution, water pollution is major problem as water has capacity to dissolve most of the substance as compared to any other liquid present on the earth [1]. Moreover, the resources of water like oceans, rivers, lakes and ponds are flooding with plastics, chemicals, dyes and other toxic pollutants which also cause water pollution. The environment and human health are both impacted in the short and long term when untreated and poorly handled wastewater is discharged into waterways. As a result, to protect the health of residents of both rural and urban areas, environmental rules related to water pollution should be strictly enforced. According to World Water Council report, there will be around 3.9 billion peoples by 2030 who are living in water scare areas [2]. Due to water shortage, it is very necessary to treat wastewater which fit for household, manufacturing, and agricultural activities. Textile processing is a huge industry that produces a lot of wastewater all over the world. Therefore, the management of wastewater and purification of potable water are important for the rapid progress of human society while also reducing contamination and health risks.

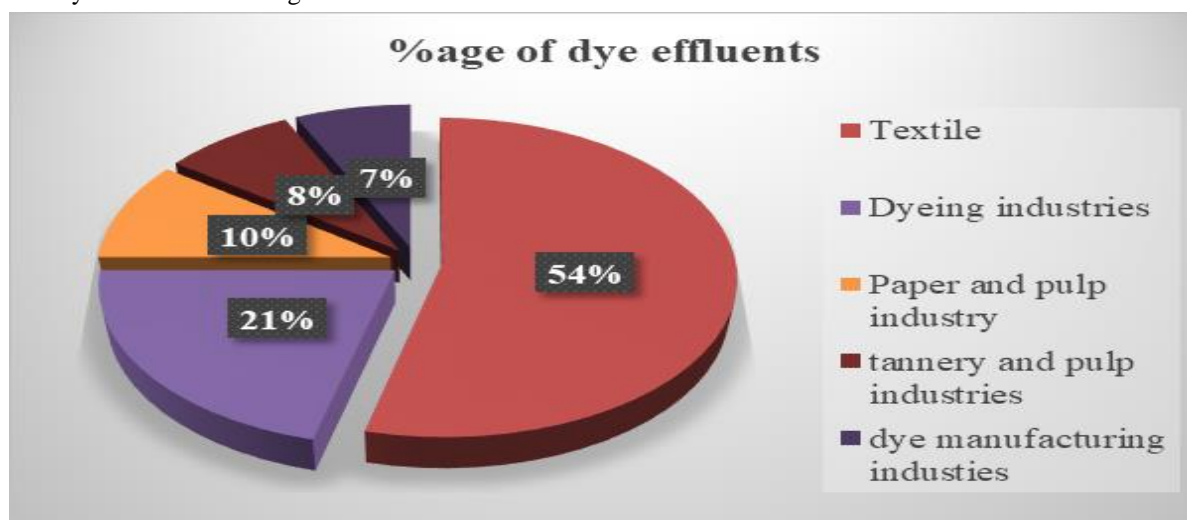


Fig. 1.1 Discharge of dye effluents from various industries

In India's major cities, approximate 38354 million litres per day (MLD) of sewage is produced, but their treatment is only 11786 MLD. Similarly, the treatment of industrial wastewater originated mainly from large-scale factories is only 60% [3]. In this situation, wastewater treatment has become foremost important. The industries like textile, paper and pulp, dye and dye intermediates, paint, pharmaceutical and tannery etc. discharge the organic contaminants into natural water supplies. Among all industries, textile industry produced more than half of all dye effluents (54%) as shown in Figure 1 [4], [5].

All over the world, approximate 10,000 types of textile dyes are generated based on color index and 7×10^5 tons of dyes are produced. The major countries have a major role in textile industries are China, United States, Pakistan, Brazil, Taiwan, Turkey, Bangladesh including India. Among all countries, India is largest textile producer where different types of raw materials like synthetic fibers, cellulose fibers are used [6]. According to a study, almost 1.6 million liters water is used by textile industries per day for the production of 8000 kg fabric where 16% of that water utilized to dye the clothes and 8% for printing as shown in Figure 2 [5].

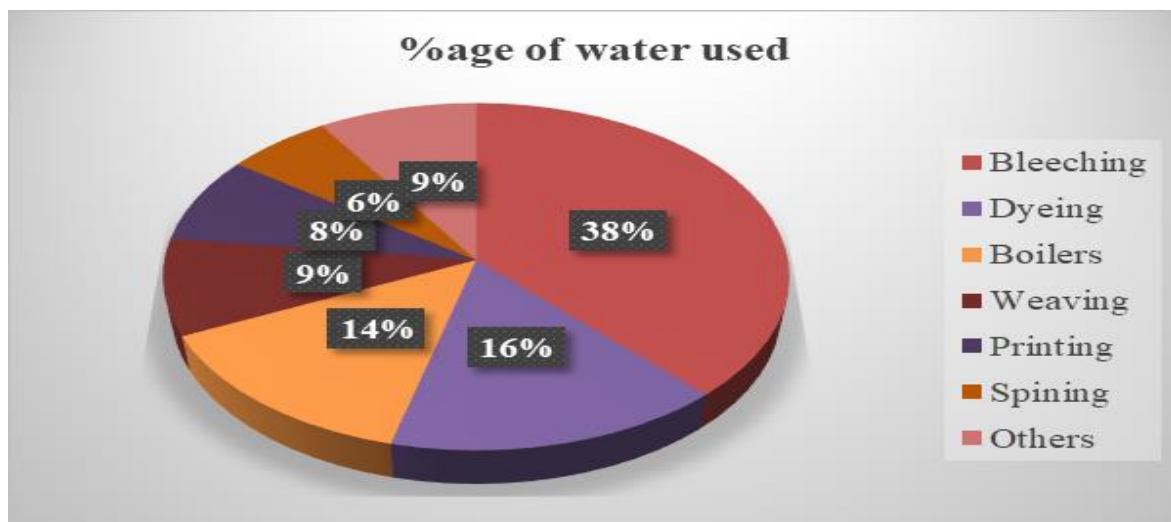


Fig. 1.2 Textile processing consuming water

The chemical processes in textile industries includes bleaching and dyeing which generates a large quantity of effluent containing a large volume of substantial contaminants such as higher chemical oxygen demand (COD), biological oxygen demand (BOD), dispersant, levelling agents, nitrogen, carriers, salts, heavy metals traces, dispersants, acids, alkali, and different types of synthetic dyes [7].

2. INDUSTRIAL DYE MATERIALS

A very common classification of the dyestuff used in textile industries is based on the source from which it is made. The most classification of dyes is done on the basis of their source from where they are originated: natural and synthetic. The synthetic dyes are further categorized into two categories: water insoluble and water-soluble dyes [8].

The most common dyes used in textile industries are acidic and basic dyes due to their bright colour, high solubility in water, low cost, and being simpler to apply to fabrics. As a result, discharge of contaminants spreads toxicity, degrades water quality and have a serious impact on photosynthesis process. Furthermore, due to low light penetration and inadequate oxygen intake, it has a major effect on the aquatic environment. The studies also revealed about genotoxicity and carcinogenic nature of dyes. They can cause various kinds of diseases like bladder cancer, dermatitis, kidney disorder after entering into skin through inhalation, ingestion or skin pores.

Therefore, effluents must be properly treated before being discharged results in enhancement of alternative of water reusability. By 2030, the United Nations has set a goal to enhance “water quality by removing pollutants, eliminating disposal, and reducing the discharge of toxic chemicals and products, percentage of contaminated water results in significantly improving recycling and reuse of water”. The environmental technology market of India is also booming, with plenty of business prospects for pollution-reduction technology developments [1].

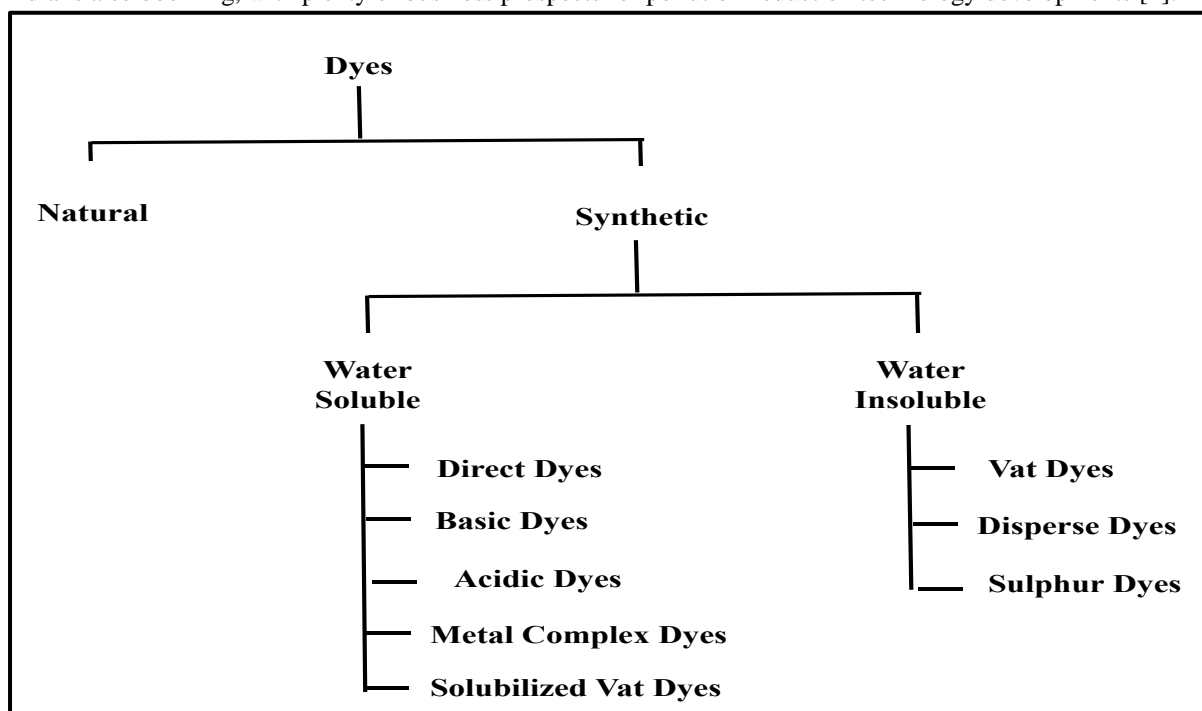


Fig. 2.1 Classification of dyes

3. TECHNIQUES USED FOR REMOVING DYES FROM WATER BODIES

From past few decades, different techniques such as ion exchange, membrane separation, coagulation/flocculation, photodegradation, charcoal filtration, reverse osmosis, ultra-filtration and some biological methods are used for removal of dyes on a large scale. There are some drawbacks of these methods like consumption of high energy, complex design and extended operation times due to which these methods can not be afforded by textile industries especially in developing countries like India [9].

Therefore, one of the most suitable and effective method for eliminating of the dyes from discarded water is adsorption as it is cost-effective with flexible design, more availability, and high energy efficient. Generally, adsorption is a surface process in which the pollutants adhered onto adsorbent's surface [10].

Adsorption is a unit procedure used to separate contaminants from industrial wastewater. Adsorbents used for elimination of dyes are zeolite, charcoal, naturally occurring clay minerals, fly ash, chitosan, fruit waste, rice husk, scrap tyres, petroleum waste, metal nanoparticles, graphene oxides etc [11].

Among all the adsorbents, graphene oxide is known as promising adsorbent to adsorb dyes effluents from water bodies. As graphene has high theoretical specific surface area, high negative charge density, it is largely used for removal of contaminants. The surface of graphene oxide is hydrophobic due to the delocalized π -electron system which provide stability to graphite over other adsorbents. They are also easily synthesized using exfoliation/chemical oxidation method on large scale from abundant natural graphite [12].

The purpose of the review is to study current state of graphene oxide and their composites to remove the dyes from water bodies. The review also focusses on adsorption efficiency of graphene-based composites and mechanisms for removing the dyes with their regeneration.

4. DYES REMOVAL USING DIFFERENT FORMS OF GRAPHENE OXIDE

Different types of dyes present in water bodies are harmful not only for aquatic life but for human being and environment also results in raising the global concern. Graphene oxides and its composites are known as one of the most effective adsorbents to remove the dye effluents like methylene blue, crystal violet, rhodamine-G, indigo carmine etc. with much higher adsorption capacities than other adsorbents.

Methyl orange and basic red 12 were removed by applying graphene oxide from wastewater. 6.83 mg/g of methyl orange and 63.69 mg/g for basic red 12 dye adsorb onto graphene oxide within 100 minutes of contact time at pH 3 of the media. The adsorption efficiency of graphene oxide was more for basic red 12 due to electrostatic interaction between them whereas repulsion was observed between methyl orange and graphene oxide due to having same negative charge. The endothermic nature of the adsorption process was revealed by the effect of temperature [13].

Sharma et al. (2013) employed graphene oxide efficiency to remove methyl green (MG) from aqueous media. 5.496 mmol/g uptake of dye was recorded at pH 5 which is further confirmed from Langmuir adsorption isotherm. Furthermore, enhancement in the adsorption of dye onto graphene oxide was observed with increase in temperature [14].

Magnetic graphene oxide functionalized with Xanthate groups ($\text{Fe}_3\text{O}_4\text{-xGO}$) were synthesized by Cui et al, (2015) where xanthate groups are linked to graphene magnetic material ($\text{Fe}_3\text{O}_4\text{-GS}$). The synthesized composite showed adsorption efficiency for Hg^{2+} 118.55 mg/ g within 180 minutes of contact time at pH 7 and 526.32 mg/ g for methylene blue within 120 minutes at pH 5.5 respectively. The adsorption process was endothermic and spontaneous as confirmed from the thermodynamic studies ($\Delta G < 0$, $\Delta H > 0$, $\Delta S > 0$) [15].

Polydopamine functionalized GO was synthesized by self – polymerization process to remove several dyes like methylene blue (MB), methyl orange (MO), methyl violet (MV), basic fuchsin (BF), Coomassie brilliant blue (CBB), rhodamine B (RHB), malachite green oxalate (MGO) and neutral red (NR) and toxic ions like Pb(II), Cu(II), Cd(II) and Hg(II). According to Langmuir adsorption isotherm, maximum removal efficiency of PDA functionalized graphene oxide (15% polydopamine –GO) was 2.181 mg/g for methylene blue dye which was ten times higher as compared to individual polydopamine or GO [16].

The hydrogel of graphene oxide and chitosan (GO-CS) were synthesized using graphene oxide suspension with Chitosan solution and used for elimination of both methylene blue, a cationic dye and Eosin Y, anionic dye from aqueous media. The efficiency to adsorb both cationic and anionic dyes (>300 mg/g) was higher for both hydrogels due to their porous structure. The adsorption efficiency varies with change in the composition of hydrogels. As the concentration of GO increased, methylene blue dye adsorption was more and on increasing the concentration of chitosan, Eosin Y adsorption was high which is due to the electrostatic interaction as GO shows negative charge on its surface and chitosan have positive charge respectively for different cationic and anionic dyes [17].

A simple sol gel method developed for synthesis of graphene oxide/ cellulose beads composites to remove cationic dye, Malachite green from water bodies. The results showed over 96% dye removal (Zhang et al, 2015). Dye adsorption increased on increasing amount of composite beads. These composites beads can be reused for five time more through simple filtration process [18].

Sheng et al. (2016) synthesized a novel adsorbent based on graphene oxide using chitosan, fly ash and graphene oxide where cross-linking of fly ash was with both GO and chitosan takes place. The synthesized adsorbent used for removal of both cationic (Acid Red R) (38.87 mg/g) and anionic dye (Red X-5GN) (64.50 mg/g) [19].

Rong et al, (2015) revealed the adsorption efficiencies of NiO/graphene nanosheets against Congo red, an acidic dye. The nanosheets which are fabricated through hydrothermal method showed 99.56% uptake of dye in 180 minutes using 1.0% adsorbent dose of dye concentration e at room temperature. Further, they explained the

adsorption mechanism through isotherm and kinetic model where the equilibrium data fitted well in pseudo-second order kinetic model and Redlich-Peterson model [20].

Table-4.1 Adsorption of various dyes using different forms of graphene oxide

Adsorbent	Dye	Results	Isotherm and Kinetic model	References
Graphene oxide (GO), fluorinated graphene oxide (F-GO) and interconnected reduced graphene oxide (IC-rGO)	Methylene blue (MB) and Rhodamine B (RhB),	Adsorption isotherm revealed high value of q_e at any C_e for GO. 403.3 mg/g for MB 686.6 mg/g for RhB for GO. F-GO: The removal efficiency was below 95.1% at 120 mg/L initial concentration. ICrGO: 47.6% removal efficiency for both dyes	Langmuir and Pseudo-second order kinetic model	[10]
Graphene oxide (GO)-based polymer nanocomposites (GO-PDA-PSPSH)	Methylene blue	279.57 mg/g in 58 minutes at pH 7	Langmuir and Pseudo-second order kinetic model	[21]
Graphene oxide (GO)/poly(N-isopropylacrylamide) (PNIPAM)	Rhodamine B	GO: 610, 412 and 223 mg/g uptake of dye at initial concentrations of dye (0.05, 0.1 and 0.2 mg/mL) GO/PNIPAM: 982, 494 and 267 mg/g dye adsorbed at concentrations of dye (0.05, 0.1 and 0.2 mg/mL)	Langmuir and Pseudo-second order kinetic model	[22]
Graphene oxide intercalated montmorillonite nanocomposites	Crystal violet	MtGO nanocomposite: Increase in equilibrium adsorption capacity from 184.67 to 583.08 mg/g with increasing dye concentration ranging from 50 to 200 mg/L within 5 minutes of contact time	Langmuir and Pseudo-second order kinetic model	[23]
Magnetic adsorbent GO-APTS-poly(AMPS-co-MA)/Fe ₃ O ₄)	Crystal violet (CV) and Methylene blue (MB)	Methylene blue = 416.06 mg/g Crystal violet = 440.97 mg/g. with 6 hrs of contact time at pH 6 and 8	Chemisorption, spontaneous, and endothermic Langmuir and Pseudo-second order kinetic model	[24]
Nafion, Nafion-TiO ₂ , Nafion-GO, Nafion-GOSULF	Methyl Orange	Nafion = 47% Nafion-GO = 46%	Langmuir and Pseudo-second order kinetic model	[25]

5. MECHANISM OF INTERACTION OF GRAPHENE OXIDE WITH ANIONIC AND CATIONIC DYES

The most common mechanism for adsorption of dyes onto graphene oxide is either due to hydrogen bonding or π - π interaction between adsorbate and adsorbent. Most of dyes either they are water soluble or insoluble are π -electron rich as they have aromatic rings in their structure results in interaction with π -electrons of graphene oxide as shown in Fig. 5.1 and 5.2 [36]. Besides these interactions, there are some other factors also like hydrophobic effects due to aromatic rings of organic dyes and surface topology of graphene oxides and its derivatives and size of organic molecule which perform an essential part during adsorption of dyes [37].

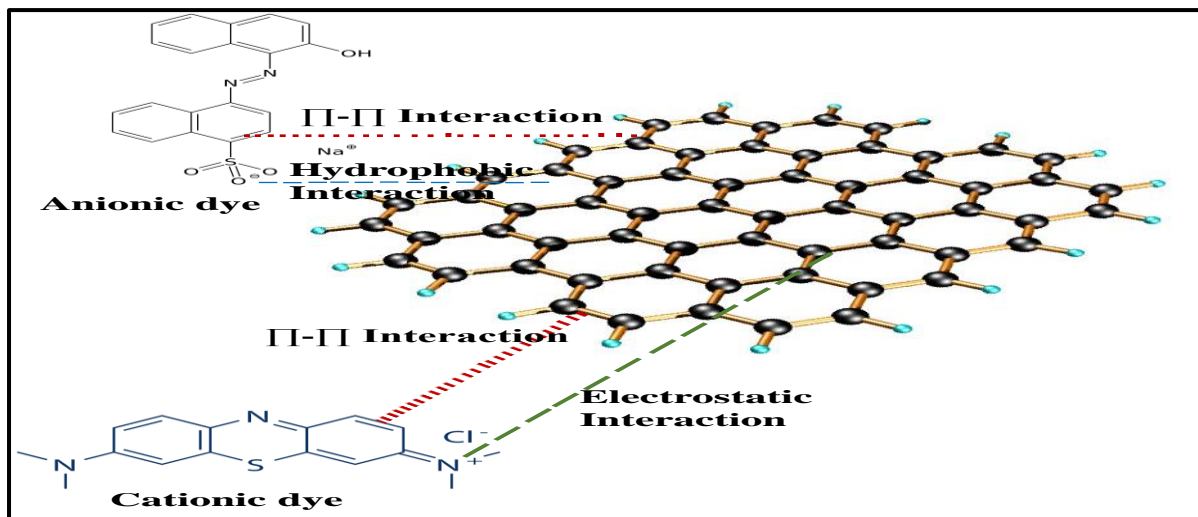


Fig. 5.1 Mechanism of interaction of cationic and anionic dyes with graphene oxide

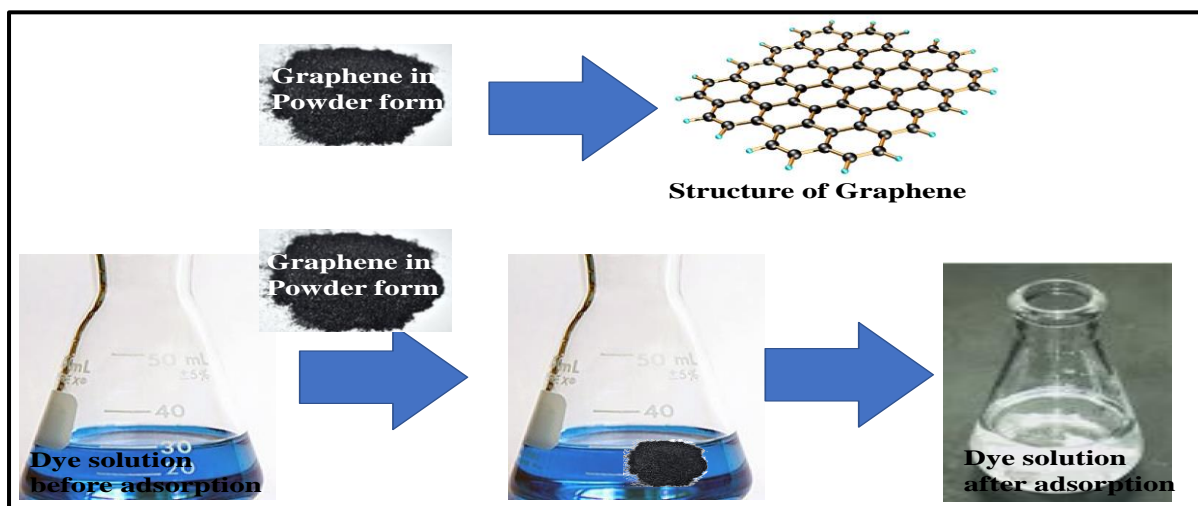


Fig. 5.2 Dye solution before and after adsorption onto graphene oxide adsorbent

CONCLUSION

The dyes used in textile and other different industries for coloring purposes are directly discarded into the environment which cause hazardous effect on human health as well as environment. Therefore, an effective treatment method is required to remove the effluents from waterbodies to avoid their deleterious effects on humans and aquatic organisms on their exposure. Attempts are being made to remove the dye effluents using graphene oxide and its derivatives due to their enhanced catalytic activities, high specific surface area and easy recovery. These composites removed the dyes either through adsorption process or free-radical mechanism, electrostatic and π - π interactions. In the last, it is concluded that the removing efficiency can be enhanced by combining with other water purifying technologies so that the superior quality of water can be achieved.

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